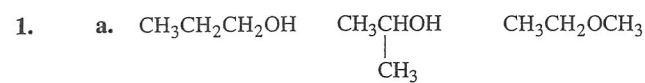
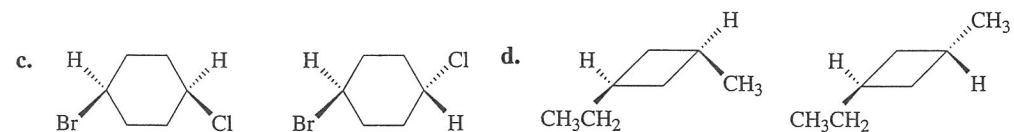
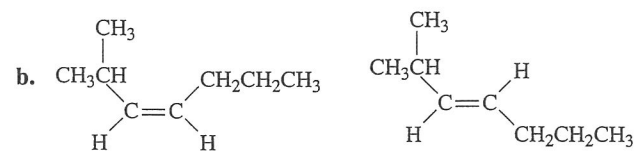
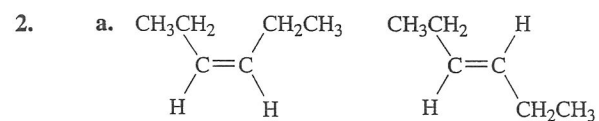
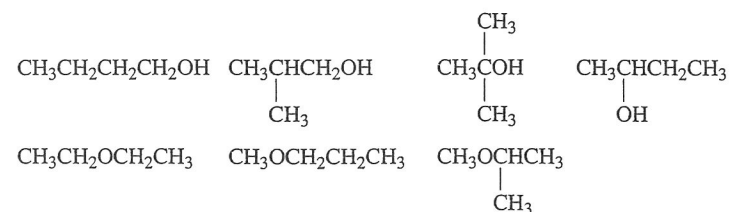


Solutions to Problems



b. There are seven constitutional isomers with molecular formula $\text{C}_4\text{H}_{10}\text{O}$.



3. a, b, c, f, and h are chiral.
d, e, and g are each superimposable on its mirror image. These, therefore, are achiral.

4. a. F, G, J, L, N, P, Q, R, S, Z

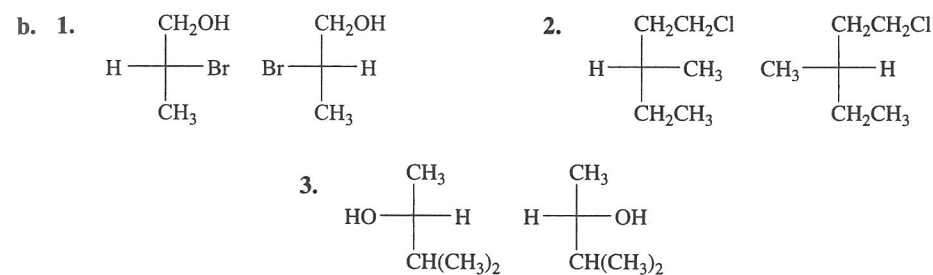
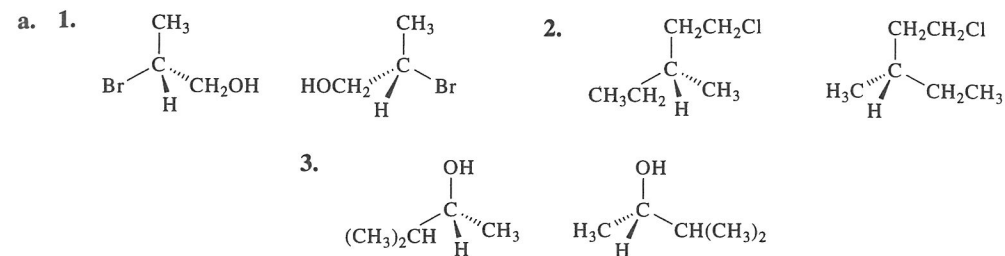
b. A, H, I, M, O, T, U, V, W, X, Y

5. a, c, and f have asymmetric centers.

6. Solved in the text.

7. a, c, and f, because in order to be able to exist as a pair of enantiomers, the compound must have an asymmetric center (except in the case of certain compounds with unusual structures. See Problem 96.)

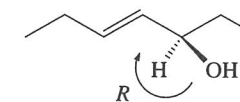
8. Draw the first enantiomer with the groups in any order you want. Then draw the second enantiomer by drawing the mirror image of the first enantiomer. Your answer might not look exactly like the ones shown below because the first enantiomer can be drawn with the 4 groups on any of the 4 bonds. The next one is the mirror image of the first one.



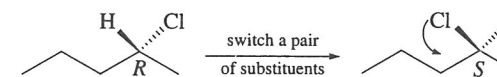
9. A, B, and C are identical.

10. a. *R* b. *R*

c. To determine the configuration. Add the fourth bond to the asymmetric center. Remember that it cannot be drawn between the two solid bonds.



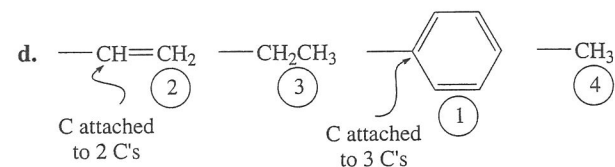
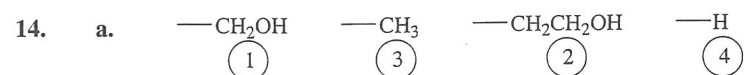
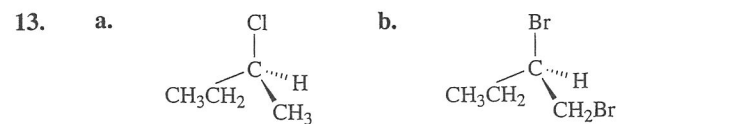
d. Draw the structure with the fourth bond to the asymmetric center. Switch a pair so that the H is on a dotted bond. The configuration of the compound with the switched pair is *S*. Therefore, the configuration of the compound given in the question is *R*.



11. a. *S* b. *R* c. *S* d. *S*

12. The easiest way to determine whether two compounds are identical or enantiomers is to determine their configurations: If both are *R* (or both are *S*), they are identical. If one is *R* and the other is *S*, they are enantiomers.

a. identical b. enantiomers c. enantiomers d. enantiomers



15. a. levorotatory b. dextrorotatory

16.
$$\text{specific rotation} = \frac{\text{observed rotation}}{\text{concentration} \times \text{length}}$$

$$[\alpha] = \frac{+13.4^\circ}{\frac{2}{50} \times 2 \text{ dm}} = \frac{+13.4^\circ}{0.08} = +168$$

17. a. -24 b. 0

18. a. 50% of the mixture is excess (+)-mandelic acid
- $$\text{optical purity} = 0.50 = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}}$$
- $$0.50 = \frac{\text{observed specific rotation}}{+158}$$
- observed specific rotation = +79

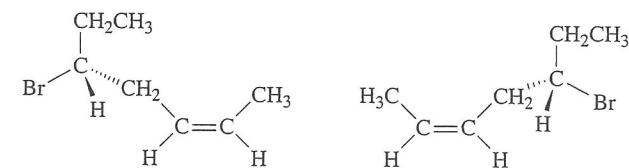
- b. 0 (It is a racemic mixture.)

- c. 50% of the mixture is excess (-)-mandelic acid.
observed specific rotation = -79

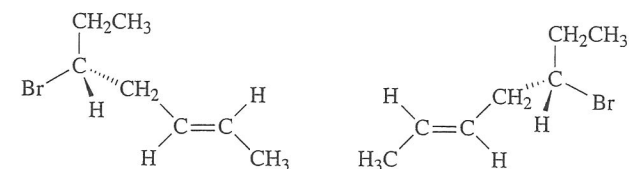
19. a. From the data given, you cannot determine what the configuration of naproxen is.
b. 97% of the commercial preparation is (+)-naproxen; 3% is a racemic mixture
Therefore, the commercial preparation forms 98.5% (+)-naproxen and 1.5% (-)-naproxen.

20. Solved in the text.

21. As a result of the double bond, the compound has a cis isomer and a trans isomer. Because the compound also has an asymmetric center, the cis isomer can exist as a pair of enantiomers and the trans isomer can exist as a pair of enantiomers.

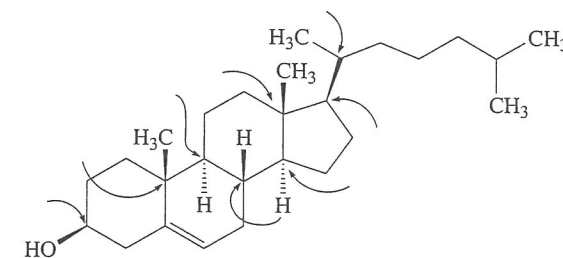


cis enantiomers



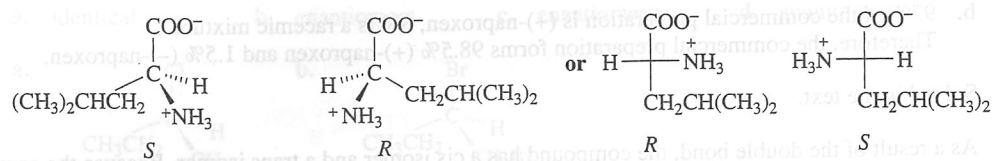
trans enantiomers

22. The statement is not correct. For example, the sp^2 carbons of cis and trans isomers are stereocenters. Therefore, *trans*-2-butene has two stereocenters but only two stereoisomers. Another example is the compound shown in Problem 21; it has three stereocenters but only four stereoisomers.
23. a. enantiomers
b. identical compounds (Therefore, they are not isomers.)
c. diastereomers
24. a. First find the sp^3 carbons that are bonded to four different substituents; these are the asymmetric centers. Cholesterol has eight asymmetric centers. They are indicated by arrows.

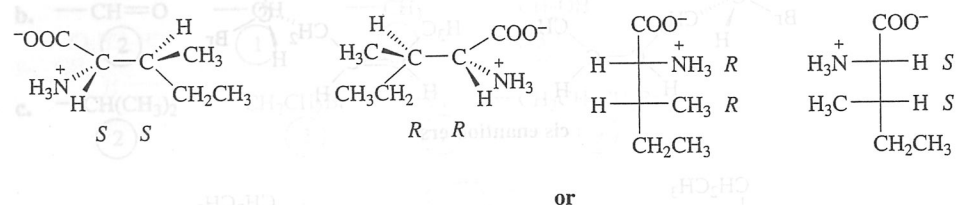


- b. $2^8 = 256$ Only the stereoisomer shown above is found in nature.

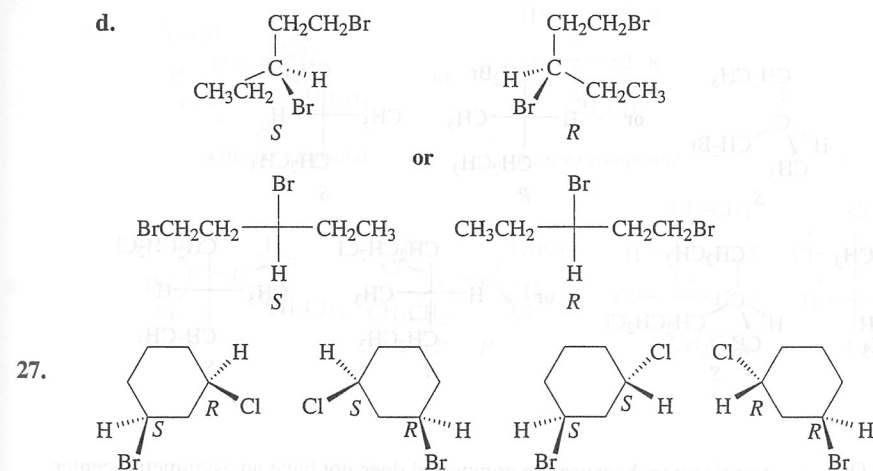
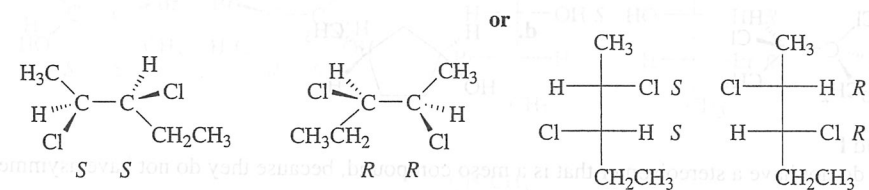
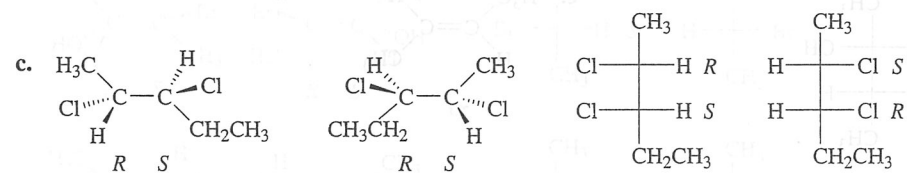
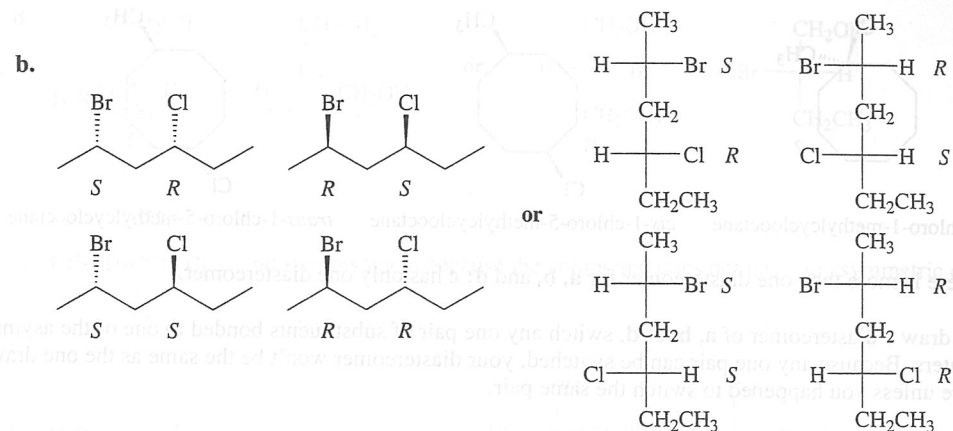
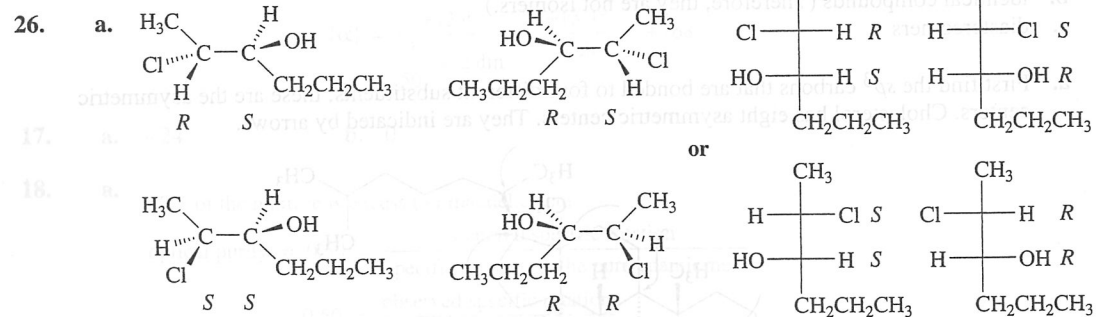
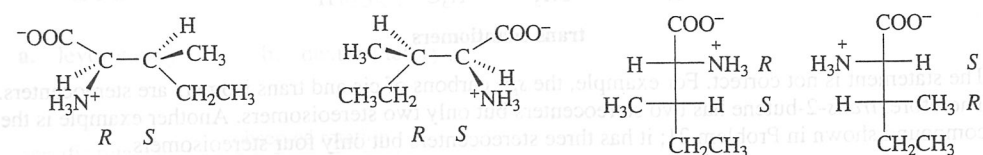
25. Your perspective formulas may not look exactly like the ones drawn here because you can draw the first one with the groups attached to any bonds you want. Just make certain that the second one is a mirror image of the first one.

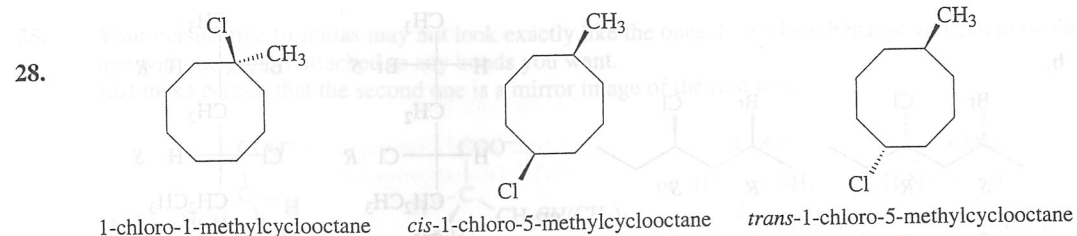


Again your perspective formulas may not look exactly like the ones drawn here. To make sure you have all four, determine the configuration of each of the asymmetric centers. You should have *R,R*, *S,S*, *R,S*, and *S,R*.



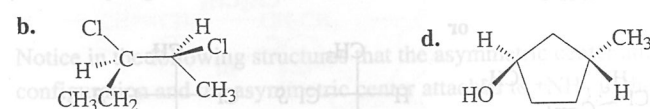
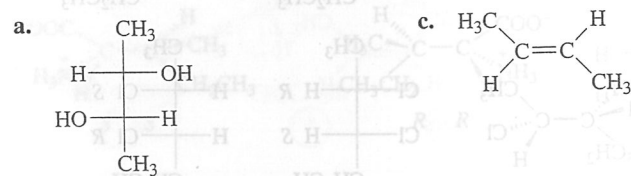
Notice in the following structures that the asymmetric center attached to $+NH_3$ in one structure has the *R* configuration and the asymmetric center attached to $+NH_3$ in the other structure has the *S* configuration.





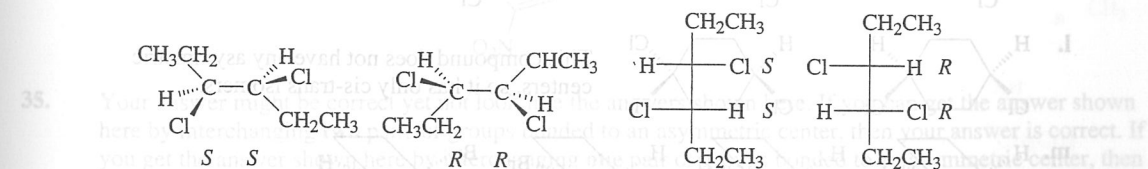
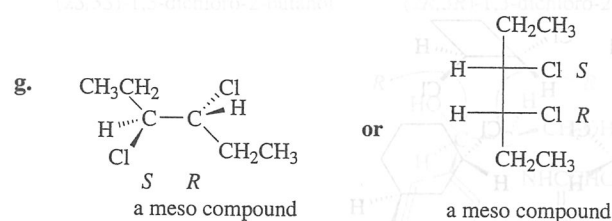
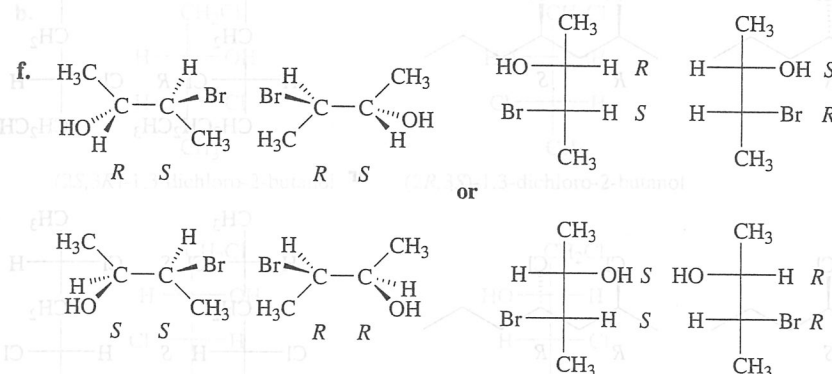
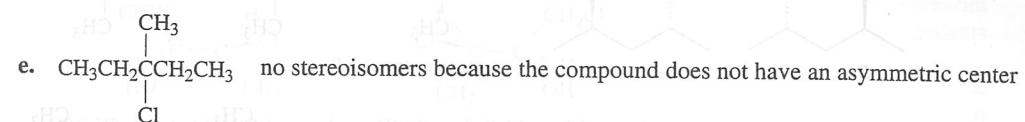
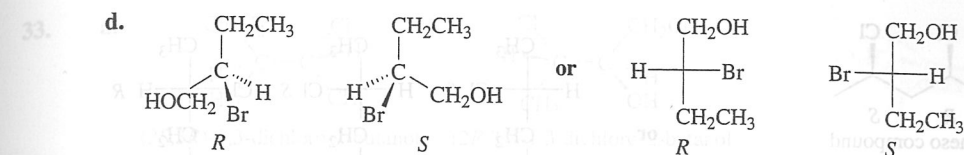
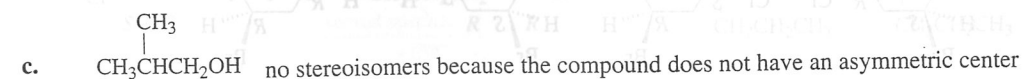
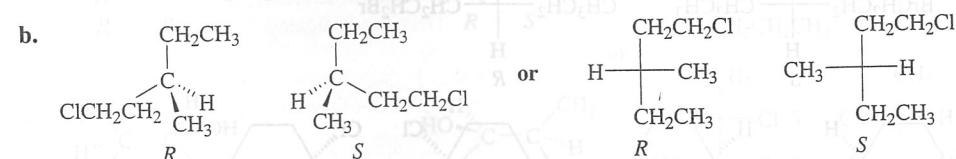
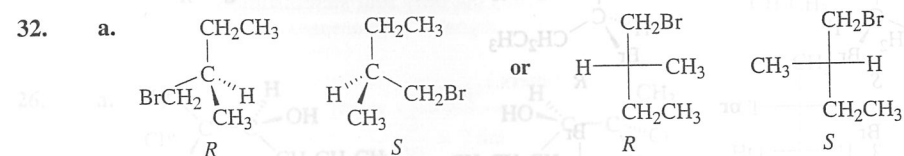
29. There is more than one diastereomer for **a**, **b**, and **d**; **c** has only one diastereomer.

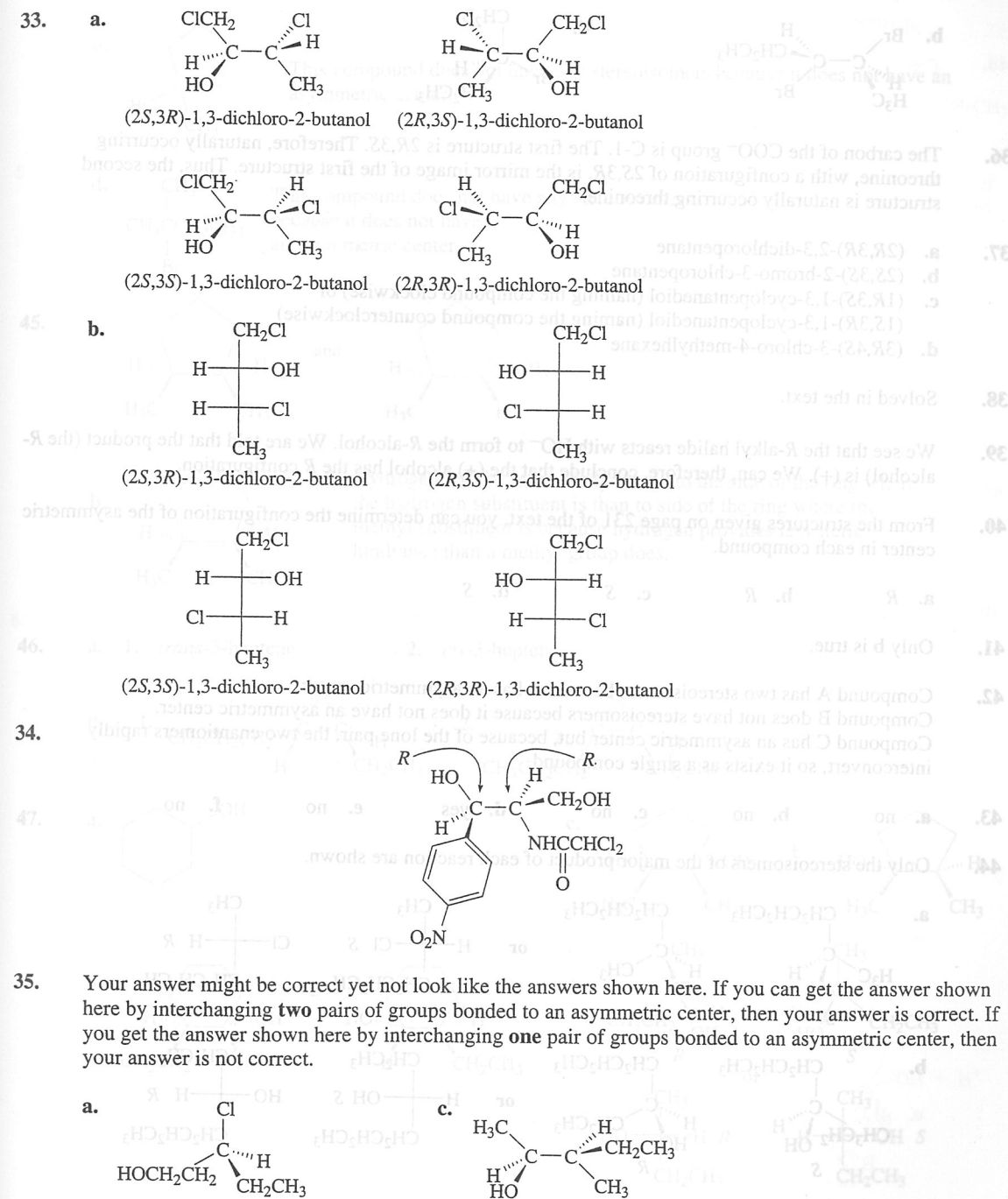
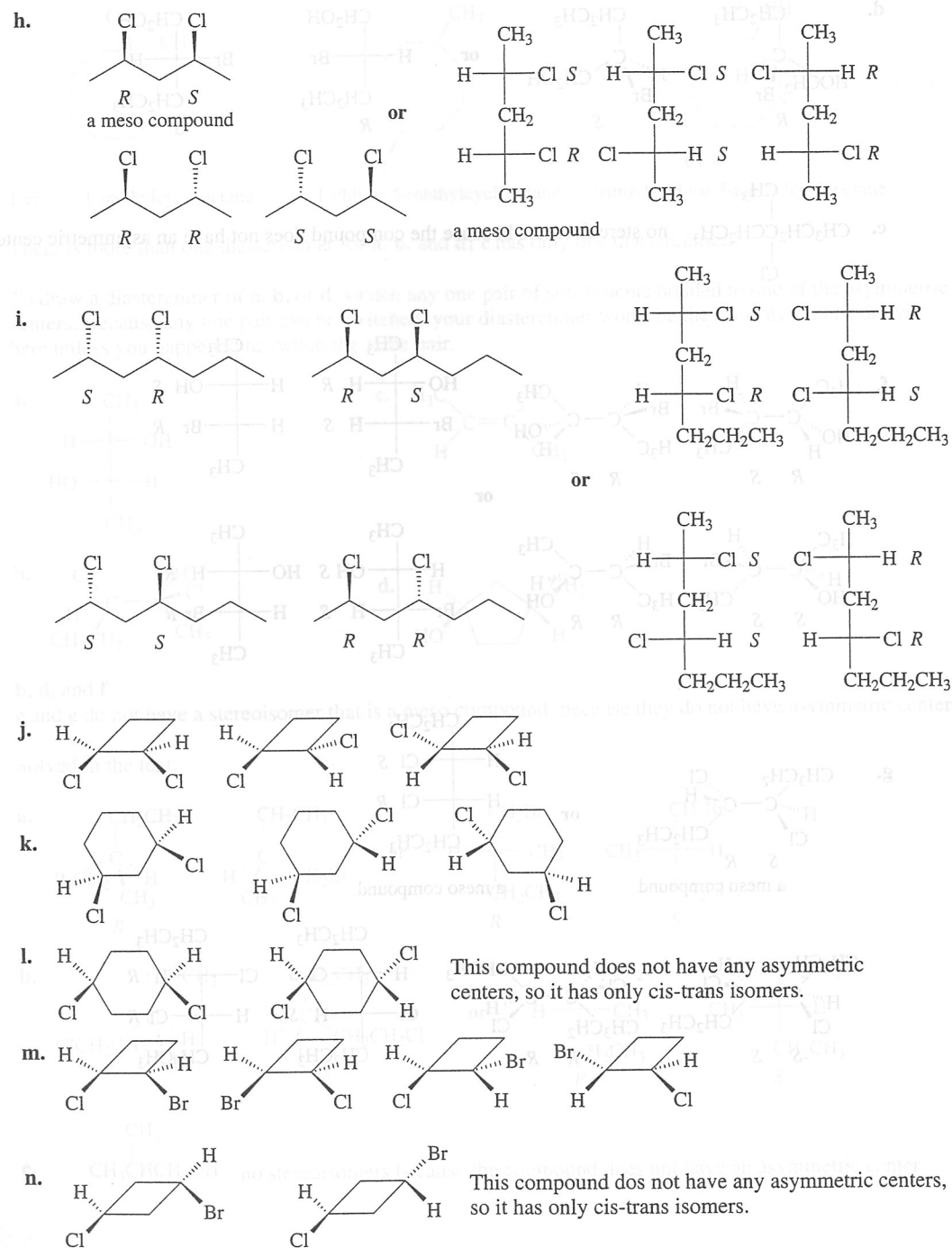
To draw a diastereomer of **a**, **b**, or **d**, switch any one pair of substituents bonded to one of the asymmetric centers. Because any one pair can be switched, your diastereomer won't be the same as the one drawn here unless you happened to switch the same pair.

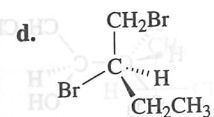
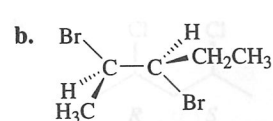


30. **b**, **d**, and **f**
c and **e** do not have a stereoisomer that is a meso compound, because they do not have asymmetric centers

31. Solved in the text.







36. The carbon of the COO^- group is C-1. The first structure is $2R,3S$. Therefore, naturally occurring threonine, with a configuration of $2S,3R$, is the mirror image of the first structure. Thus, the second structure is naturally occurring threonine.

37. a. $(2R,3R)$ -2,3-dichloropentane
 b. $(2S,3S)$ -2-bromo-3-chloropentane
 c. $(1R,3S)$ -1,3-cyclopentanediol (naming the compound clockwise) or $(1S,3R)$ -1,3-cyclopentanediol (naming the compound counterclockwise)
 d. $(3R,4S)$ -3-chloro-4-methylhexane

38. Solved in the text.

39. We see that the R -alkyl halide reacts with HO^- to form the R -alcohol. We are told that the product (the R -alcohol) is (+). We can, therefore, conclude that the (+) alcohol has the R configuration.

40. From the structures given on page 231 of the text, you can determine the configuration of the asymmetric center in each compound.

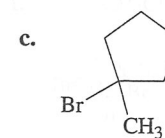
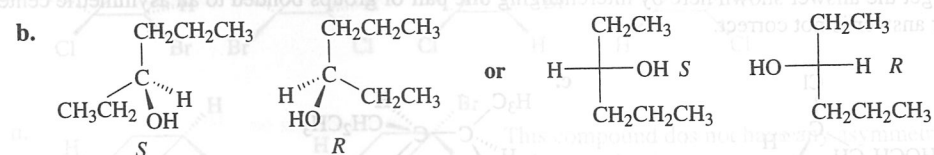
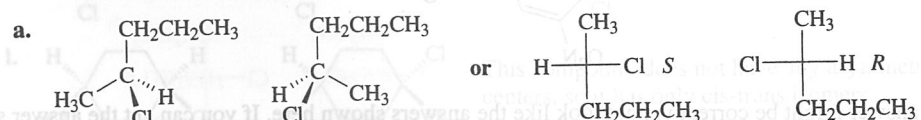
a. R b. R c. S d. S

41. Only b is true.

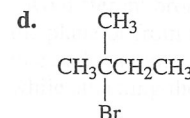
42. Compound A has two stereoisomers because it has an asymmetric center. Compound B does not have stereoisomers because it does not have an asymmetric center. Compound C has an asymmetric center but, because of the lone pair, the two enantiomers rapidly interconvert, so it exists as a single compound.

43. a. no b. no c. no d. yes e. no f. no

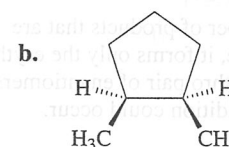
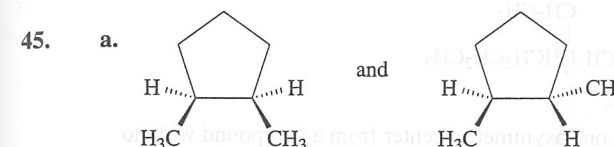
44. Only the stereoisomers of the major product of each reaction are shown.



This compound does not have any stereoisomers because it does not have an asymmetric center.

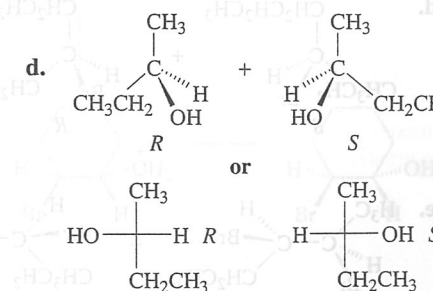
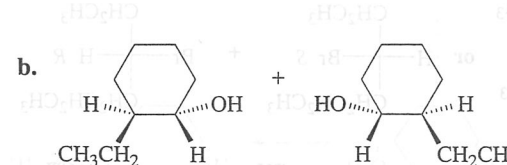
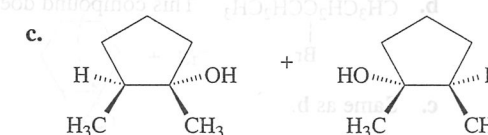
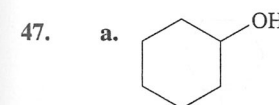
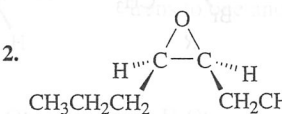
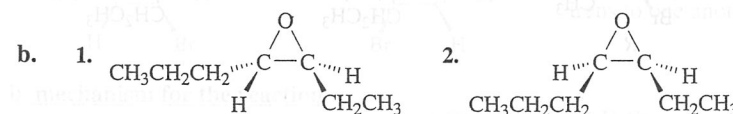


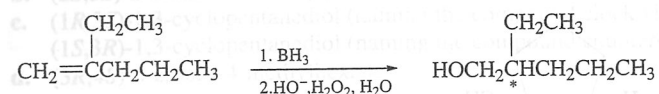
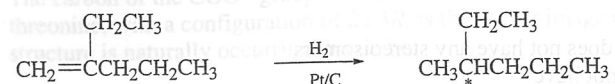
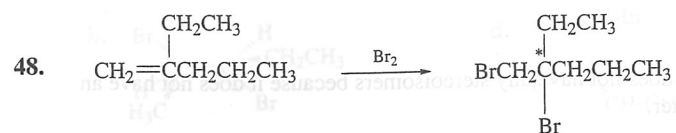
This compound does not have any stereoisomers because it does not have an asymmetric center.



Hydrogen will be more likely to add to the side of the ring where the hydrogen substituent is than to side of the ring where the methyl substituent is because hydrogen provides less steric hindrance than a methyl group does.

46. a. 1. *trans*-3-heptene 2. *cis*-3-heptene

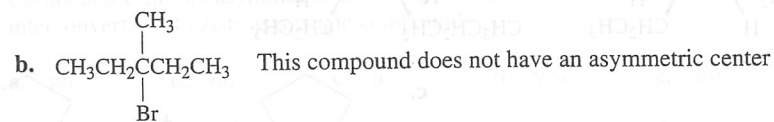
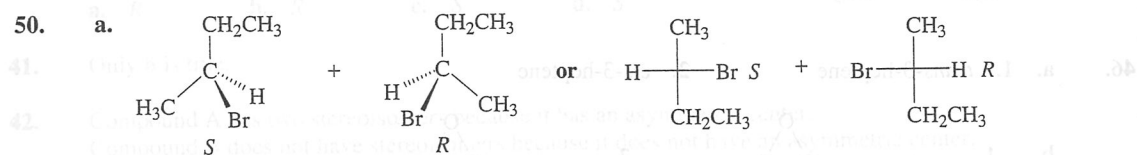




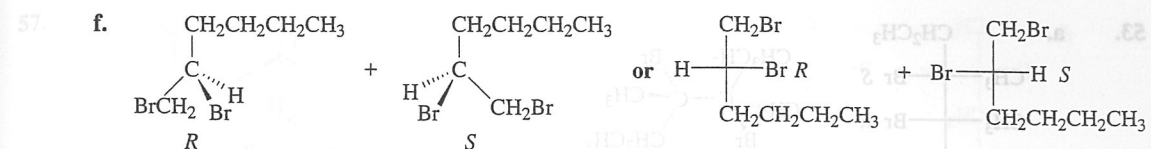
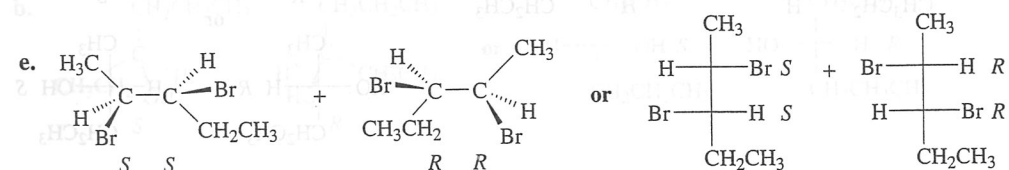
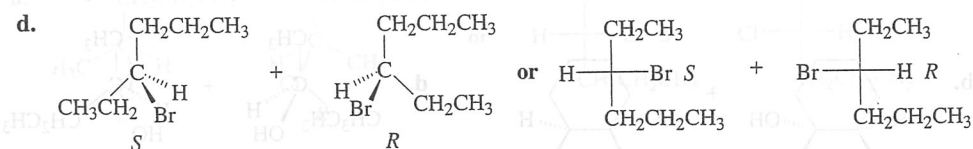
(* indicates an asymmetric center)

Each of the reactions forms a compound with one asymmetric center from a compound with no asymmetric centers. Therefore, each of the products is a racemic mixture.

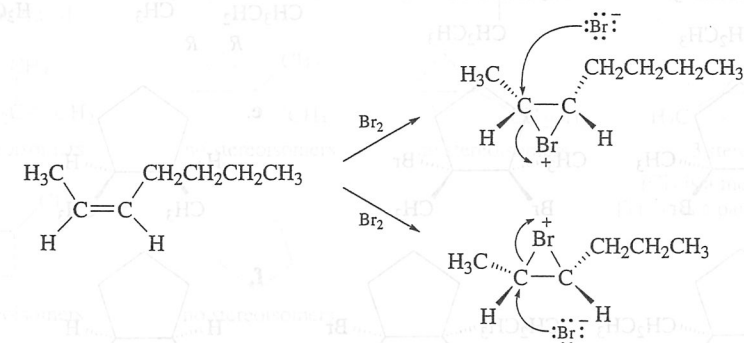
49. You could identify the intermediate that is formed by determining the number of products that are formed. Because *trans*-2-butene forms a cyclic bromonium ion intermediate, it forms only the erythro enantiomers. If the reaction formed a carbocation intermediate, both the erythro pair of enantiomers and the threo pair of enantiomers would be formed because both syn and anti addition could occur.



c. Same as b.

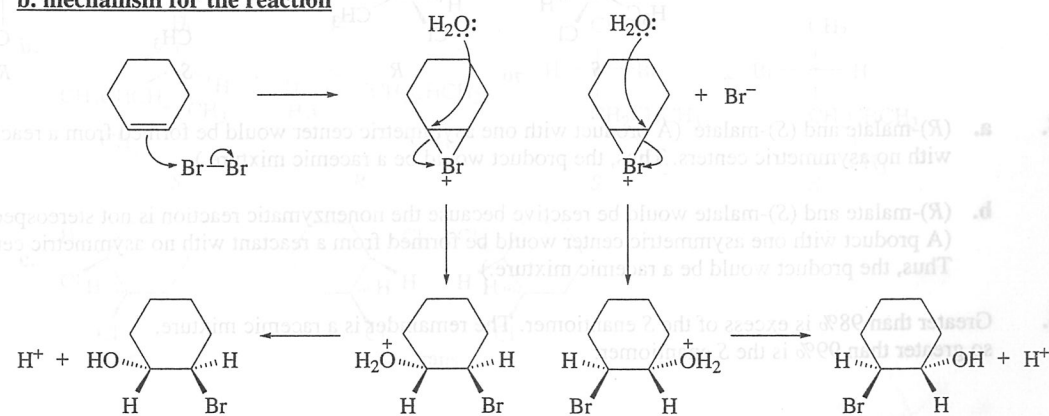


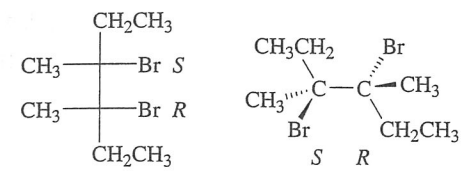
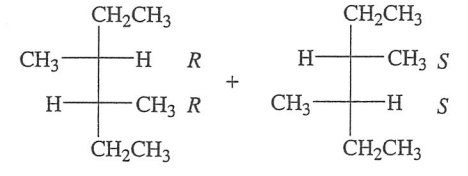
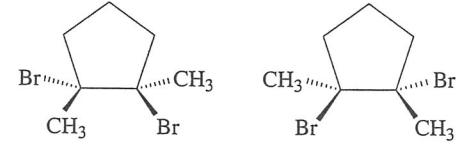
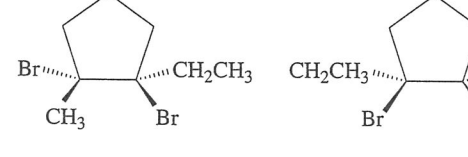
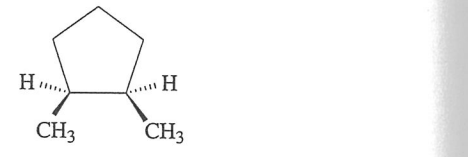
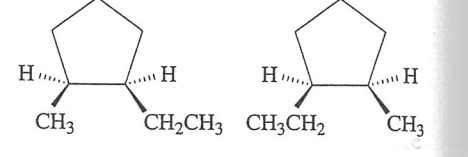
51. Two different bromonium ions are formed because Br^+ can add to the double bond either from the top of the plane or from the bottom of the plane defined by the alkene, and the two bromonium ions are formed in equal amounts. Attacking the less hindered carbon of one bromonium ion forms one stereoisomer, while attacking the less hindered carbon of the other bromonium ion forms the other stereoisomer.

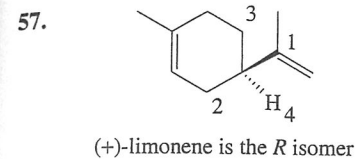


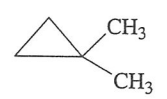
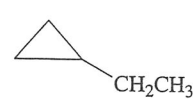
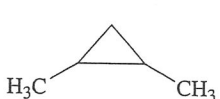
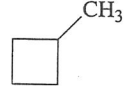
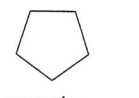
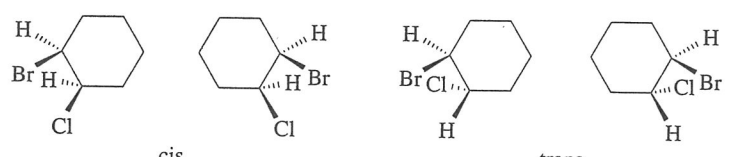
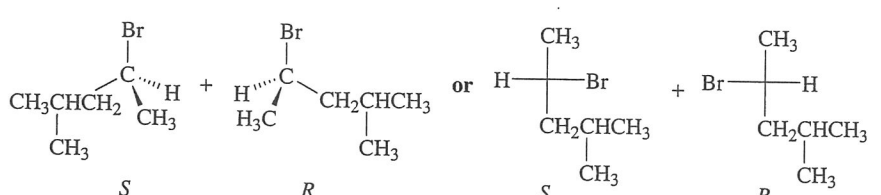
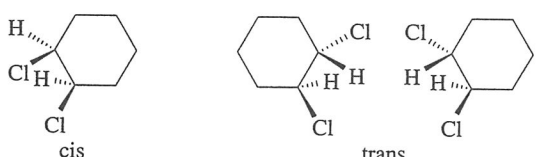
52. a.
$$\begin{array}{c} \text{HO} \\ | \\ \text{C}_6\text{H}_{10} \\ | \\ \text{H} \quad \text{Br} \end{array} \text{ and } \begin{array}{c} \text{H} \\ | \\ \text{C}_6\text{H}_{10} \\ | \\ \text{Br} \quad \text{OH} \end{array}$$
 The addition of Br and OH are anti, so in a cyclic compound these two substituents are trans to one another.

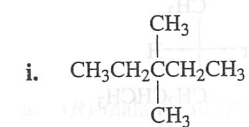
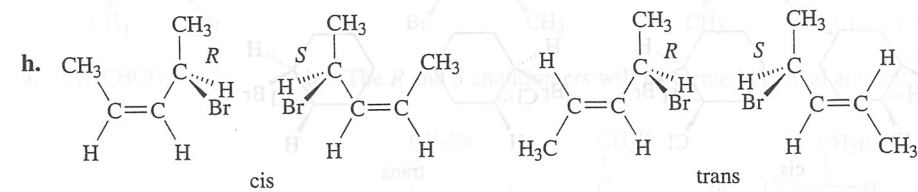
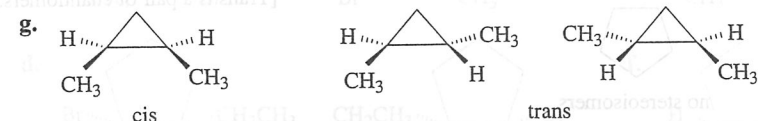
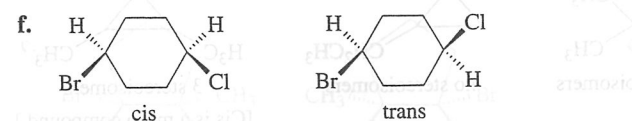
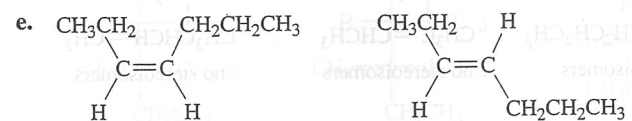
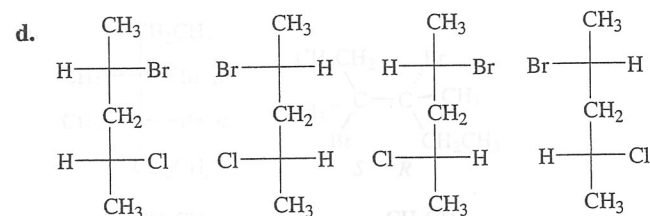
b. mechanism for the reaction



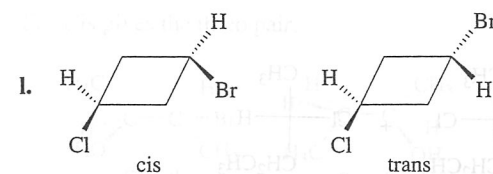
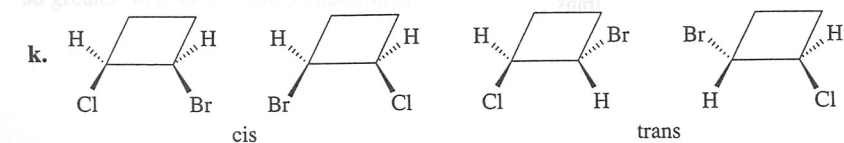
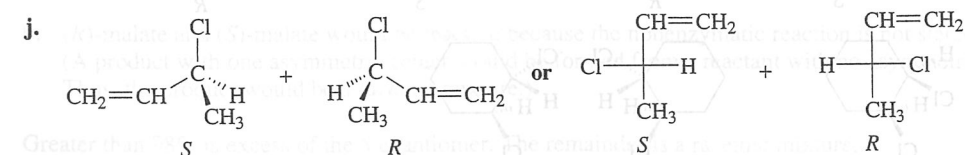
53. a. 
- b. 
- c. 
- d. 
- e. 
- f. 
54. a. $\text{CH}_3\text{CHCH}_2\text{Br}$
|
Cl
- b. The *R* and *S* enantiomers will be formed in equal amounts.
55. a. (*R*)-malate and (*S*)-malate (A product with one asymmetric center would be formed from a reactant with no asymmetric centers. Thus, the product would be a racemic mixture.)
- b. (*R*)-malate and (*S*)-malate would be reactive because the nonenzymatic reaction is not stereospecific. (A product with one asymmetric center would be formed from a reactant with no asymmetric centers. Thus, the product would be a racemic mixture.)
56. Greater than 98% is excess of the *S* enantiomer. The remainder is a racemic mixture, so greater than 99% is the *S* enantiomer.



58. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$ 2 stereoisomers [cis and trans]
- $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$ no stereoisomers
- $\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_3$ no stereoisomers
- $\text{CH}_3\text{CHCH}=\text{CH}_2$ no stereoisomers
- $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$ no stereoisomers
-  no stereoisomers
-  no stereoisomers
-  3 stereoisomers [Cis is a meso compound.] [Trans is a pair of enantiomers.]
-  no stereoisomers
-  no stereoisomers
59. a. 
- b. 
- c. 



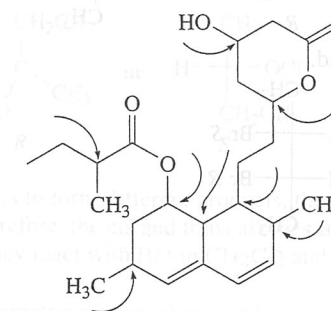
No isomers are possible for this compound because it does not have an asymmetric center.



60. Only the fourth one (CHFBrCl) is optically active.

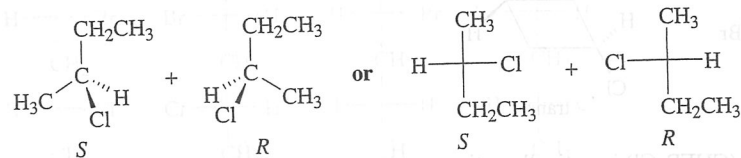
61. a. (R)-3-methyl-1-pentene
 b. (E)-1-bromo-2-chloro-2-fluoro-1-iodoethene
 c. (2R,3R)-3-chloro-2-pentanol
 d. (Z)-2-bromo-1-chloro-1-fluoroethene
 e. 8-bromo-2-ethyl-1-octene
 f. (E)-1,3-dibromo-4,7-dimethyl-3-octene
 g. (S)-2-methyl-1,2,5-pentanetriol
 h. (2S,3S)-1,2-dibromo-2-methyl-3-pentanol
 i. (E)-4-(2-chloroethyl)-2,3-dimethyl-3-octene

62. Mevacor has eight asymmetric centers.

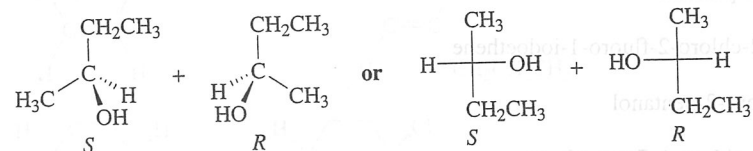


63. a. diastereomers
 b. enantiomers
 c. constitutional isomers
 d. diastereomers
 e. diastereomers
 f. identical
 g. diastereomers
 h. identical

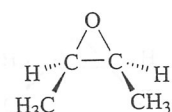
64. 1. Both cis and trans give these products.



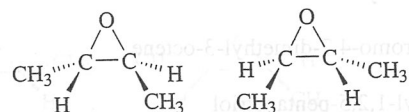
2. Both cis and trans give these products.



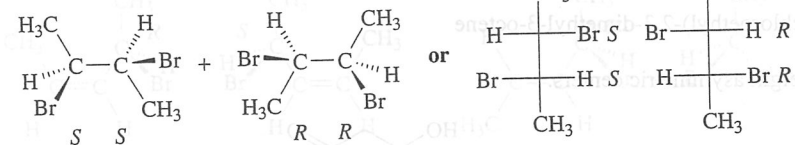
3. Cis gives a meso compound.



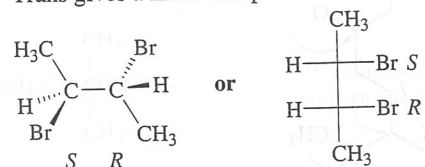
Trans gives a pair of enantiomers.



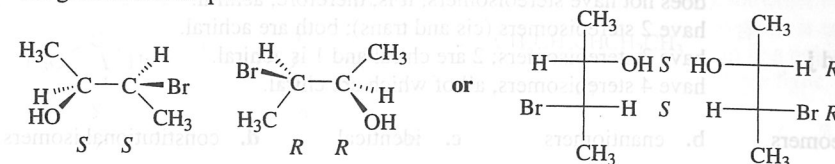
4. Cis gives the threo pair.



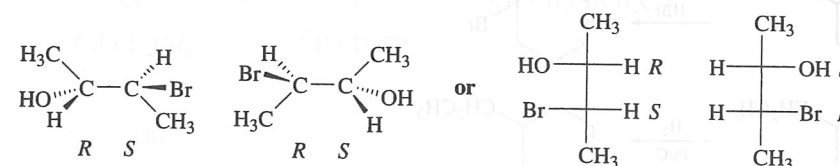
Trans gives a meso compound.



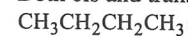
5. Cis gives the threo pair.



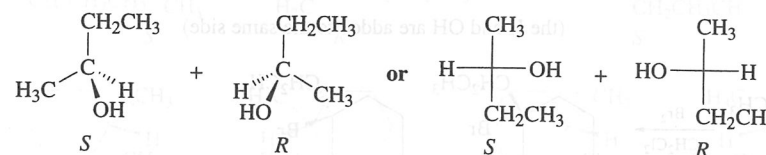
Trans gives the erythro pair.



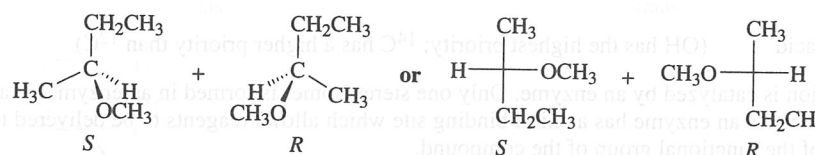
6. Both cis and trans give this product.



7. Both cis and trans give these products.



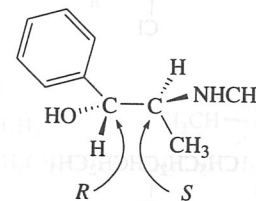
8. Both cis and trans give these products.

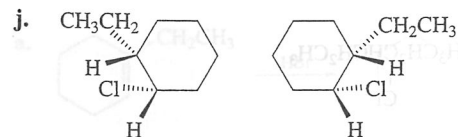
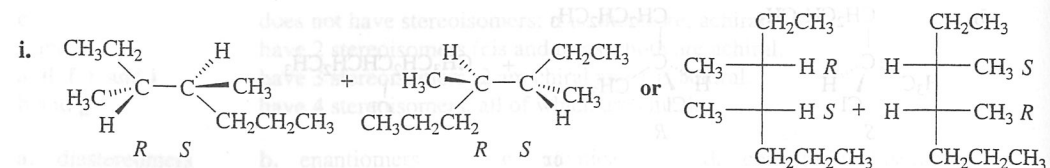


- b. For the cis and trans isomers to form different products, the reaction must form two new asymmetric centers in the product. Therefore, the cis and trans alkenes form different products when they react with a peroxyacid, when they react with Br
- ₂
- in CH
- ₂
- Cl
- ₂
- and when they react with Br
- ₂
- in H
- ₂
- O.

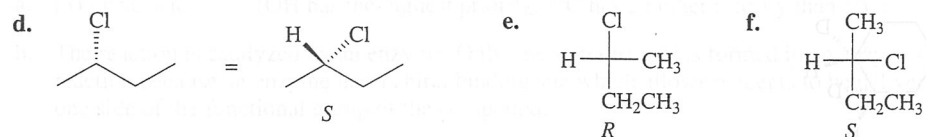
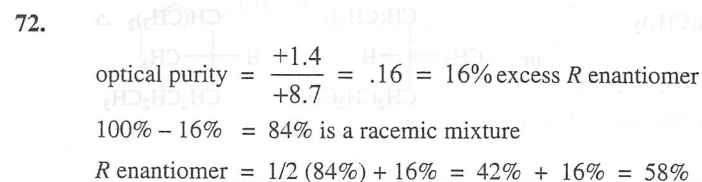
65. a. Because there are two asymmetric centers, there are four possible stereoisomers.

- b.



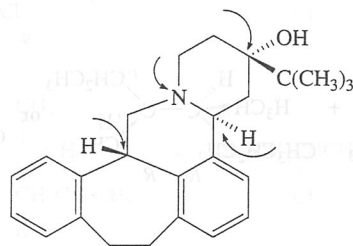


71. a. identical e. constitutional isomers
 b. identical f. diastereomers
 c. enantiomers g. constitutional isomers
 d. constitutional isomers h. enantiomers

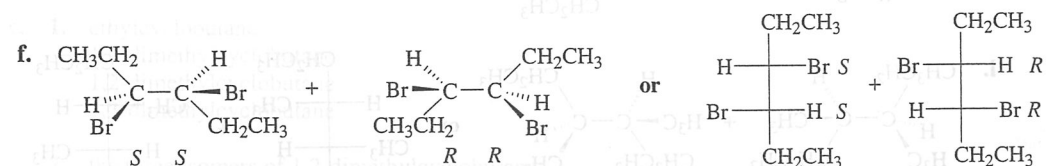
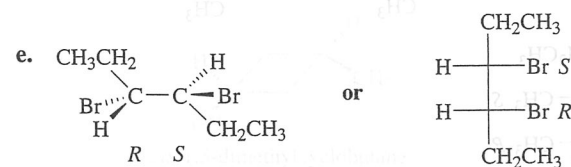
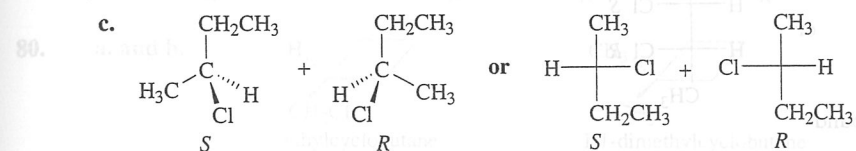
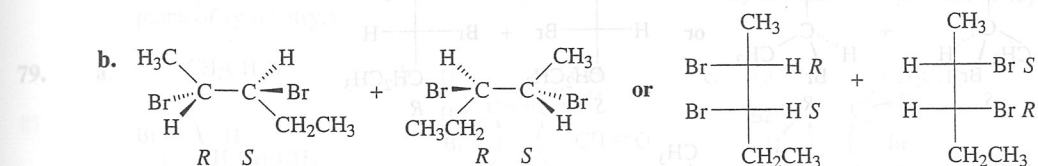
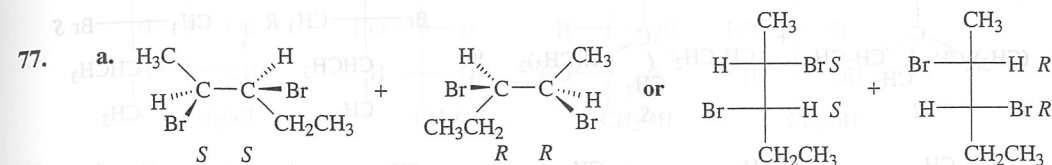


74. $[\alpha] = \frac{\alpha}{l \times c} = \frac{-1.8^\circ}{[2.0\text{dm}][0.15\text{g/mL}]} = -6.0$

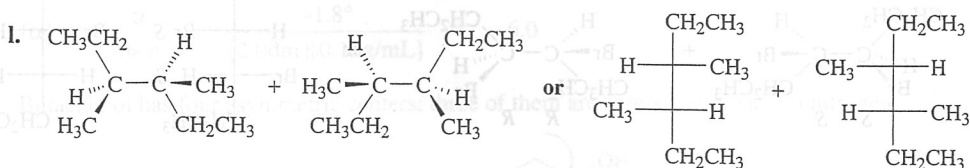
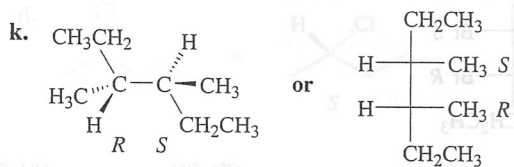
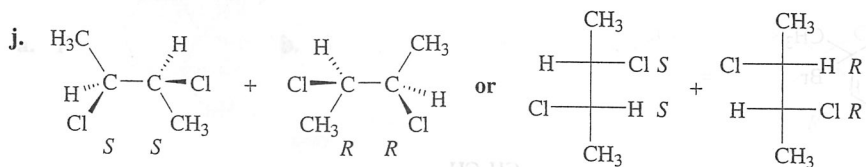
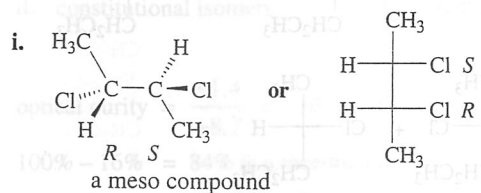
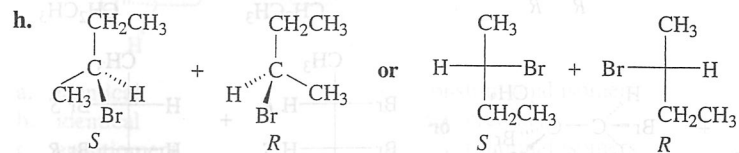
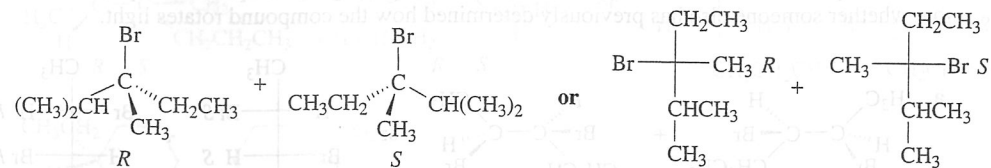
75. Butaclamol has four asymmetric centers; three of them are carbons and one is a nitrogen.



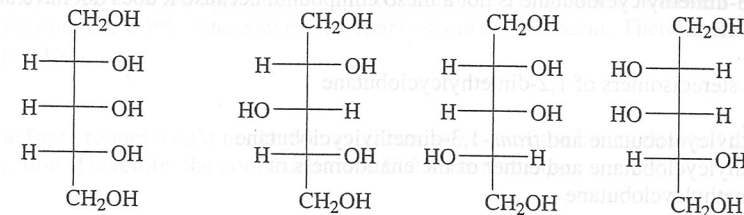
76. *R* and *S* are related to (+) and (-) in that if one configuration (say, *R*) is (+), the other one is (-). Because some compounds with the *R* configuration are (+) and some are (-), there is no way to determine whether a particular *R* enantiomer is (+) or (-) without putting the compound in a polarimeter or finding out whether someone else has previously determined how the compound rotates light.



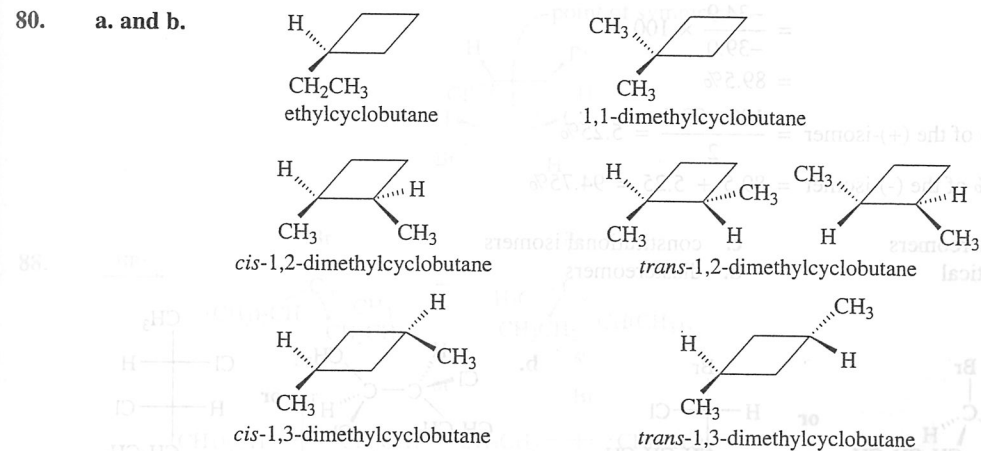
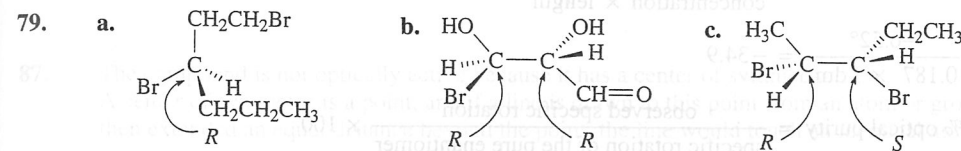
- g. The initially formed carbocation is secondary. It undergoes a 1,2-methyl shift to form a tertiary carbocation that gives the products shown below.



78. a. The compound has four stereoisomers.



- b. The first two stereoisomers are optically inactive because they are meso compounds. (They have a plane of symmetry.)



- c. 1. ethylcyclobutane
1,1-dimethylcyclobutane
1,2-dimethylcyclobutane
1,3-dimethylcyclobutane
2. the three isomers of 1,2-dimethylcyclobutane
the two isomers of 1,3-dimethylcyclobutane
3. *cis*- and *trans*-1,2-dimethylcyclobutane
cis- and *trans*-1,3-dimethylcyclobutane
4. the two *trans* stereoisomers of 1,2-dimethylcyclobutane
5. all the isomers except the two *trans* stereoisomers of 1,2-dimethylcyclobutane

6. *cis*-1,2-dimethylcyclobutane
(Note: *cis*-1,3-dimethylcyclobutane is not a meso compound, because it does not have any symmetric centers.)
7. the two *trans* stereoisomers of 1,2-dimethylcyclobutane
8. *cis*-1,3-dimethylcyclobutane and *trans*-1,3-dimethylcyclobutane
cis-1,2-dimethylcyclobutane and either of the enantiomers of *trans*-1,2-dimethylcyclobutane

81.

$$\text{observed specific rotation} = \frac{\text{observed rotation}}{\text{concentration} \times \text{length}}$$

$$\frac{-6.52^\circ}{0.187 \times 1 \text{ dm}} = -34.9$$

$$\% \text{ optical purity} = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}} \times 100$$

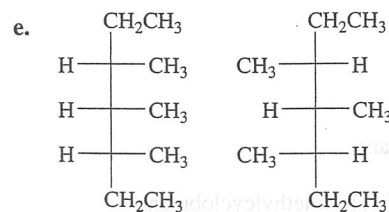
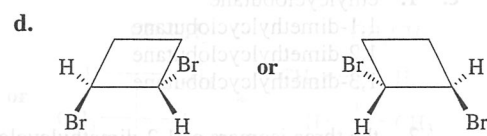
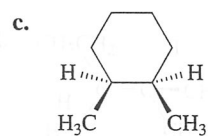
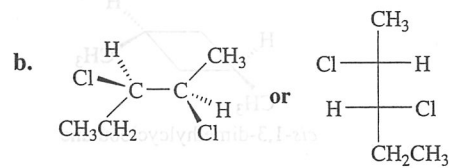
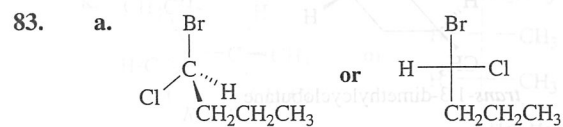
$$= \frac{-34.9}{-39.0} \times 100$$

$$= 89.5\%$$

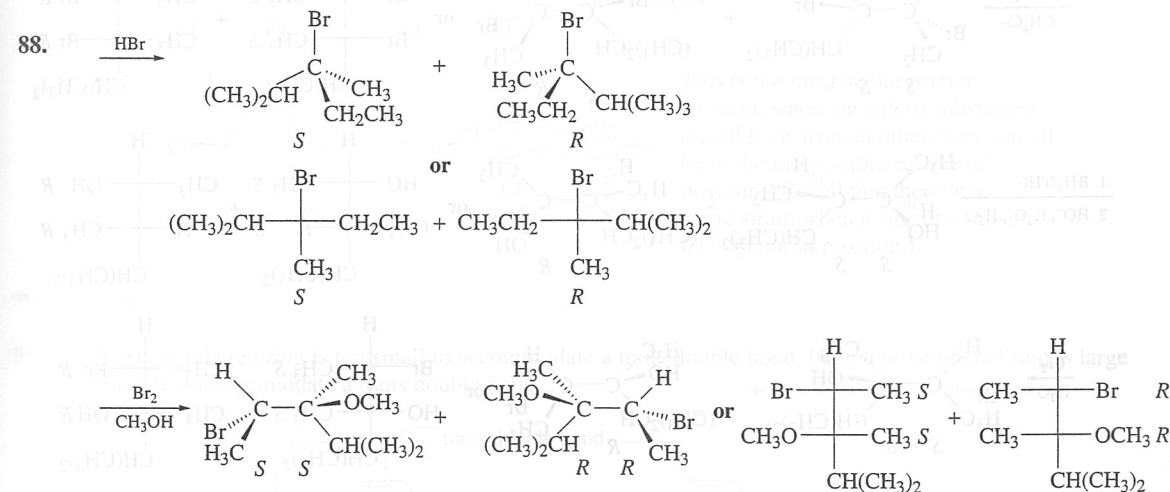
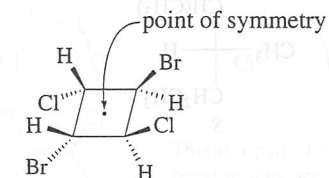
$$\% \text{ of the (+)-isomer} = \frac{100 - 89.5}{2} = 5.25\%$$

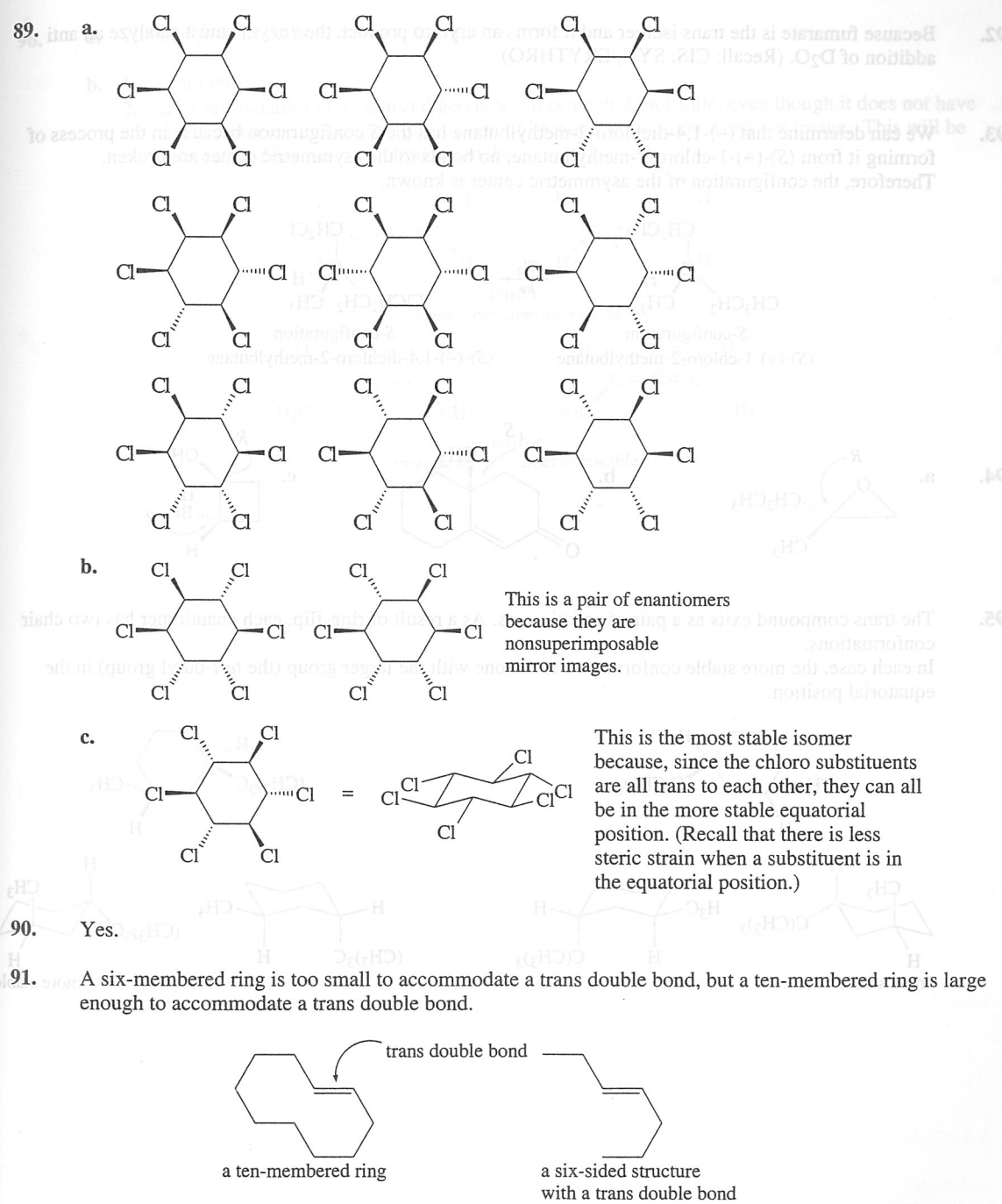
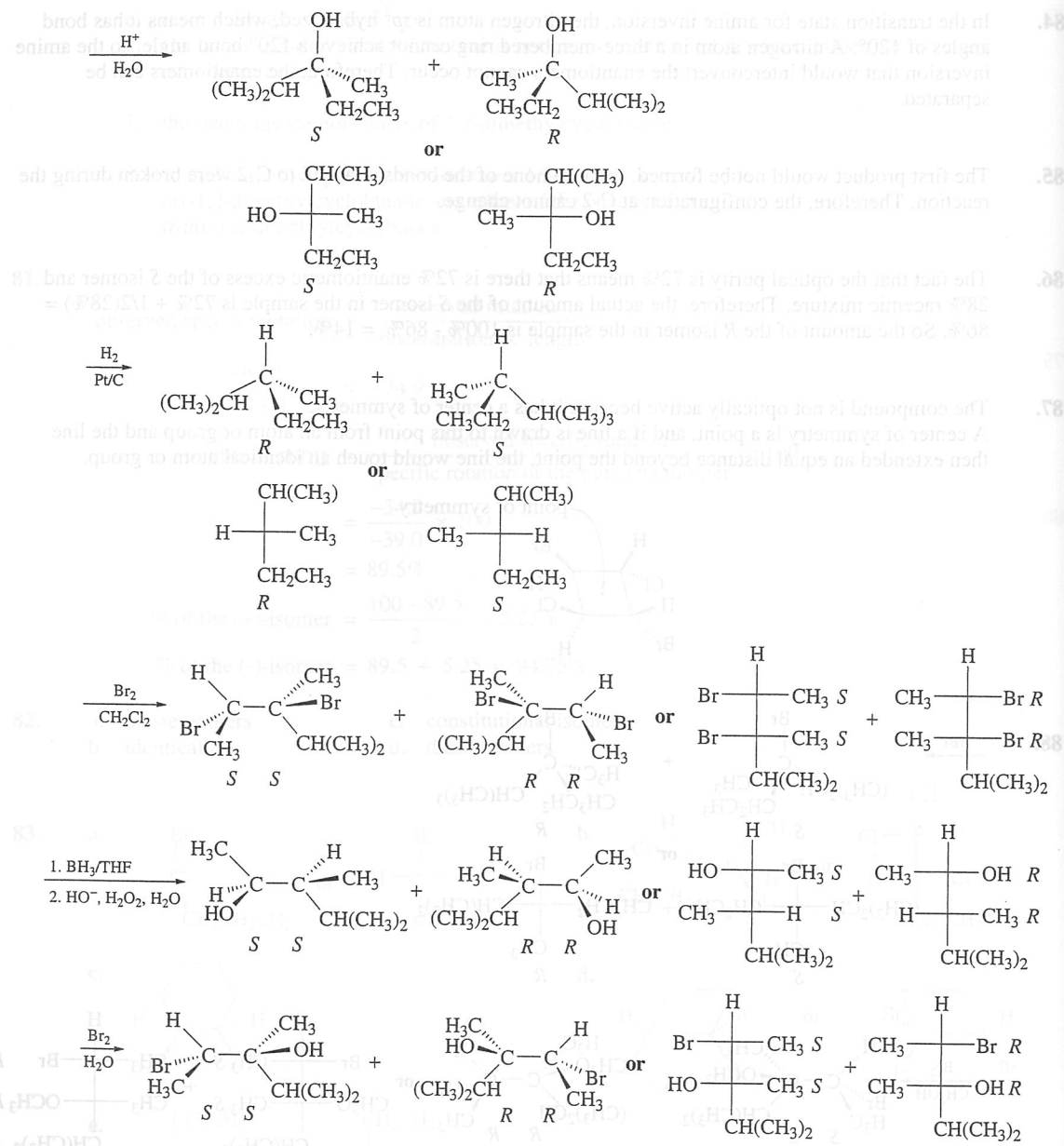
$$\% \text{ of the (-)-isomer} = 89.5 + 5.25 = 94.75\%$$

82. a. diastereomers c. constitutional isomers
b. identical d. diastereomers

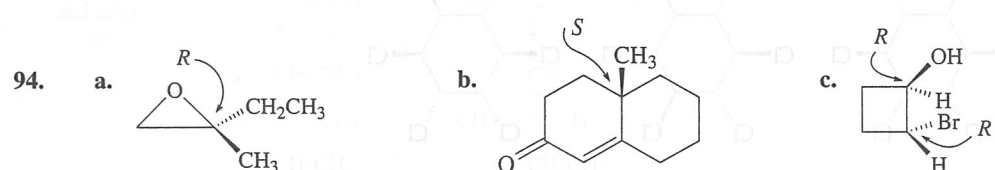
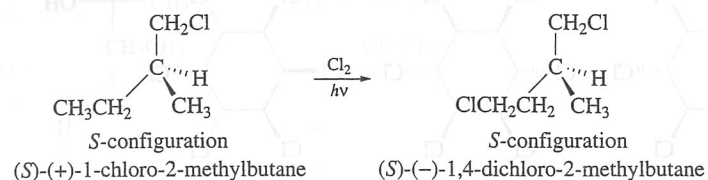


84. In the transition state for amine inversion, the nitrogen atom is sp^2 hybridized, which means it has bond angles of 120° . A nitrogen atom in a three-membered ring cannot achieve a 120° bond angle, so the amine inversion that would interconvert the enantiomers cannot occur. Therefore, the enantiomers can be separated.
85. The first product would not be formed, because none of the bonds attached to C-2 were broken during the reaction. Therefore, the configuration at C-2 cannot change.
86. The fact that the optical purity is 72% means that there is 72% enantiomeric excess of the *S* isomer and 28% racemic mixture. Therefore, the actual amount of the *S* isomer in the sample is $72\% + 1/2(28\%) = 86\%$. So the amount of the *R* isomer in the sample is $100\% - 86\% = 14\%$.
87. The compound is not optically active because it has a center of symmetry. A center of symmetry is a point, and if a line is drawn to this point from an atom or group and the line then extended an equal distance beyond the point, the line would touch an identical atom or group.

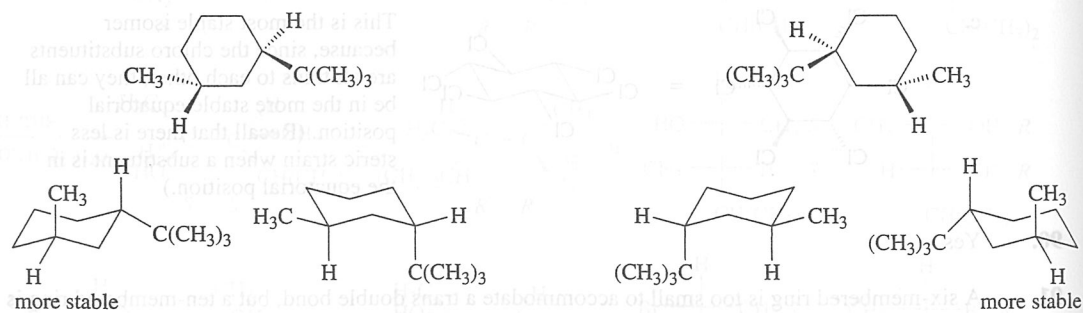




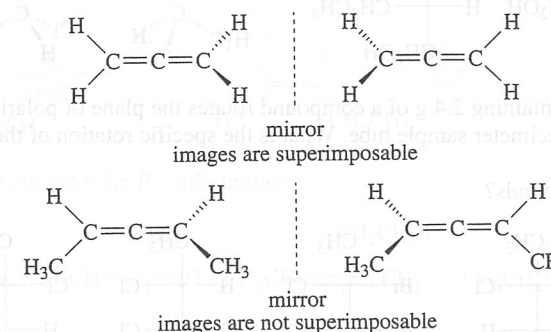
92. Because fumarate is the trans isomer and it forms an erythro product, the enzyme must catalyze an anti addition of D_2O . (Recall: CIS, SYN, ERYTHRO)
93. We can determine that $(-)$ -1,4-dichloro-2-methylbutane has the *S* configuration because in the process of forming it from (S) - $(+)$ -1-chloro-2-methylbutane, no bonds to the asymmetric center are broken. Therefore, the configuration of the asymmetric center is known.



95. The trans compound exists as a pair of enantiomers. As a result of ring-flip, each enantiomer has two chair conformations. In each case, the more stable conformation is the one with the larger group (the *tert*-butyl group) in the equatorial position.



96. a. The compounds do not have any asymmetric centers.
- b. 1. is not chiral.
2. is chiral. Because of its unusual geometry, it is a chiral molecule, even though it does not have any asymmetric centers, because it cannot be superimposed on its mirror image. This will be easier to understand if you build models.



10. Draw the stereoisomers of:
- a. 2,3-dibromopentane
- b. 2,3-dibromopentane
11. Give the stereochemistry of the products that would be obtained from each of the following reactions:
- a. 1-pentene + HCl
- b. 2-pentene + HBr
- c. trans-3-pentene + HBr
- d. trans-3-pentene + HBr
12. R - $(-)$ -2-methyl-1-butanol can be oxidized to (+)-2-methylbutanoic acid without breaking any of the bonds to the asymmetric center. What is the configuration of $(-)$ -2-methylbutanoic acid?
13. Which of the following is a chiral molecule?
- a. b. c. d. e. f. g. h. i. j. k. l. m. n. o. p. q. r. s. t. u. v. w. x. y. z. aa. ab. ac. ad. ae. af. ag. ah. ai. aj. ak. al. am. an. ao. ap. aq. ar. as. at. au. av. aw. ax. ay. az. ba. bb. bc. bd. be. bf. bg. bh. bi. bj. bk. bl. bm. bn. bo. bp. bq. br. bs. bt. bu. bv. bw. bx. by. bz. ca. cb. cc. cd. ce. cf. cg. ch. ci. cj. ck. cl. cm. cn. co. cp. cq. cr. cs. ct. cu. cv. cw. cx. cy. cz. da. db. dc. dd. de. df. dg. dh. di. dj. dk. dl. dm. dn. do. dp. dq. dr. ds. dt. du. dv. dw. dx. dy. dz. ea. eb. ec. ed. ee. ef. eg. eh. ei. ej. ek. el. em. en. eo. ep. eq. er. es. et. eu. ev. ew. ex. ey. ez. fa. fb. fc. fd. fe. ff. fg. fh. fi. fj. fk. fl. fm. fn. fo. fp. fq. fr. fs. ft. fu. fv. fw. fx. fy. fz. ga. gb. gc. gd. ge. gf. gg. gh. gi. gj. gk. gl. gm. gn. go. gp. gq. gr. gs. gt. gu. gv. gw. gx. gy. gz. ha. hb. hc. hd. he. hf. hg. hh. hi. hj. hk. hl. hm. hn. ho. hp. hq. hr. hs. ht. hu. hv. hw. hx. hy. hz. ia. ib. ic. id. ie. if. ig. ih. ii. ij. ik. il. im. in. io. ip. iq. ir. is. it. iu. iv. iw. ix. iy. iz. ja. jb. jc. jd. je. jf. jg. jh. ji. jj. jk. jl. jm. jn. jo. jp. jq. jr. js. jt. ju. jv. jw. jx. jy. jz. ka. kb. kc. kd. ke. kf. kg. kh. ki. kj. kl. km. kn. ko. kp. kq. kr. ks. kt. ku. kv. kw. kx. ky. kz. la. lb. lc. ld. le. lf. lg. lh. li. lj. lk. ll. lm. ln. lo. lp. lq. lr. ls. lt. lu. lv. lw. lx. ly. lz. ma. mb. mc. md. me. mf. mg. mh. mi. mj. mk. ml. mn. mo. mp. mq. mr. ms. mt. mu. mv. mw. mx. my. mz. na. nb. nc. nd. ne. nf. ng. nh. ni. nj. nk. nl. nm. no. np. nq. nr. ns. nt. nu. nv. nw. nx. ny. nz. oa. ob. oc. od. oe. of. og. oh. oi. oj. ok. ol. om. on. oo. op. oq. or. os. ot. ou. ov. ow. ox. oy. oz. pa. pb. pc. pd. pe. pf. pg. ph. pi. pj. pk. pl. pm. pn. po. pp. pq. pr. ps. pt. pu. pv. pw. px. py. pz. qa. qb. qc. qd. qe. qf. qg. qh. qi. qj. qk. ql. qm. qn. qo. qp. qq. qr. qs. qt. qu. qv. qw. qx. qy. qz. ra. rb. rc. rd. re. rf. rg. rh.