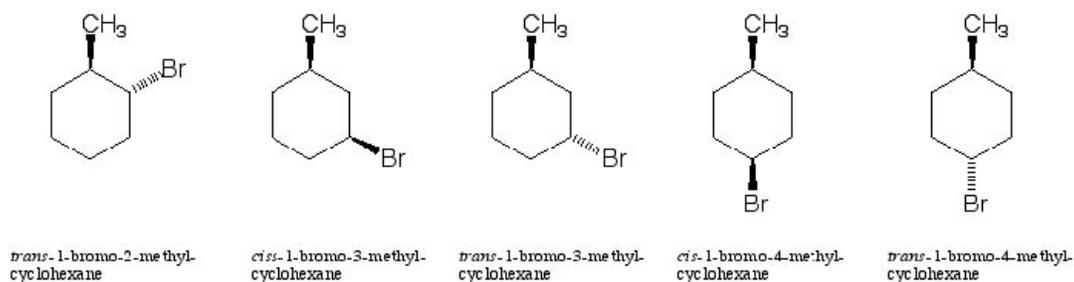**4-1** You must work this exercise with molecular models to understand the shapes and flexibilities of the various cyclic compounds.

4-2 This exercise is worked out on page 134 as "Working with Concepts".

4-3 Remember that at UCSD, faculty do not require that students be able to properly name structures, only to be able to draw structures from names. You can practice the latter with these compounds and names.

trans-1-bromo-2-methyl-cyclohexane   ciss-1-bromo-3-methyl-cyclohexane   trans-1-bromo-3-methyl-cyclohexane   cis-1-bromo-4-methyl-cyclohexane   trans-1-bromo-4-methyl-cyclohexane

4-4 The methyl groups in the *cis* isomer are too close to each other and thus, the *cis* isomer is less stable than is the *trans*. For isomeric structures, the less stable isomer releases for energy in an exothermic reaction (as is combustion).
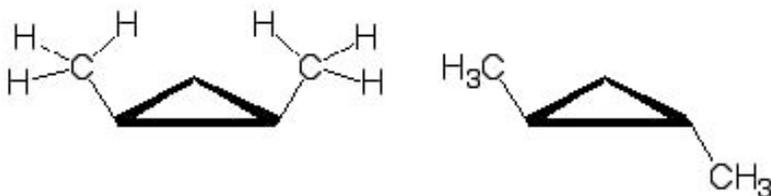
4-5 This exercise is worked out, but poorly, on page 138 as "Working with Concepts". Here is the basic idea. We want to estimate the energy release for the illustrated reaction in which the following bond changes occur:

Bonds broken	energy	Bonds made	energy	Delta
C—C	85.5	C—H	98.5	
H—H	104	C—H	98.5	
	189.5		197.0	7.5

We can find these energies values in Tables 3-1, 3-2, be careful to note the particular

type of bond that we are dealing with in this example. However, in addition to the change in bond energies that accompanies this reaction, there is the relief of ring strain as the three- and four-membered rings go away and a five-memebered ring takes their place. The difference between the ring strain of the smaller rings (27.6 and 26.3, total 53.9, from Table 4-2) and the five-membered ring (6.5) means that an additional 47.4 kcal/mole will be released only because of the change in ring size. Combining the energy released as a result of bond changes (7.5) to that from ring strain relief (47.4) we arrive at an estimated heat of reaction of -54.9, as compared to the observed value of -56. This is a remarkable correspondence given that we would not anticipate that the ring strain of the four and three membered rings in the starting material would be the same as in cyclobutane and cyclopropane.

4-6 Having worked through the details of Exercise 4-5, we simple add the ring strain to the value for the reaction of a $C—C$ bond with $H—H$ (50.7 + 7.5 = 58.2) .

4-7 This is a prime example of why this author took it upon himself to provide detailed answers to the in-chapter exercises. Let's start with cyclopropane, which is planar. Looking down any one of the three identical $C—C$ bonds, we see that the conformation is eclipsed.
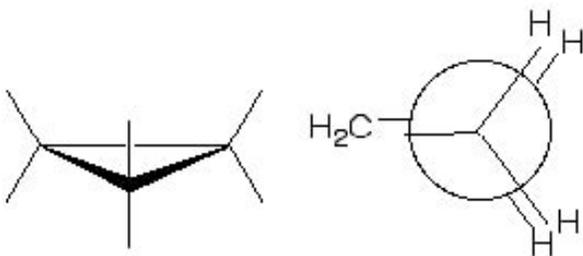
Here we use a variant of the Newman projection for an eclipsed conformation where, instead of a slight rotation about the bond to show the bonds on the rear atom, we simply offset the bonds slightly. Either works and both are correct.

We know that cyclobutane is not planar but rather one atom is moved out of the plane of the other three. Nonetheless, all atoms are identical as three atoms define a plane. Unfortunately, molecular models "know" nothing about eclipsing interactions and respond only to bond angles (there is one exception: Drieding molecular models have atoms specifically made for each ring size so the bias of the tetrahedral carbon is absent-even these models are not biased for eclipsing interactions). So when you build a four-membered ring with models that have tetrahedral carbon atoms, the ring will have a strong bias for being planar.
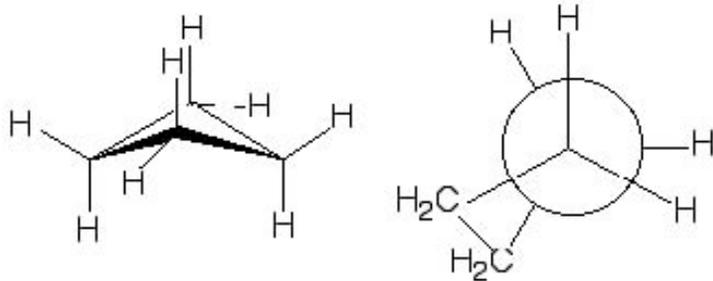
Now with cyclopentane, the exercise becomes enormous. We know that there are two nearly equal energy conformation of cyclopentane, the envelope and the half chair. Let's start with the envelope which has one atom out of the plane of the other four. Thus, we have three unique types of carbon atoms in the envelope: the one that is out of the plane; the two attached directly to the one out of the plane; and the other two. And, as a result, there are three unique types of bonds. One of which is fully eclipsed (can you find it?). Moving to the half chair, we know that there are two adjacent atoms out of the plane defined by the other three, one above and one below that plane. Once again, there are three unique carbon atoms and three unique bonds, conformationally speaking. One of these if fully staggered (can you find this one?).

The primary value of this exercise is that it forces you to pick up your models and work with them.

4-8 This is nothing but simple math, solving the equation: $\log K = -G/1.36$ or $K = 10\exp(-G/1.36)$.

$K = 10\exp(-1.25) = 0.056$

Note that K derived from the ratio given of 95:5 back calculates to a value of 1.73 kcal/mole for G. Thus, the difference is the result of the lack of precision in the given value of G.

4-9 This exercise is worked out on page 146 as "Working with Concepts".

4-10 Note that there are two cyclohexane rings that can be traced from the 11 ring carbon atoms in these isomers. Isomer A has one of the rings as a rigid boat (make models to convince your self that the other ring prevents the boat from becoming a twist boat.

4-11 As with exercise 4-6, this is a math problem. First, we find the energy difference between how much each group involved is disfavored in the axial position. Then, we use the same equation as in 4-6: $K = 10\exp(-G/1.36)$
    (a) methyl 1.70; ethyl 1.75, difference 0.05. $K = 1.09$
    (b) The difference is the same, we are look for how much difference there is between a methyl axial and an ethyl axial.
    (c) Now both groups will be either axial or equitorial. So the values become additive. $G= 3.45$, $K = 344$.

4-12 A good rule to remember is that when two substituents on different carbon atoms are cis to each other, the *other* two substituents are also *cis*.
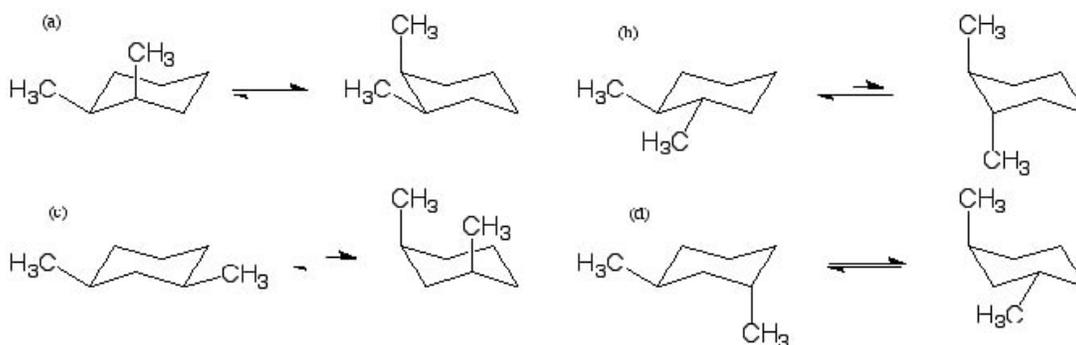

**4-13** This exercise is worked out on page 147-8 as "Working with Concepts".

4-14 While we focus on the 1.3-diaxial interactions the result from axial substituents on cyclohexane, we should not forget to look for ALL gauche butane-like interactions. When the methyl groups of *trans* 1,2-dimethylcyclohexane are equatorial, they are in a gauche butane-like arrangement to each other.

4-15 You must work this exercise with molecular models to understand the shapes and flexibilities of the various cyclic compounds.

4-16 There are three substituents on the cyclohexane ring of menthol. We can see from Table 4-3 that the isopropyl group has the greatest preference for being equitorial. Thus, we start by drawing a chair cyclohexane and adding an isopropyl group in an equitorial position. Now we can add an OH group trans on the adjacent carbon of the ring and a methyl group trans on the carbon on the opposite side of the ring.
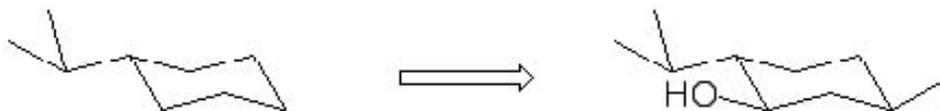
4-17 Terpenes are classified by the number of carbon atoms present. The upper structure has 15 carbon atoms and is thus a sesquiterpene whereas the lower structure has 10 carbon atoms and is a monoterpene.
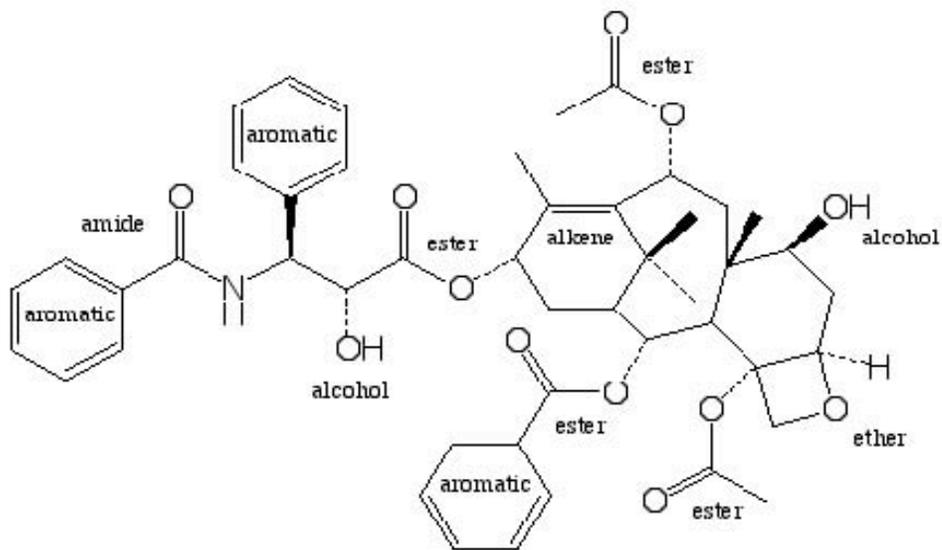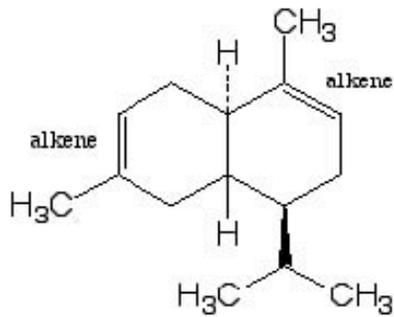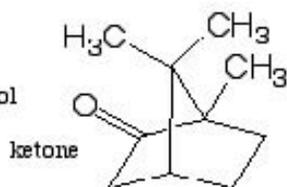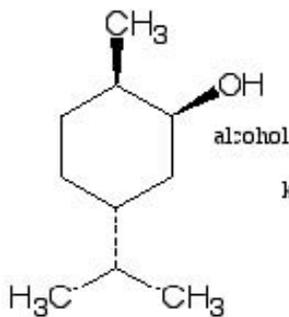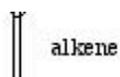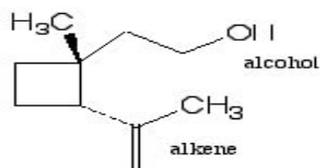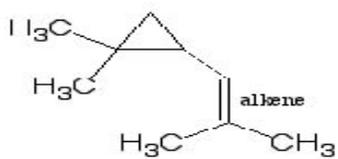
4-18 See the answer at the back of the book.