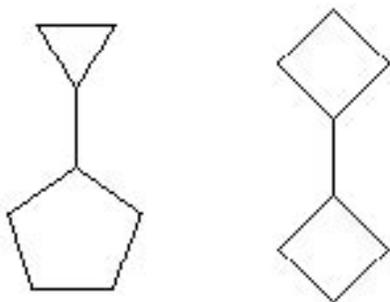


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5-1 These two molecules, cyclopropylcyclopentane and cyclobutylcyclobutane have the same number of carbon and hydrogen atoms and thus they are constitutional isomers.

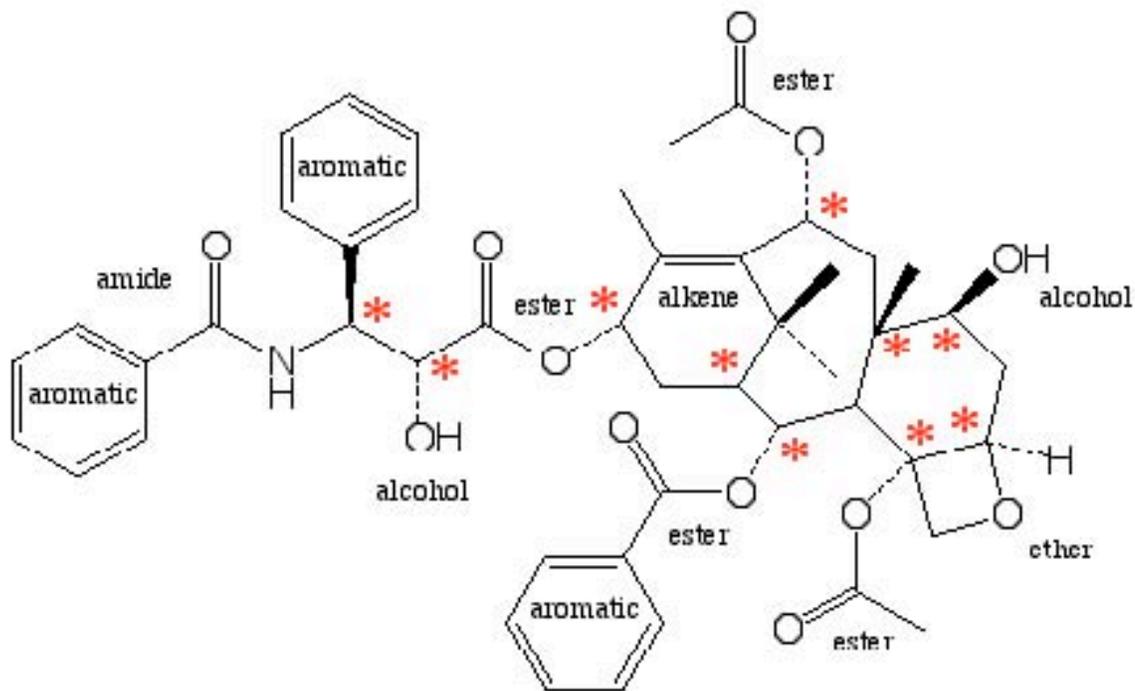
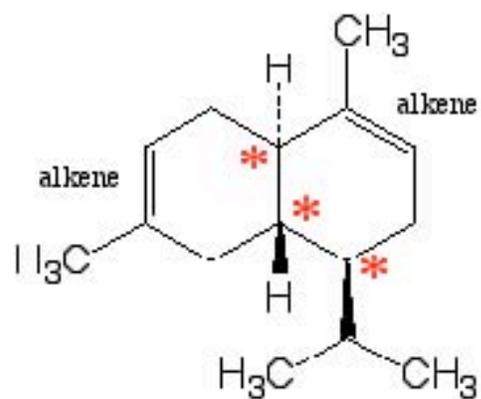
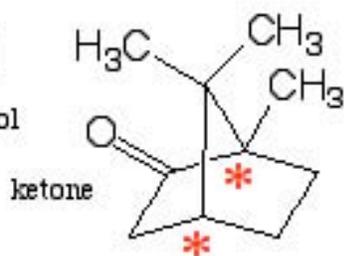
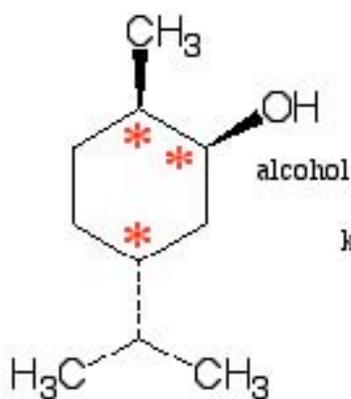
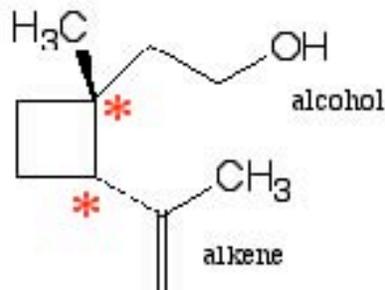
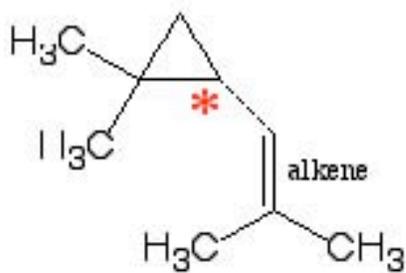


5-2 For any given cyclohexane, there are only two possible chair conformations. As both are given for methylcyclohexane above the exercise (equatorial on the left and axial on the right), the exercise is asking for conformations other than chairs. We know that there is only one other conformation that represents an energy minimum---the twist boat. Although the brief answer in the book includes the boat which represents an local energy maximum, few faculty would be looking for this as an answer. Indeed, if this is what the authors of the textbook were looking for, they should have included the half-chair conformation (see page 142).

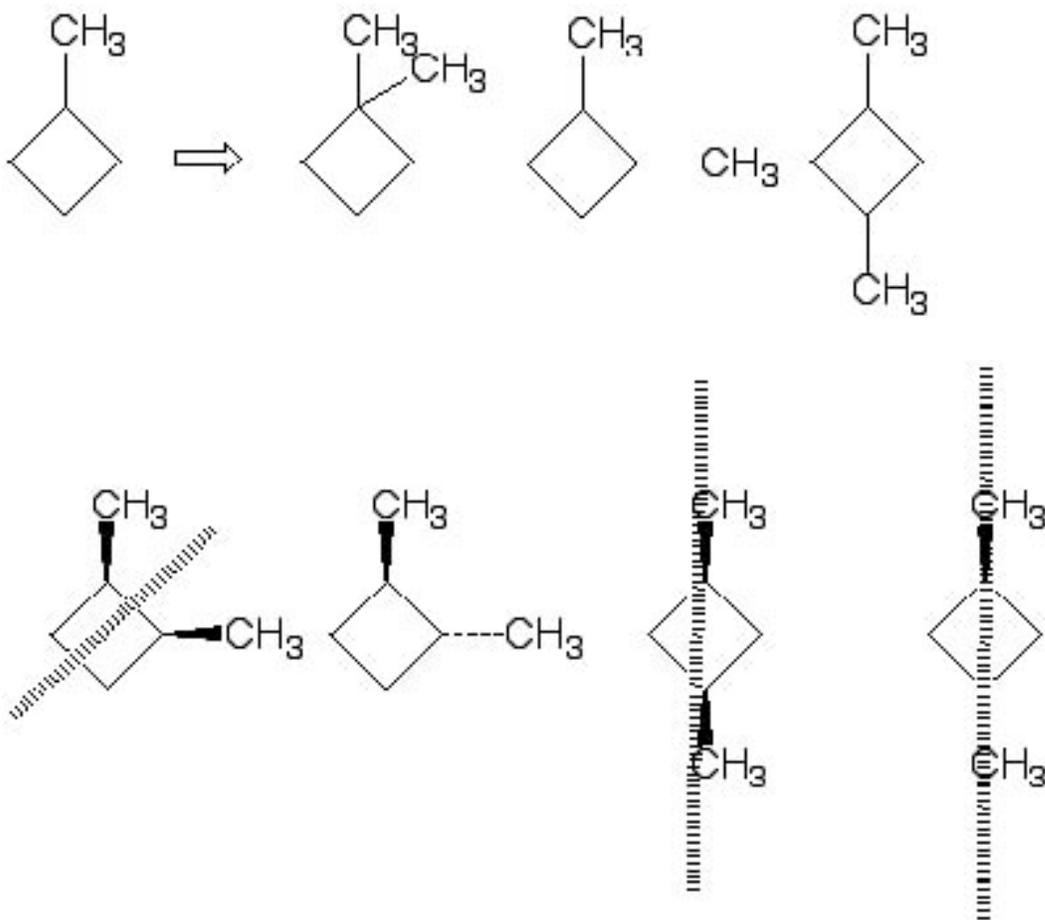
The twist boat is an interesting conformation of cyclohexane as, like the chair, all of the carbon atoms are identical. Nonetheless, there are two unique positions to which a substituent can be added. The twist boat is virtually impossible to represent as a three-dimensional object using a two-dimensional drawing so, once again, it is essential here that you use your models.

5-3 The stereocenters in each of the terpenes are marked below with a *. The presence of a single stereocenter is sufficient for a molecule to be chiral. With more than one stereocenter, the molecule will be chiral unless there is symmetry where stereocenters are present that have all

the same substituents but opposite stereochemistry. None of these molecules fall into this category so all are chiral.



5-5 We start by adding a single methyl group to cyclobutane to form methylcyclobutane and then recognize that there are three unique carbon atoms to which we could add the second methyl group: Now, we consider stereochemistry. The first, 1,1-dimethylcyclobutane has not stereocenter as all of the carbon atoms have two identical groups (either two methyls or two hydrogens). Forming 1,2-dimethylcyclobutane allows us to add the second methyl group either *cis* or *trans* to the first one. When the methyl groups are *cis*, there is a mirror plane and thus the molecule is achiral. Adding the second methyl to form 1,3-dimethylcyclobutane can again be done in two ways, to form *cis* and *trans* isomers. However, both have a mirror plane of symmetry.



5-6 The specific rotation is calculated from the experimentally observed rotation, α , from the equation:

$$[\alpha] = \alpha / l \times c.$$

The key to a problem such as this one is being sure to use the correct units for the length, l , and the concentration, c . The length is quite unusual as it is in decimeters and the concentration is in g/mL. Thus,

$$[\alpha] = 6.65/1 \times 0.1 = 66.5.$$

Enantiomers have equal but opposite rotations so the specific rotation for the enantiomer of natural sucrose is -66.5 .

5-7 This exercise is worked out on page 177 as "Working with Concepts".

5-8 The rotation of a sample is found simply by multiplying the specific rotation by the optical purity, or in this case, $+23.1 \times 0.75 = +17.3$. Note that with rotational values, we always include the plus sign for a positive rotation.

We can work the ratio part of this exercise as a purely mathematical one by rearranging the equation for optical purity at the bottom of page 176 in the textbook. But there is another way that may help you understand better why the answer comes up the way it does. Recall that enantiomers have equal rotation but with opposite sign. Also, the optical purity is a number that reflects the degree to which a mixture of enantiomers rotates light compared with a pure sample of a single enantiomer. Thus, the optical purity indicates how much of one enantiomer is present compared to a 1:1 mixture of both. For a sample that has an optical purity of 75%, 75% is a single enantiomer and the remaining 25% is a 1:1 mixture of the two enantiomers, which, as they cancel each others rotation, contribute nothing to the rotation of the sample. Thus, present is 75% + 12.5% of one enantiomer and 12.5% of the other. For 50% optical purity, the ratio is 50% + 25% to 25%. And for 25%, it is 25% + 37.5% to 25%. So in general, we subtract the optical purity from 100%, divide that by two, and add the result to the optical purity. That represents one enantiomer and the other is the difference between that and 100%.

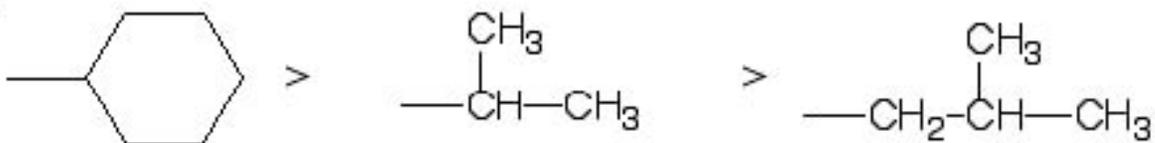
5-9 Remember, the Rules give priority to the substituent that "wins"

at the site nearest to the stereocenter regardless of what might be further removed. That is why 1-chloroethyl has higher priority than does 2-bromoethyl (d).

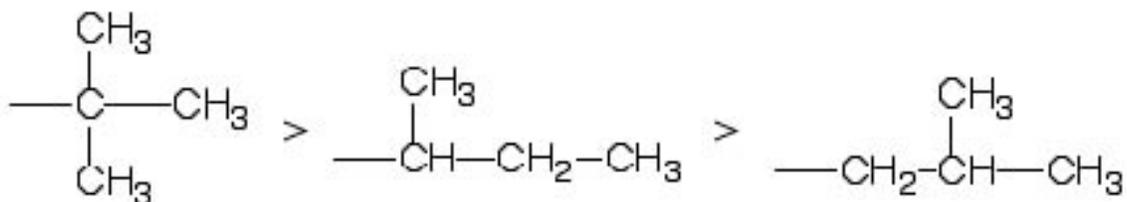
(a)



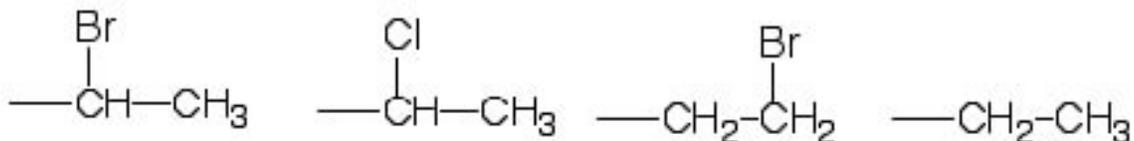
(b)



(c)



(d)

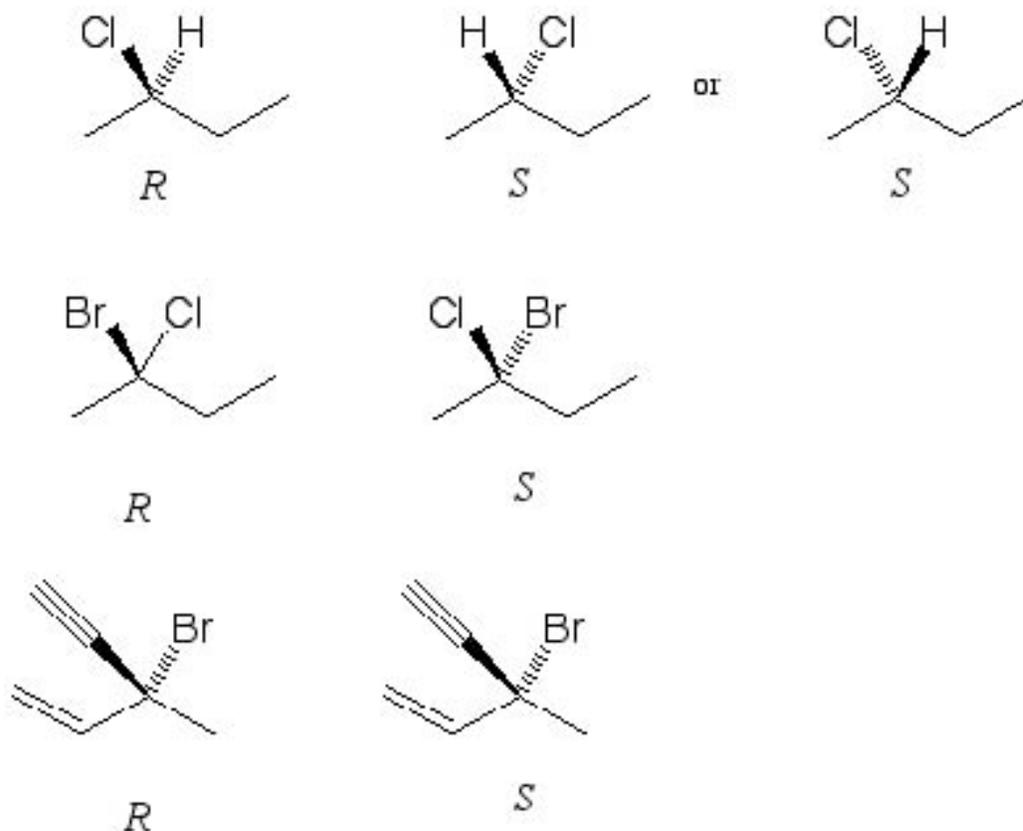


5-10 This exercise is worked out on page 181 as "Working with Concepts".

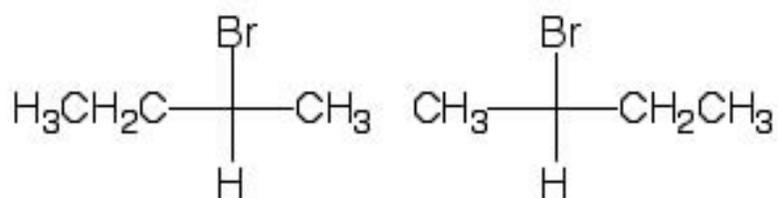
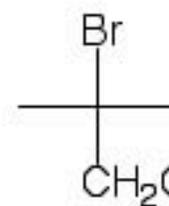
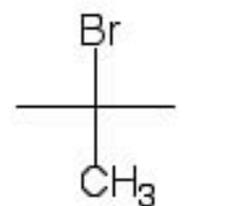
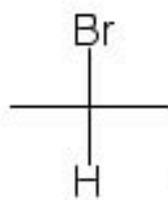
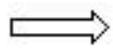
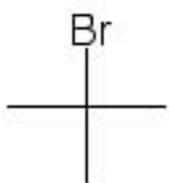
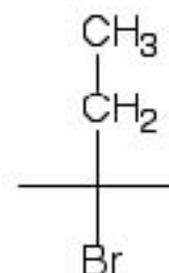
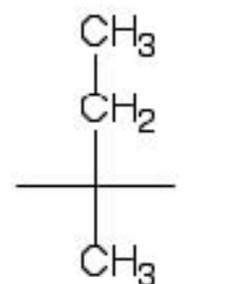
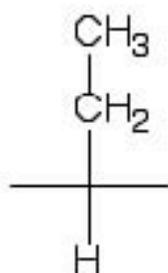
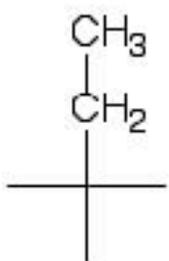
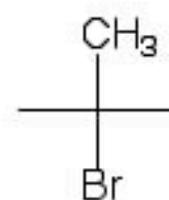
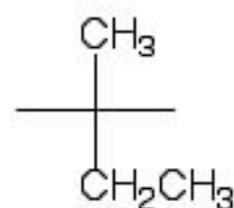
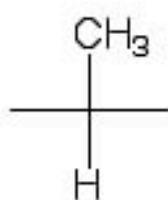
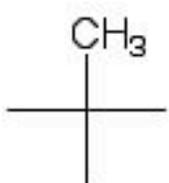
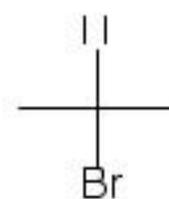
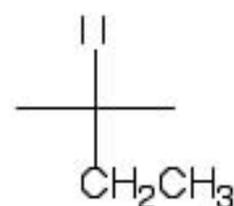
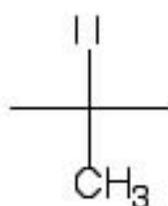
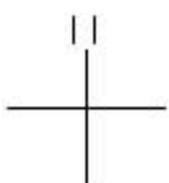
5-11 A simple "trick" you can use to assign absolute configuration is the following: take either hand and align the thumb pointing along the bond from the atom to be assigned to the lowest priority substituent. Then check to see if your fingers track the progression of substituents 1, 2, and 3 with the finger tips on 3. If they do, then the atom is *R* if you are using your right hand or *S* if you are using your left hand. If the fingers track in the opposite way, then the configuration is the opposite.

5-12 There are many correct ways to draw these structures. In general, when an organic compound contains a chain of carbon atoms, the chain is drawn in a horizontal zig-zag. Switching any two atoms on a

stereocenter results in the opposite configuration. This can be done in two ways, as illustrated for *S*-2-chlorobutane: 1) interchanging two of the substituents; or 2) switching the stereochemical indicators, in this case indicating front and back.

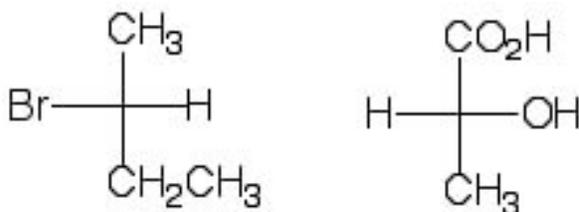


5-13 There is a serious problem with asking a question of this type as there is no rigorous set of "rules" for drawing Fischer Projections. To illustrate, we start with 2-bromobutane, the first example in Table 5-1. There is one stereocenter with four different substituents: H, CH₃, CH₂CH₃, and Br. We start by drawing the "cross" to represent the stereocenter. Now we have four choices as to what to put at the top. Now for each of these structures, we can add any one of three substituents as the second group, leading to twelve structures that are not yet finished. Finally, we add the remaining two and which way we add them determines the absolute configuration of the stereocenter.



So providing all of the correct Fischer Projections would take a huge amount of space and make it difficult to find the one that corresponds to your answer.

Now there are some friendly agreement conventions for Fischer Projections. Generally, if there is a carbon chain then the chain is represented as a vertical string with the stereocenter(s) as near the top as possible. If one end of the chain has a carbon based functional group, it is typically placed at the top and if there is one at each end, that with the higher oxidation state carbon is placed at the top. Thus, the first and last example in Table 5-1 would be represented as:

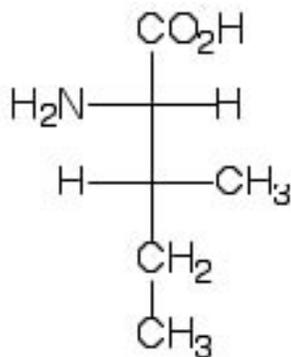
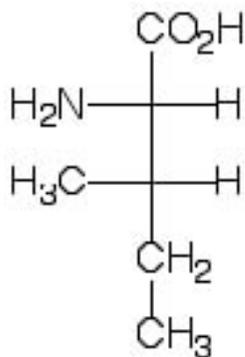


5-14 This is 2-chlorobutane which we drew with wedges and dashes in Exercise 5-10:

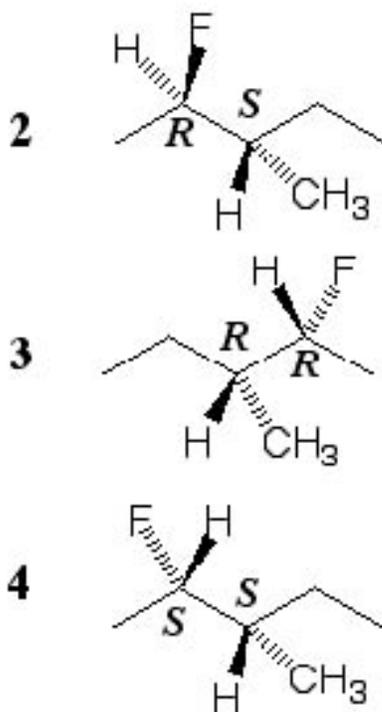
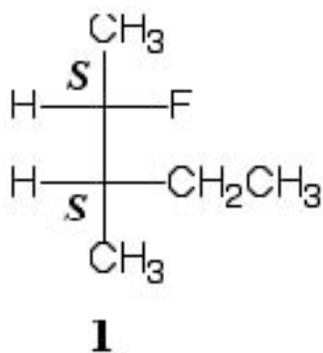


5-15 This exercise is worked out on page 186 as "Working with Concepts".

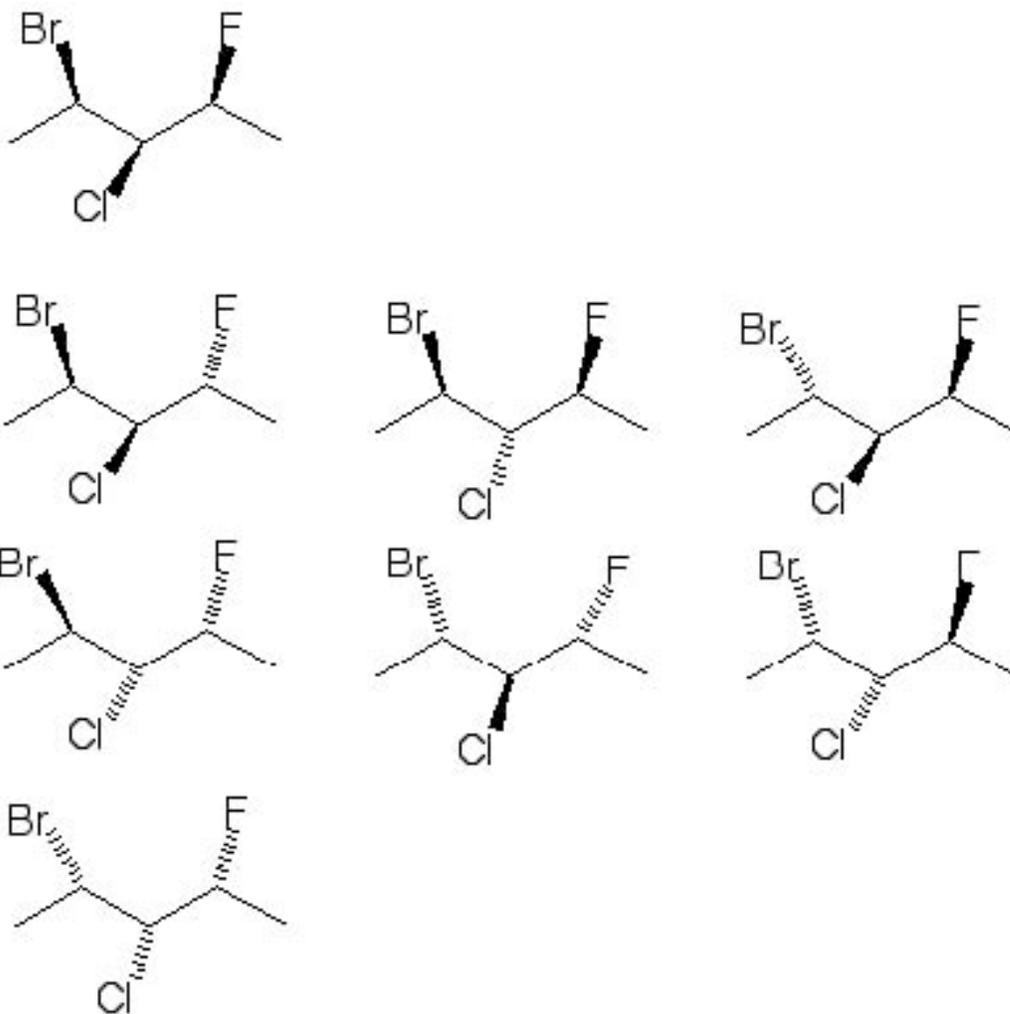
5-18 In this exercise, the book has followed the convention of placing the main chain of carbon atoms vertically with the end of highest oxidation state at the top. Each of these stereoisomers has two stereocenters and as only one is different between them, they must be diastereomers.



5-19 The rigorous approach to solving this exercise is to first assign stereochemistry (*R,S*) to each stereocenter. Then it becomes easy to see the relationships: *S-S* is the enantiomer of *R-R*, *S-S* is a diastereomer of both *R-S* and *S-R*.

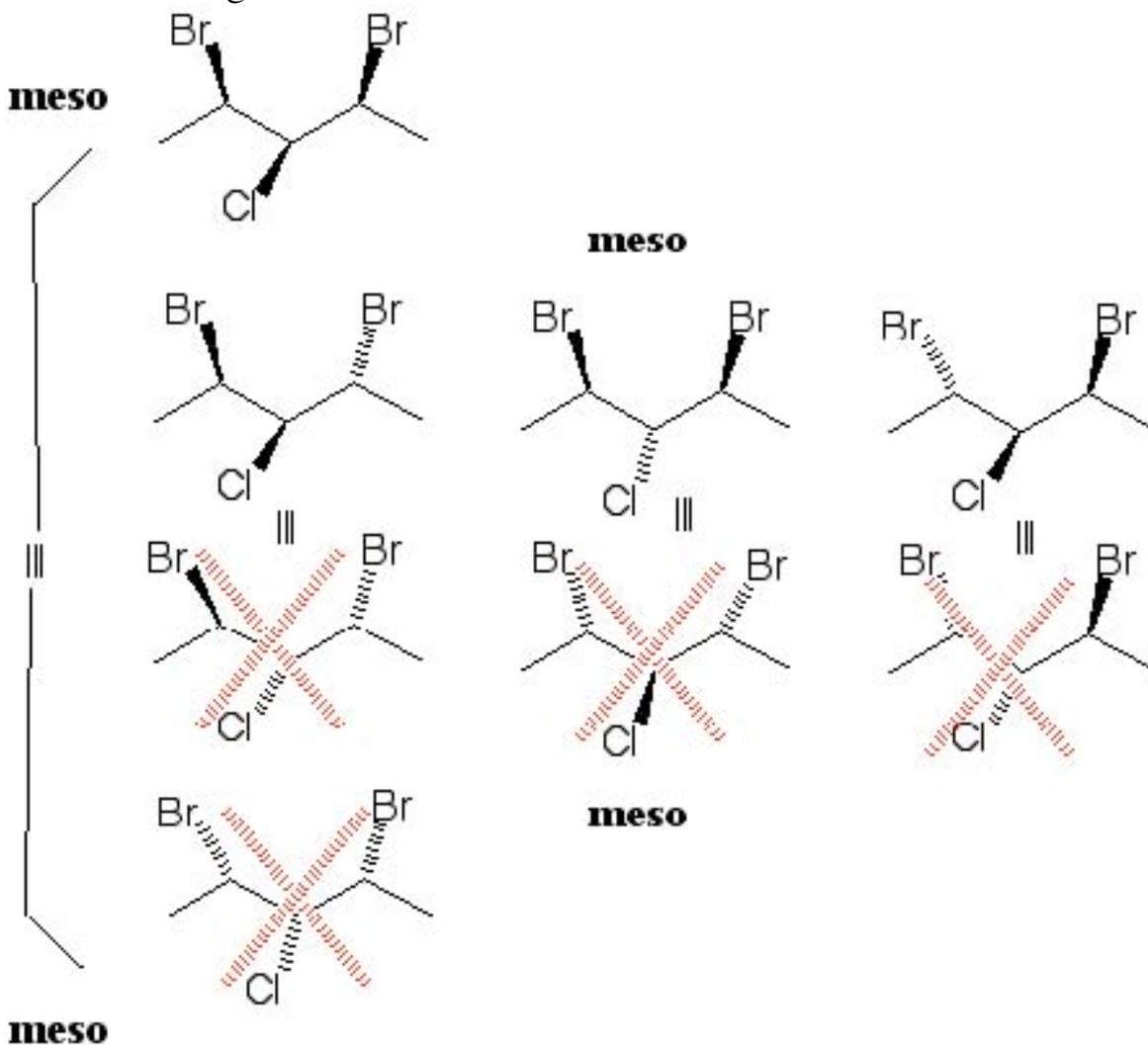


5-20 This is really an exercise in finding all of the permutations. To make it easy, we will start with all of the substituents on the five-carbon chain to the front and then systematically change them to find all possible combinations. Because there are three stereocenters none of which have the same substituents, we know that there are 2^n isomers, or 8.

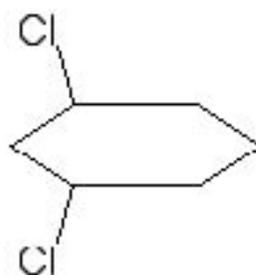
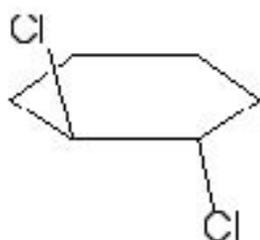
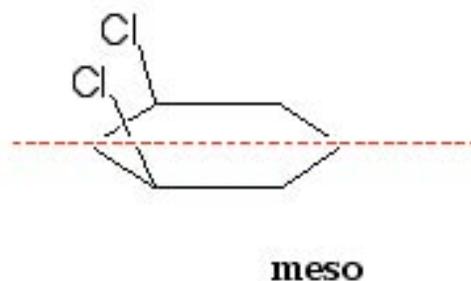
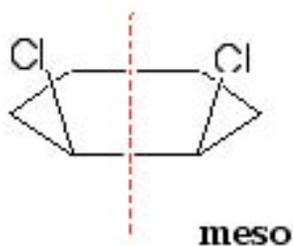
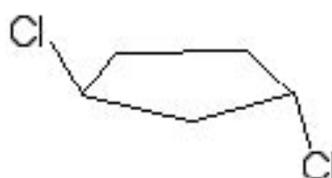
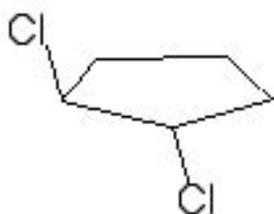
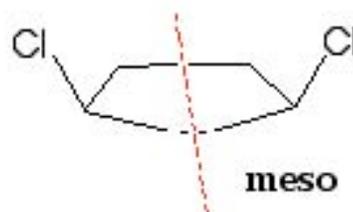
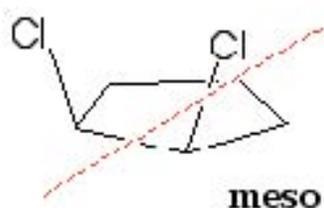


5-21 This is essentially the same exercise as 5-17 except now two of the stereocenters have the same substituents so we have the possibility of meso isomers. We use the same systematic approach, drawing all permutations and then looking for those that have a mirror plane. As meso isomers are identical to their mirror images, this approach will lead to duplicates that we must remove. We can find the meso isomers easily as the two centers with the same substituents must have opposite stereochemistry. However, this is a very special situation and we have arrived at additional duplicates by our systematic approach. Note that when the two stereocenters on the "outside" (those bearing bromine) have the same configuration, then the central carbon bearing chlorine is NOT a stereocenter as it does not have four different things attached. Thus, the two structures in the middle on the left and on the right have duplicates. (Think of it this way: because the two end stereocenters

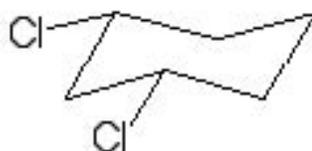
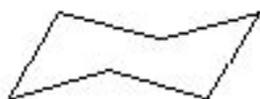
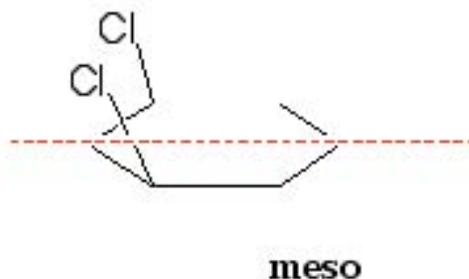
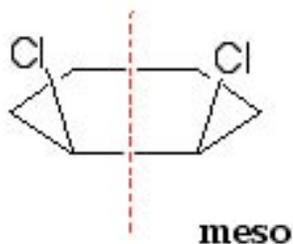
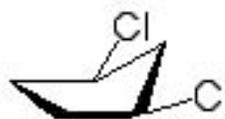
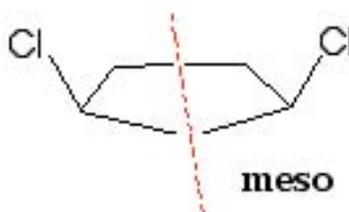
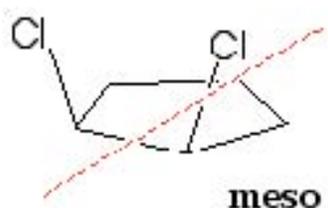
have the same substituents AND the same stereochemistry, we can rotate the molecule about a vertical axis through the central carbon and not change anything about the two bromine-bearing stereocenters. But, we will move the chlorine from the front to the back or the back to the front and doing so does not create a new isomer.



5-22 Only the *cis* isomers can be meso.



5-23 This is a poorly worded exercise as we have already provided the answer by solving Exercise 5-22. The question should have been: "For each of the meso compounds in Exercise 5-22, provide a low energy conformation that contains a mirror plane."



No chair conformation has a mirror plane of symmetry for *cis*-1,2-dichlorocyclohexane

Only the boat has such a plane.

5-21 The key here is that halogenation involves the formation of a radical which has only three substituents and therefore is not a stereocenter. Thus, halogenation of 2-bromobutane at C-2 will result in a racemic mixture (addition of the second halogen will occur at equal rates from both sides). With chlorine or fluorine, racemic mixtures will result whereas bromination will result in an achiral product (2,2-dibromobutane). All of these will be optically inactive. Halogenation at

C-1, C-3, or C-4 will preserve the stereocenter at C-2 and the product will be optically active.

5-22 You will learn little of practical value from working this exercise as all of the molecules exist as planar rings only at transition states for conformational changes.

5-23 Ditto.

5-24 We begin by noting that there are five unique carbon atoms in (*S*)-2-bromopentane and thus adding a second bromine atom to each of these five will result in five unique constitutional isomers.