Study Guide/Solutions Manual to Accompany Organic Chemistry

Fifth Edition

MAITLAND JONES, Jr.

New York University

HENRY L. GINGRICH

Princeton University

STEVEN A. FLEMING

Temple University

W · W · NORTON & COMPANY NEW YORK · LONDON

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Printed in the United States of America

Composition by codeMantra
Manufacturing by Courier Kendallville

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ISBN 978-0-393-93659-9

W. W. Norton & Company, Inc., 500 Fifth Avenue, New York, NY 10110
www.wwnorton.com

W. W. Norton & Company Ltd., Castle House, 75/76 Wells Street, London W1T 3QT

1 2 3 4 5 6 7 8 9 0

Contents

Introduction

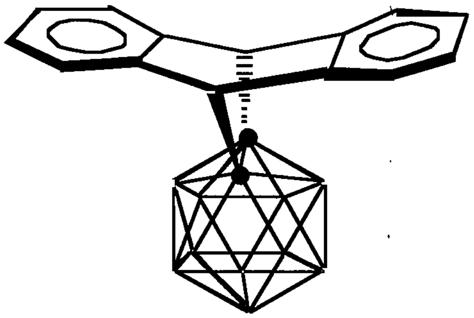
In this Study Guide we try to go beyond straightforward "bare bones" answers to problems. Once one gets past simple questions, problem solving in organic chemistry becomes very hard to teach. The answers to many problems are intuition-intensive, and therefore it becomes difficult to explain in explicit terms how to proceed. Nonetheless, there are things that can be said that may help; there are techniques of problem solving that can be learned. In this collection of comments on solutions to all the problems that are not solved in the text itself, we try to help you to do that. As in the text, we seek in these pages to show you how to approach problems in organic chemistry in general, not just how we got from here to there in specific cases.

The exercises in these chapters become much easier when we have an idea of where we are going. What exactly are we trying to do in this problem? What tasks must be accomplished? What bonds are we trying to make or break? What rings must be closed or opened? Such questions seem simple, but it is amazing how few people really start problems with the simple question: "What happens in this reaction?" Analyze! Once a goal is in mind, the path to that goal becomes much, much easier. In a sense, a good problem solver has learned, first and foremost, to avoid "thrashing." We know that is a flip remark, but it is, nonetheless, true. A person solving a tough problem is like a bacterium swimming up a food gradient—he or she (or it) is following a pathway that "feels good." We will try to show you how to do that in this Study Guide, but there can be no denying that experience is important, and experience can be gained only by practice. Practice and more practice will teach you what feels good in terms of problem solving—of how to swim up that food gradient—but we will try to give you some hints along the way.

The problems solved in the Study Guide will recapitulate each chapter, and thus will generally start off with the easier examples and then go on to tougher stuff. Don't worry if the hard problems at the end of the sections do not come so easily; they are meant to tax you, to demand some hard work and careful thought. Some difficult problems will be dealt with best over time. If a problem resists solution, and some will, come back to it after a while; let your subconscious work on it for a while. Most research chemists carry unsolved problems around in their heads for a long time, sometimes for years, returning to them now and then. There is nothing wrong with emulating that process. People think at vastly different rates, and it is a rare situation that requires a rapid solution of a problem. (Hour exams may be an exception, unfortunately.)

Many of us who actually do organic chemistry for a living (believe it or not there are such people) typically get great pleasure from problem solving. We hope that you will be similarly stimulated. In a fundamental way that is what we humans are about. We have evolved to be curious and to turn over rocks to see what is underneath. Perhaps, thinks our ancestral hunter-gatherer, I will find something good to eat! From such imperatives we humans have become problem solvers, and it gives us pleasure to work out what's happening in unknown situations.

Here is one favorite example, which makes an important point about problem solving. This lesson is so simple as to be trivially obvious and yet at the same time so profound as to be most difficult in practice. MJ and HG had been working for some time on the synthesis of the following pterodactyl-shaped compound:



One of us (MJ) had become entrapped in devising increasingly clever "solutions" that a series of graduate students and undergraduates had not been able to make work—and for good reasons. Those clever solutions were complicated, and extraordinarily hard to carry out in a practical sense. While MJ was away one July, HG had the wit to avoid all the foolish "cleverness" and to do what we beseech our students to do—to "think simple." HG went back to basics, did the work himself, and solved the problem. MJ arrived back in Princeton and was presented with a vial containing exquisitely beautiful crystals of the long-sought compound. What's the lesson? Don't be too clever. If you ground yourself in the basics, analyze what you want to do, and then apply those basics, you will prosper.

Remember, think simple. As Ted Williams is supposed to have said: "If you don't think too good, don't think too much."

Maitland Jones, Jr.
Henry L. Gingrich
Steven A. Fleming

1

Atoms and Molecules; Orbitals and Bonding

In this chapter, you are learning a bit about atomic structure and acquiring skills that you will need throughout your study of organic chemistry. In a sense, you are learning vocabulary and grammar that will enable you to write sentences a little later and eventually to compose whole paragraphs and short stories. The problems of this chapter concentrate on tool building and require less thought and imagination than those of later chapters. That does not mean that they are unimportant. Even though much of this chapter may review what you already know, please do not skip past it until you are certain that you can write Lewis structures easily, determine the position of charges without error, and use the arrow formalism to write resonance forms with ease. These skills will be as necessary in Chapter 24 as they are now.

Problem 1.2 See Problem 1.1. If the fifth and sixth electrons in a carbon atom occupied the same orbital with parallel spins, they would have the same values for all four quantum numbers, a violation of the Pauli principle. If they occupy the same orbital, their spin quantum numbers (s) *must* be opposite (paired).

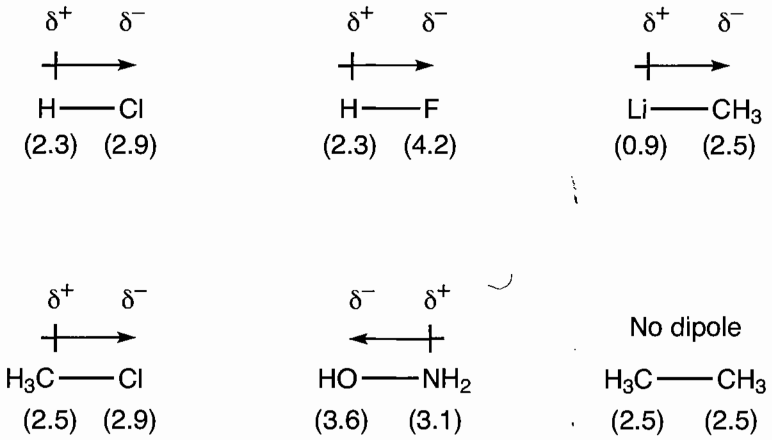
Problem 1.3 In this row, we fill the $n = 3$ energy levels, first filling the $3s$ orbital, then moving on to the higher energy $3p$ orbitals.

$_{11}$Na $1s^2\ 2s^2\ 2p_x^{\,2}\ 2p_y^{\,2}\ 2p_z^{\,2}\ 3s$
$_{13}$Al $1s^2\ 2s^2\ 2p_x^{\,2}\ 2p_y^{\,2}\ 2p_z^{\,2}\ 3s^2\ 3p_x$
$_{15}$P $1s^2\ 2s^2\ 2p_x^{\,2}\ 2p_y^{\,2}\ 2p_z^{\,2}\ 3s^2\ 3p_x\ 3p_y\ 3p_z$
$_{16}$S $1s^2\ 2s^2\ 2p_x^{\,2}\ 2p_y^{\,2}\ 2p_z^{\,2}\ 3s^2\ 3p_x^{\,2}\ 3p_y\ 3p_z$
$_{18}$Ar $1s^2\ 2s^2\ 2p_x^{\,2}\ 2p_y^{\,2}\ 2p_z^{\,2}\ 3s^2\ 3p_x^{\,2}\ 3p_y^{\,2}\ 3p_z^{\,2}$

Problem 1.4 A bond dipole will result when two atoms of different electronegativities are attached to each other. This problem requires you only to look up the electronegativities of the two atoms in the bond. The electronegativity (Table 1.8, p. 15) of each atom in the bond is shown in parentheses. As you see below, the atom of greater electronegativity will be at the negative end of the dipole. The answer uses an arrow to represent the direction of the dipole, $\delta^{+} \longmapsto \delta^{-}$.

(continued)

Problem 1.4 *(continued)*



Problem 1.5 This classic problem is asked in many textbooks. It requires you to estimate the net dipole in a molecule by summing the bond dipoles. In carbon tetrachloride (CCl_4), the four dipoles cancel, and there is no net dipole. In chloroform ($CHCl_3$), the dipoles do not cancel, and a net dipole exists.

Here, the four dipoles cancel..............................but in this molecule they do not.

Problem 1.6 In each part of this problem, we will first determine the number of electrons available for bonding on each atom. For atoms in the second row of the periodic table, this will be the atomic number of the atom, less the two 1*s* electrons. Then we will see how many bonds between atoms are possible using these electrons. Finally, be careful to write the leftover nonbonding (lone pair) electrons as a pair of dots.

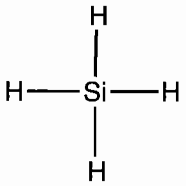
(b) H_2Be

Beryllium ($_4Be$) has two electrons available for bonding (4 – 2 1*s* electrons), and each hydrogen contributes one electron. Two beryllium–hydrogen single bonds are formed. There are no nonbonding electrons.

$$H\cdot \qquad \cdot Be \cdot \qquad \cdot H \quad \longrightarrow \quad H{:}Be{:}H \quad = \quad H—Be—H$$

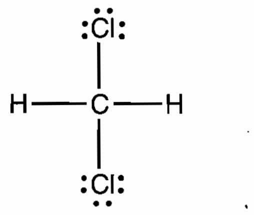
(c) SiH_4

Silicon has four valence electrons. We know that hydrogen has only one valence electron and that hydrogen only makes one bond. So the structure for SiH_4 must be



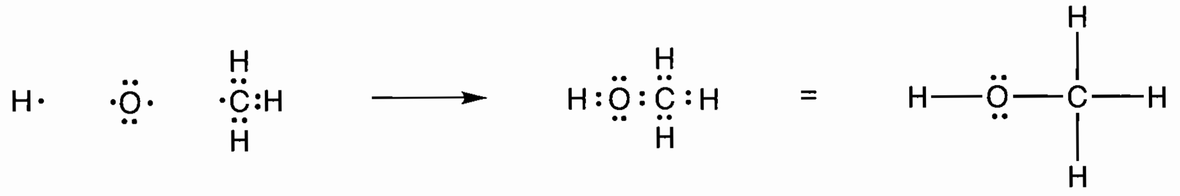
(d) CH_2Cl_2

We know that carbon has four valence electrons. Each chlorine atom has seven valence electrons and must be bonded to the carbon. If a chlorine atom were bonded to hydrogen or another chlorine, then the CH_2Cl_2 would not be a single molecule. Hydrogen and chlorine fill their valence shell by making one bond, and carbon can make four bonds. So the structure of CH_2Cl_2 must be



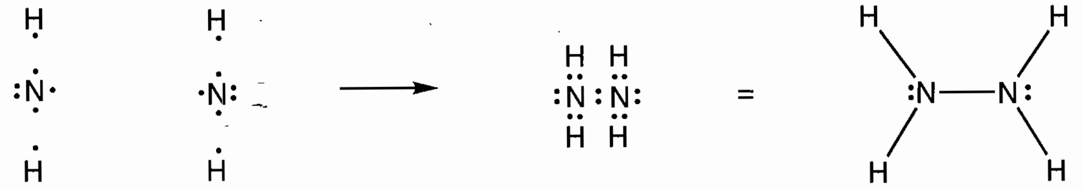
(e) $HOCH_3$

Oxygen ($_8O$) has six electrons available for bonding (8 – 2 1*s* electrons). Carbon forms three covalent single bonds with the three hydrogens, which leaves one carbon electron available for covalent bond formation between carbon and oxygen. Oxygen forms the carbon–oxygen bond as well as one covalent bond with hydrogen, leaving oxygen with two pairs of nonbonding electrons.



(f) $H_2N—NH_2$

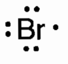
Nitrogen has five electrons available for bonding. In this molecule, each nitrogen forms covalent bonds with two hydrogens and a third with the other nitrogen. This bonding system uses three of the available electrons, leaving a nonbonding pair of electrons on each nitrogen.



Problem 1.7

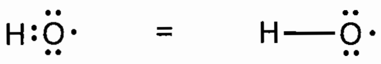
(c) Br

$_{35}$Br is in the fourth row of the periodic table, so we can ignore the 28 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 3*d* electrons. This procedure leaves seven electrons. Like the other halogens (F, Cl, and I), Br has three nonbonding pairs and a single odd electron.



(d) OH

Oxygen ($_8O$) has six electrons available for bonding. One electron is used in forming a covalent bond with hydrogen, leaving two pairs of nonbonding electrons and a single odd electron on oxygen.

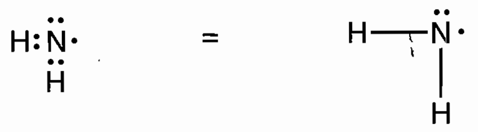


(continued)

Problem 1.7 *(continued)*

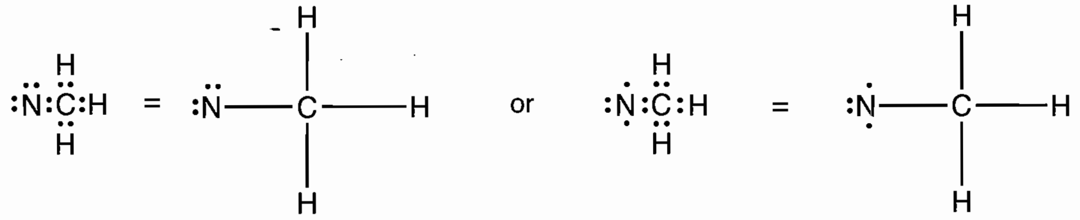
(e) NH_2

Nitrogen has five electrons available for bonding. Two covalent bonds are formed to hydrogens, leaving a nonbonding pair and a single odd electron remaining on nitrogen.



(f) $H_3C—N$

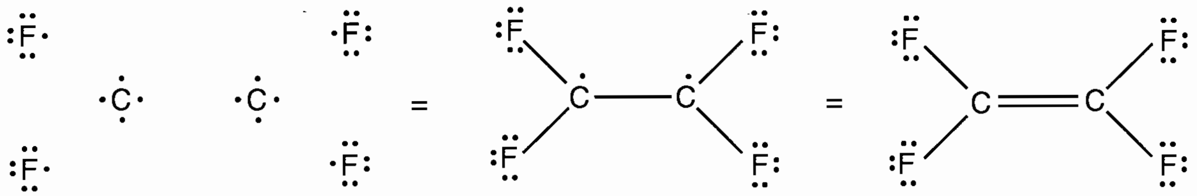
There are two possible answers to this one, and both kinds of molecule are known. Carbon has four electrons available for bonding. Three are used in forming single bonds to the three hydrogens, and the fourth is used in the single bond to nitrogen. Nitrogen has five electrons available for bonding. One covalent bond is formed to carbon, leaving four electrons. These can be used either as two pairs of nonbonding electrons or as one nonbonding pair and two odd electrons.



Problem 1.8 The question itself helps with the hard part—working out the connectivity of the atoms. Once again, this is an exercise in electron counting. First, determine the number of electrons available for bonding (atomic number less two 1*s* electrons for most atoms or a single 1*s* electron for hydrogen), then make single bonds. Finally, we look to see where multiple bonds can be formed.

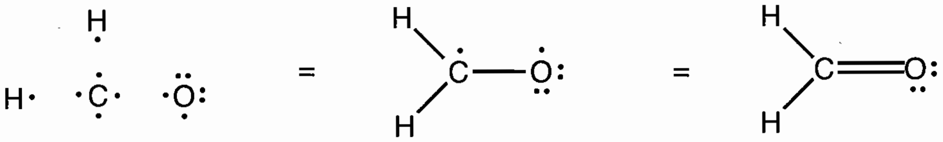
(a) F_2CCF_2

Carbon has four electrons available for bonding and fluorine seven, including a single odd electron. As in ethylene (Fig. 1.20), each carbon forms three covalent bonds, two with fluorines and one with the other carbon atom. Thus, there are three nonbonding pairs remaining on each fluorine and a single electron left over on each carbon. These are shared in a second covalent carbon–carbon bond.



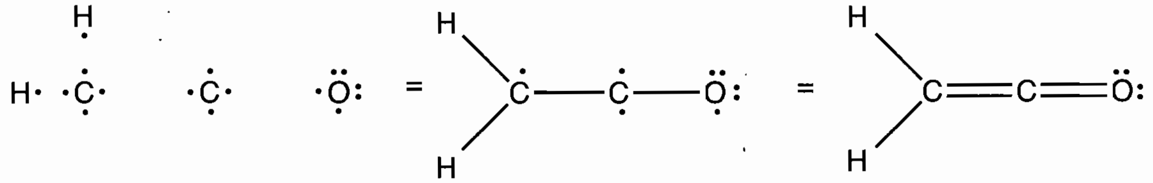
(c) H_2CO

Once again, carbon has four electrons available for bonding and oxygen six. Carbon uses two electrons to form bonds to hydrogen and one to bond to oxygen. Oxygen uses one electron in the bond to carbon, leaving one unshared electron on carbon and five on oxygen. Formation of a second carbon–oxygen bond leaves two nonbonding electron pairs on oxygen.



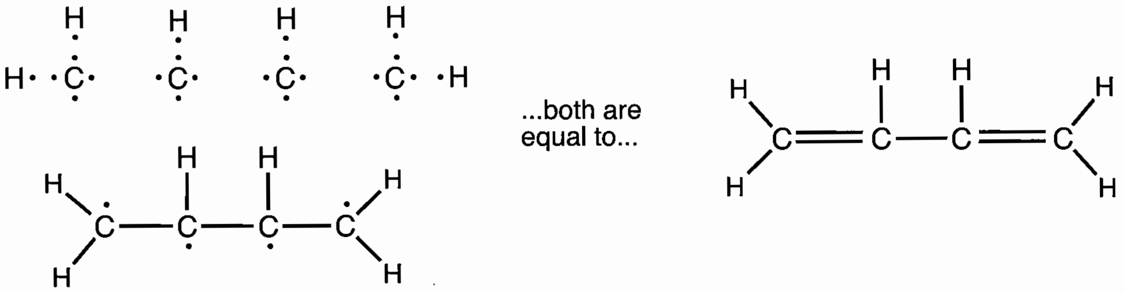
(d) H_2CCO

Each carbon has four available electrons and the single oxygen six. The left-hand carbon uses three electrons to form three covalent bonds to the two hydrogens and the adjacent carbon. The right-hand carbon uses two electrons in forming covalent bonds with the left-hand carbon and the oxygen, leaving the left-hand carbon with one electron, the right-hand carbon with two, and the oxygen with five. Formation of a second carbon–carbon bond and a second carbon–oxygen bond completes the picture, leaving the oxygen with two nonbonding pairs of electrons.



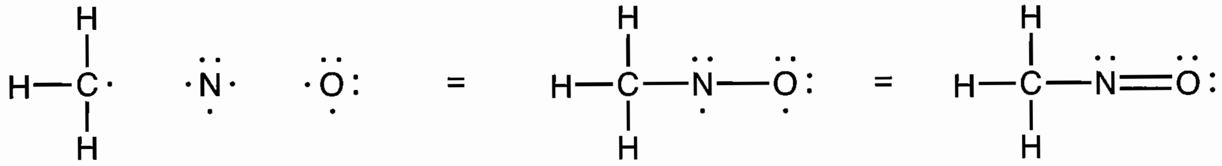
(e) $H_2CCHCHCH_2$

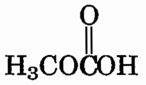
Each of the four carbons has four electrons available for bonding. The two terminal carbons form two covalent bonds with the two hydrogens and a third covalent bond with the adjacent carbon. Each internal carbon forms two covalent bonds with the adjacent carbons and a third to a hydrogen. There remains one electron on each carbon, allowing the formation of two additional carbon–carbon bonds.



(f) $H_3C.NO$

Once again there is a methyl group ($\cdot CH_3$). Nitrogen has five available electrons, and oxygen has six ($_8O$, 8 – 2 1*s* electrons = 6). A carbon–nitrogen single bond and a nitrogen–oxygen double bond can be formed. Nitrogen is left with one pair of nonbonding electrons and oxygen with two pairs.



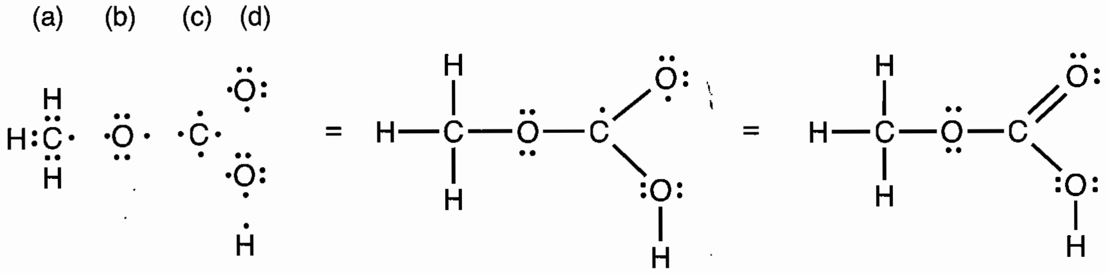
(g) 
$H_3CO\overset{\overset{O}{\|}}{C}OH$

Each carbon has four available electrons for bonding, and each oxygen has six. The left-hand carbon (a) forms three bonds to hydrogen and a fourth to one oxygen (b). Oxygen (b) forms two bonds to a pair of carbons. The remaining carbon (c) forms covalent bonds with oxygen (b) and the two other oxygens (d). Each oxygen (d) forms a covalent bond with carbon (c), and one oxygen (d) forms a bond to hydrogen. This process leaves one odd electron on carbon (c), four nonbonding electrons on the oxygen (d) bound to hydrogen, and five electrons on the non-hydrogen-bound

(continued)

Problem 1.8 *(continued)*

oxygen (d). Oxygen (b) has four electrons remaining. Formation of a carbon (c) oxygen (d) bond completes the picture.

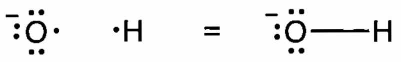


Problem 1.9 This problem is just like Problem 1.7 except that you need to make an adjustment for the charge. First, calculate the number of available electrons on the neutral atom, then add one electron for a negative charge or subtract one electron for a positive charge.

(a) ^{-}OH

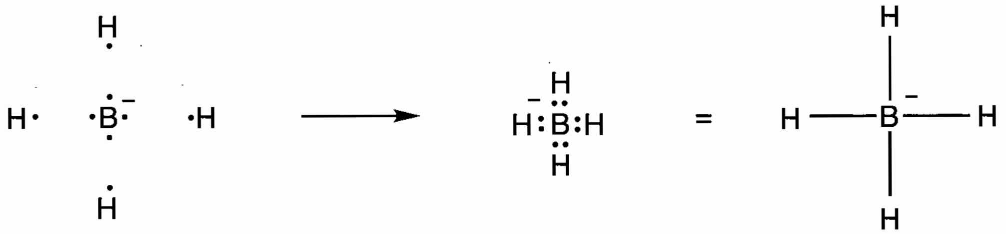
Neutral oxygen ($_8O$) has six electrons available for bonding ($8 - 2\ 1s = 6$). Therefore, negatively charged oxygen must have seven electrons.

One covalent bond can be made to the lone hydrogen, which supplies a single electron.



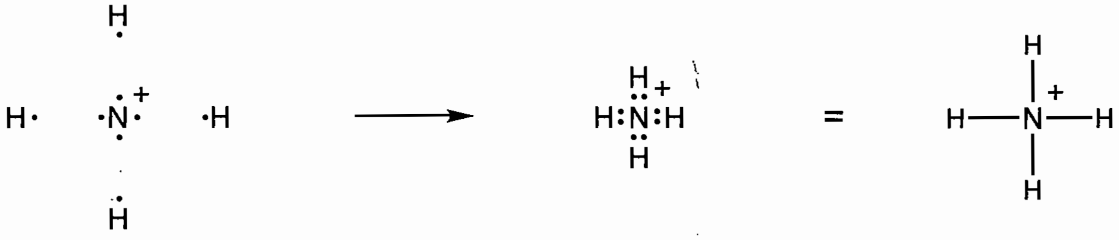
(b) $^{-}BH_4$

Neutral boron ($_5B$) has three electrons available for bonding ($5 - 2\ 1s$). Therefore, negatively charged boron must have four electrons, allowing four covalent bonds to be made to the four hydrogens, each of which supplies a single electron. Notice that there is no pair of electrons on the negatively charged boron atom. In most negatively charged species, there is a nonbonding pair of electrons. This molecule is an exception.



(c) $^{+}NH_4$

Neutral nitrogen ($_7N$) has five electrons available for bonding ($7 - 2\ 1s$). Positively charged nitrogen must have four electrons for bonding, allowing four single bonds to the four hydrogens, each of which supplies its single electron.

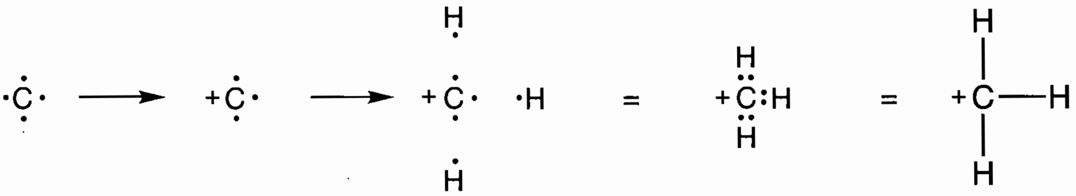


(d) ^{-}Cl

Neutral chlorine ($_{17}Cl$) has seven electrons available for bonding (ignore the 10 1*s*, 2*s*, and 2*p* electrons). Therefore, negatively charged chlorine must have eight electrons.

(e) $^{+}CH_3$

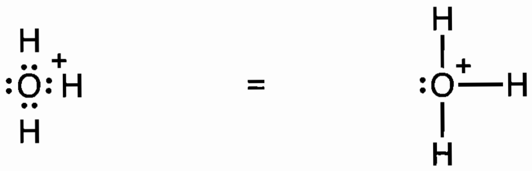
Neutral carbon ($_6C$) has four electrons available for bonding (6 – 2 1*s*). Positively charged carbon must have only three electrons for bonding, allowing three single bonds to the hydrogens, each of which supplies its single electron.



(f) $^{+}OH_3$

Neutral oxygen has six electrons available for bonding ($_8O$, 8 – 2 1*s* electrons), and so positively charged oxygen must have five electrons.

Three single bonds can be made with the three hydrogen atoms.

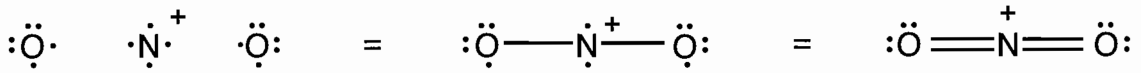


(g) $^{+}NO_2$

Nitrogen has five electrons available for bonding, so ^{+}N must have four. Each oxygen has six. Two nitrogen–oxygen double bonds can be formed, leaving each oxygen with two pairs of nonbonding electrons.

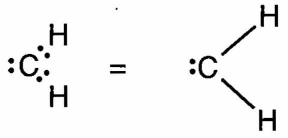
(continued)

Problem 1.9 *(continued)*



Problem 1.10 In these examples, we will first show a full Lewis structure in which each bonding electron appears as a dot, then a more schematic Lewis structure in which bonds are shown as lines and nonbonding electrons as dots. These structures will be followed by the charge calculation.

(a)



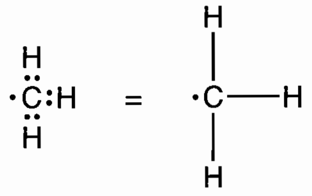
$_6C$ **6 protons = 6 positive charges**

2 1*s* electrons
2 nonbonding electrons
2 shared electrons

6 negative charges

neutral

(b)



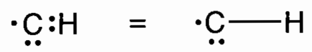
$_6C$ **6 protons = 6 positive charges**

2 1*s* electrons
1 nonbonding electron
3 shared electrons

6 negative charges

neutral

(c)



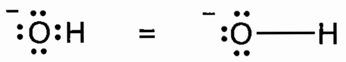
$_6C$ **6 protons = 6 positive charges**

2 1*s* electrons
3 nonbonding electrons
1 shared electron

6 negative charges

neutral

(d)



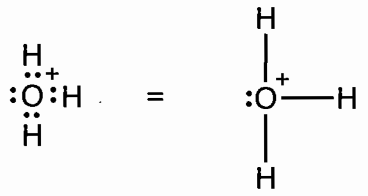
$_8O$ **8 protons = 8 positive charges**

2 1*s* electrons
6 nonbonding electrons
1 shared electron

9 negative charges

net 1^-

(e)



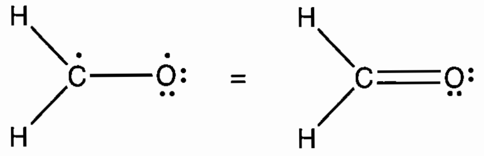
$_8O$ **8 protons = 8 positive charges**

2 1*s* electrons
2 nonbonding electrons
3 shared electrons

7 negative charges

net 1^+

(f)



$_8$O **8 protons = 8 positive charges**

2 1*s* electrons
4 nonbonding electrons
2 shared electrons

8 negative charges

neutral

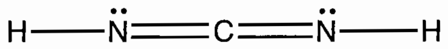
$_6$C **6 protons = 6 positive charges**

2 1*s* electrons
0 nonbonding electrons
4 shared electrons

6 negative charges

neutral

(g)



$_6$C **6 protons = 6 positive charges**

2 1*s* electrons
0 nonbonding electrons
4 shared electrons

6 negative charges

neutral

$_7$N **7 protons = 7 positive charges**

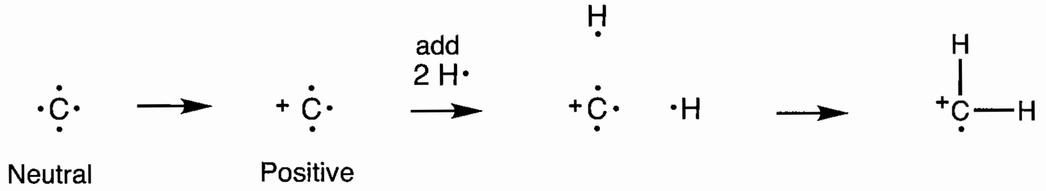
2 1*s* electrons
2 nonbonding electrons
3 shared electrons

7 negative charges

neutral

Problem 1.11 The task here is to work out the number of nonbonding electrons (if any) on the charged atom. Each answer first shows the neutral atom, then the atom with an electron added or removed to get the proper charge. Finally, electrons are used to make the bonds to the available hydrogen atoms or other groups. In (a), for example, we first see carbon with four bonding electrons ($_6$C; 6 electrons – 2 1*s* electrons = 4 bonding electrons), then with one electron removed to get $^+$C; finally, two of the remaining three electrons form single bonds to the two available hydrogens. Now we have $^+CH_2$ with a single nonbonding electron.

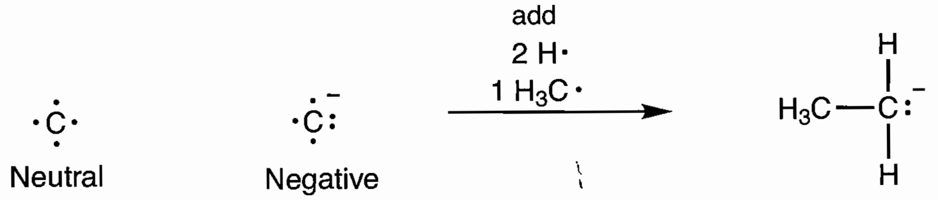
(a) $^+CH_2$



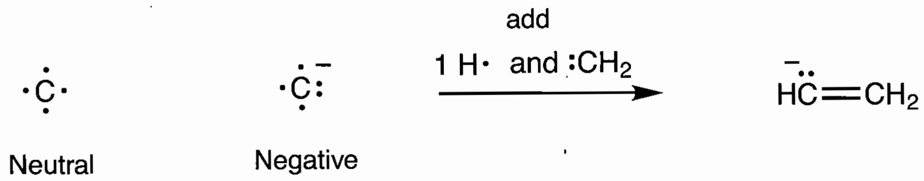
(continued)

Problem 1.11 *(continued)*

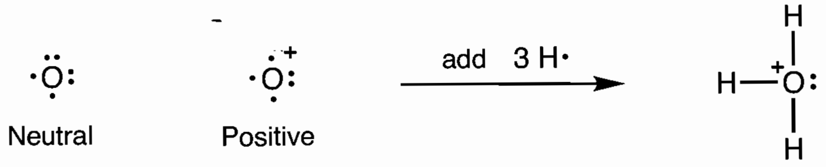
(b) $CH_3\bar{C}H_2$



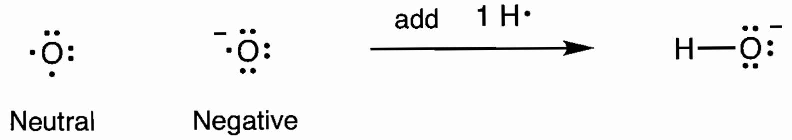
(c) $H\bar{C}{=}CH_2$



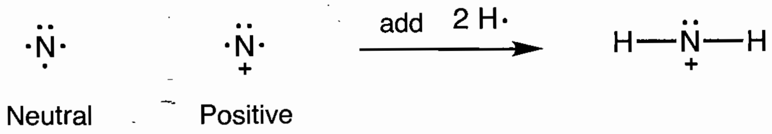
(d) H_3O^+



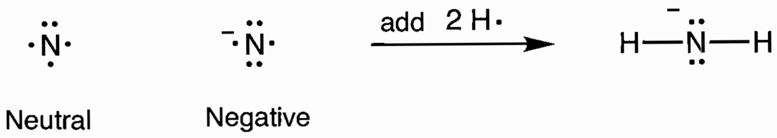
(e) HO^-



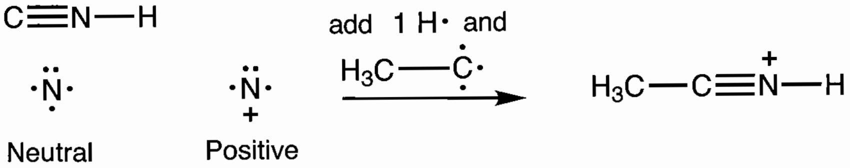
(f) $^+NH_2$



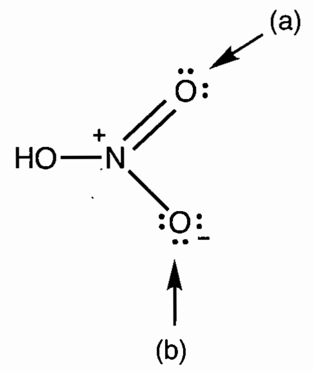
(g) $^-NH_2$



(h) $H_3C{-}C{\equiv}\overset{+}{N}{-}H$



Problem 1.12 Figure 1.26 shows the structure of nitromethane, $H_3C—NO_2$. By analogy, we can write a structure for nitric acid, $HO—NO_2$.



$_7N$ **7 protons = 7 positive charges**

2 1*s* electrons
0 nonbonding electrons
4 shared electrons

6 negative charges

net 1^+

$_8O$ (a) **8 protons = 8 positive charges**

2 1*s* electrons
4 nonbonding electrons
2 shared electrons

8 negative charges

neutral

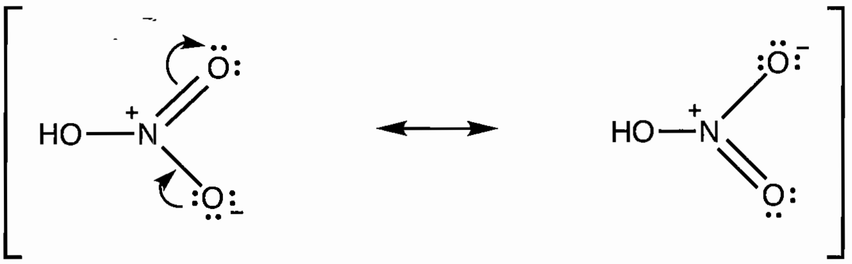
$_8O$ (b) **8 protons = 8 positive charges**

2 1*s* electrons
6 nonbonding electrons
1 shared electron

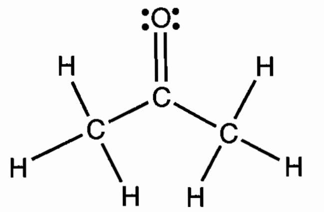
9 negative charges

net 1^-

Problem 1.13 Notice that the lower arrow pushes a nonbonding pair of electrons on one oxygen to displace a bonding pair (shown only as a line in the drawing). The displaced pair winds up as a nonbonding pair on the other oxygen, and the displacing pair winds up as a new bond between the lower oxygen atom and nitrogen.

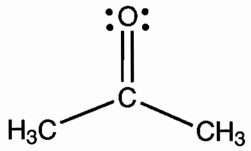


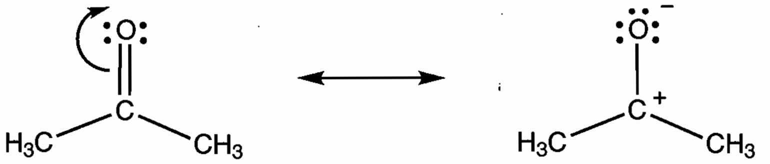
Problem 1.15



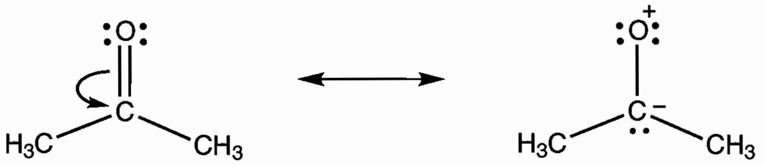
Lewis structure for acetone.

can also be written as:





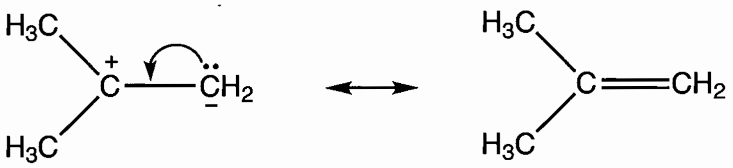
We can move the π electrons to the oxygen to give the resonance structure on the right. This species contributes significantly to the chemistry of acetone. The negative charge takes advantage of the higher electronegativity of oxygen. Note that the carbon does not have an octet in the resonance structure on the right. It only has six electrons around it.



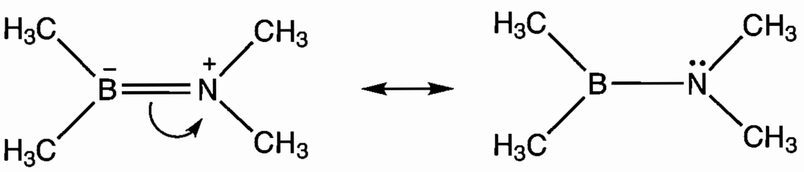
Moving the electrons from the π bond to the carbon also gives a valid resonance structure. However, this resonance structure has an oxygen without an octet (which is worse than a carbon with only six electrons, because oxygen is more electronegative). In addition, the negative charge is on the less electronegative carbon. To make matters even worse, the electronegative oxygen has a positive charge. This resonance structure does not contribute to the overall structure of acetone.

Problem 1.16 *Remember*: The double-barbed, curved arrows move pairs of electrons, and we must be careful neither to violate the rules of valence nor to move atoms. A new convention appears in the last example. When "pushing" single electrons, a single-barbed, curved arrow is used.

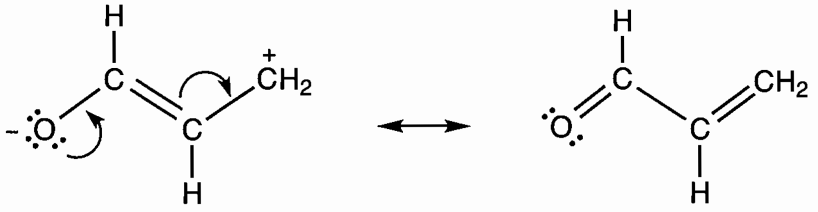
(a)



(b)



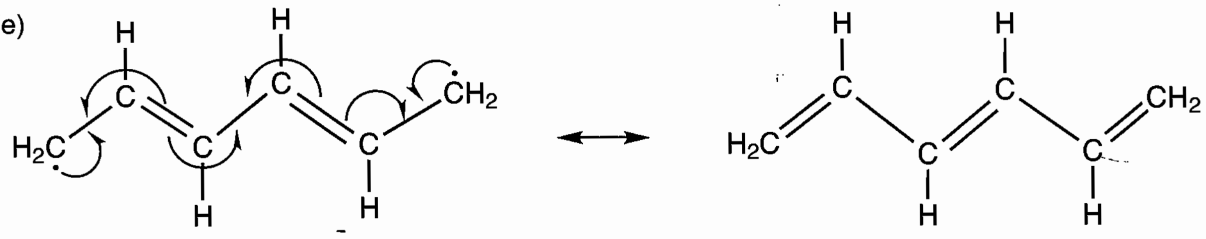
(c)



(d) Here is the tricky part to this problem. It is sooooo tempting to push the arrow as shown:

But this "pushing" makes no sense: There is no low-lying empty orbital on nitrogen to accept an electron pair and no pair of electrons on boron to push! The form on the right violates the rules of valence twice.

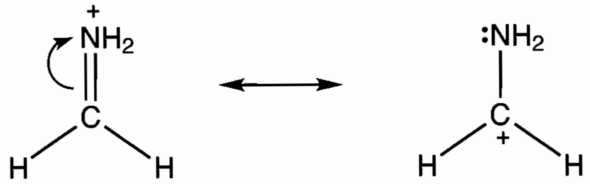
(e)



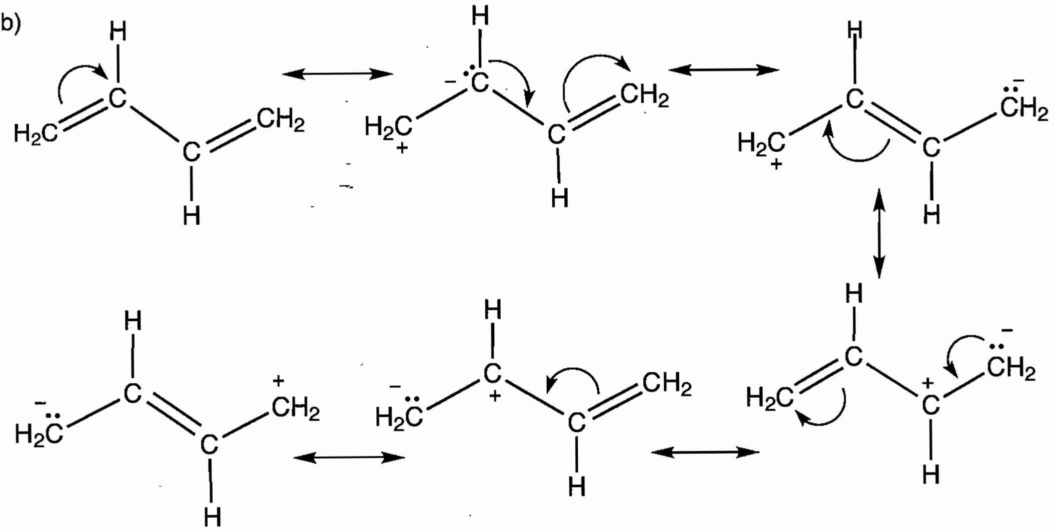
In this example, notice the use of *single-barbed,* or "fishhook," arrows to show the motion of single electrons!

Problem 1.17

(a)



(b)

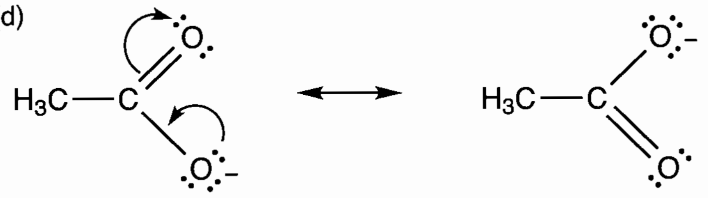


None of the resonance forms in part (b), except the first, uncharged one, is very good. Each contains one fewer bond than the first, and each requires substantial charge separation.

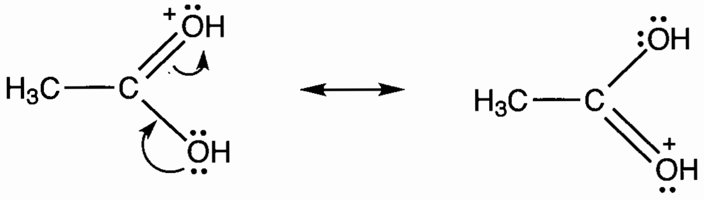
(continued)

Problem 1.17 *(continued)*

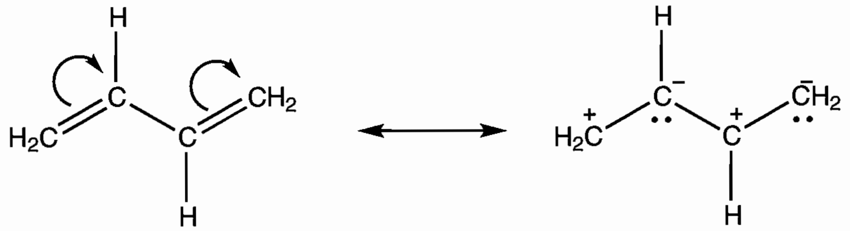
(d)

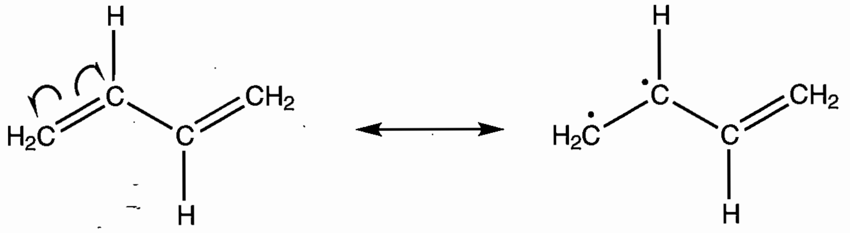


(e)



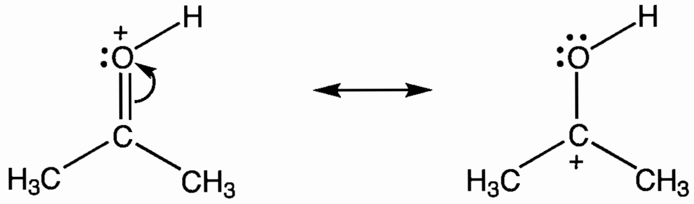
Problem 1.18 There are six resonance structures for butadiene drawn in Problem 1.17(b). Here are two more. These do not contribute significantly.



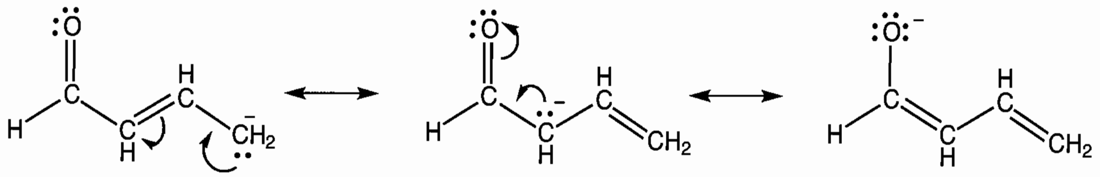


Problem 1.19

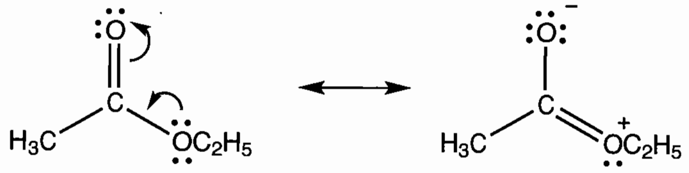
(a)



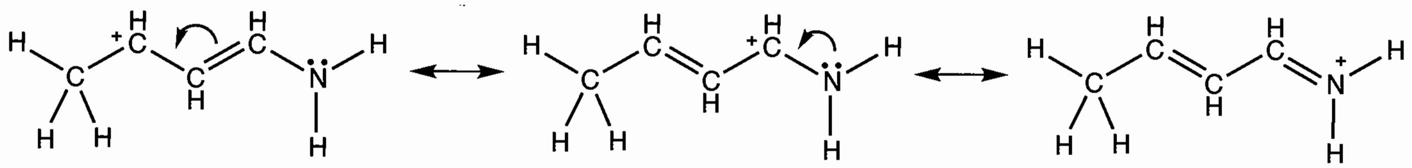
(b)



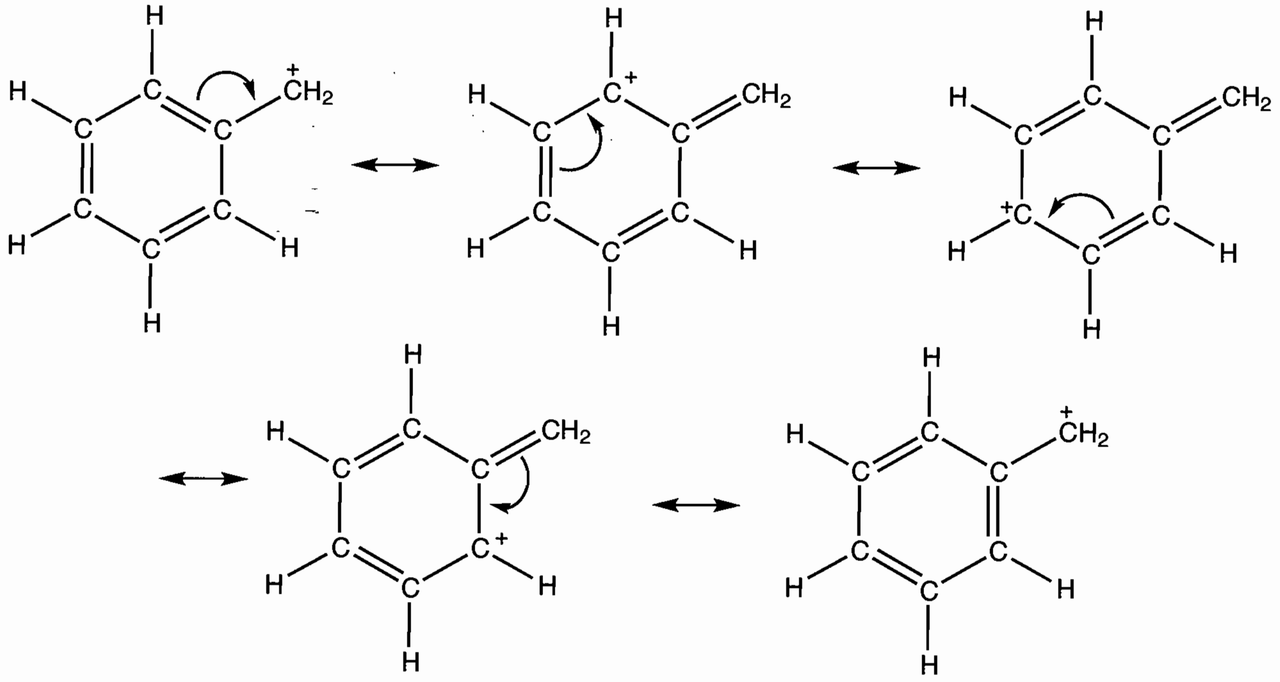
(c)



(d)



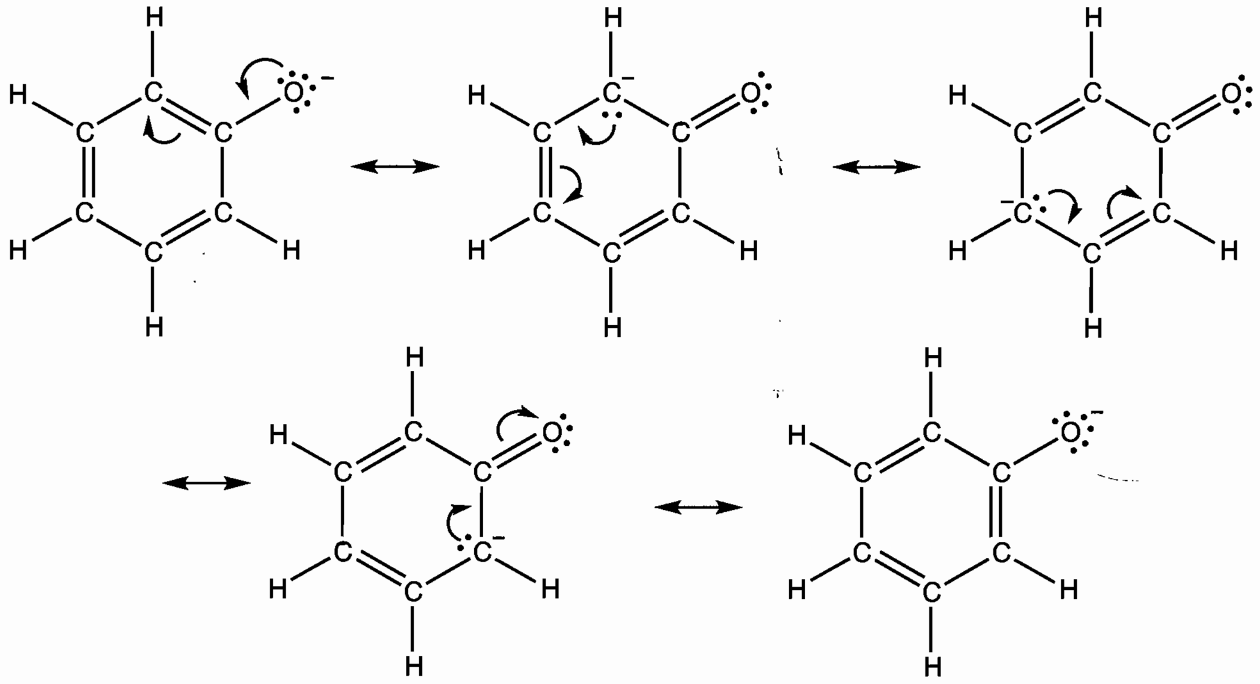
(e)



(continued)

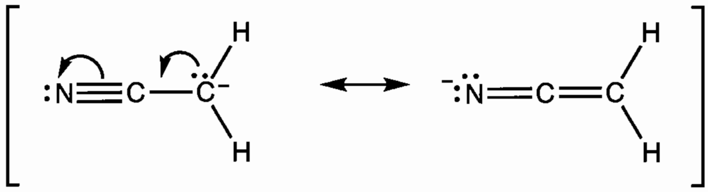
Problem 1.19 *(continued)*

(g)

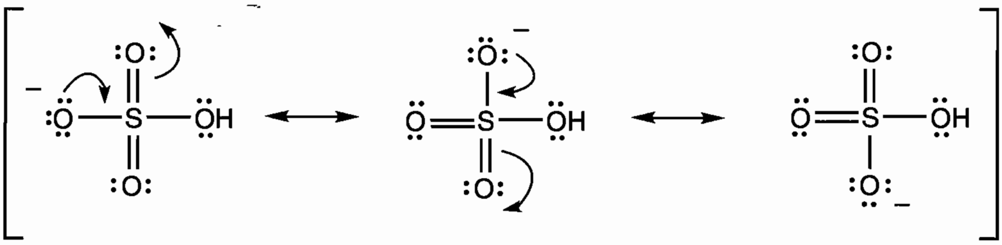


Problem 1.20

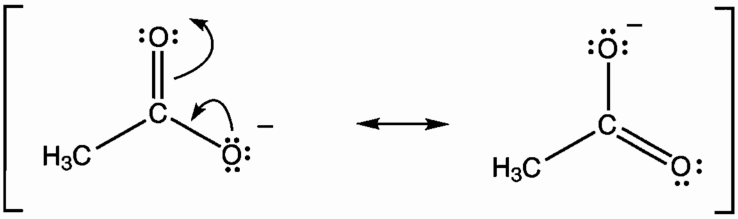
(a)



(b)

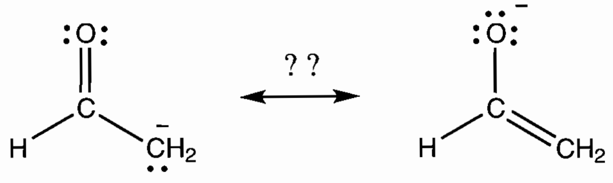


(c)

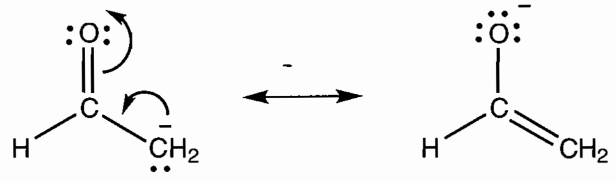


Problem 1.21

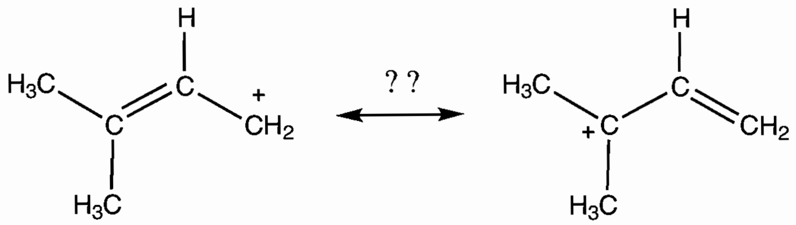
(a)



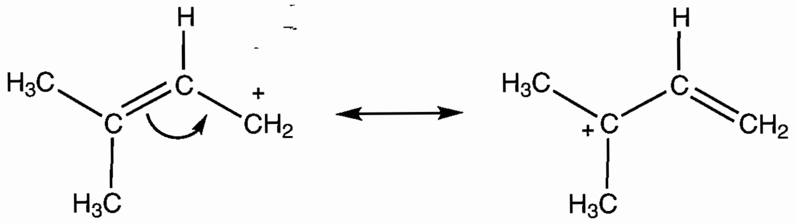
Yes, these are resonance structures. The electron pushing that allows you to go from the left structure (the aldehyde) to the right structure is shown here:



(c)

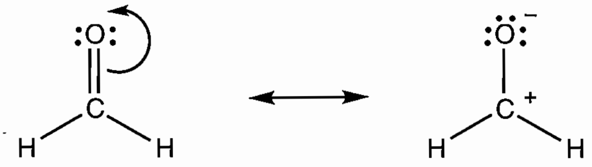


Yes, these two are resonance structures of each other. The electron pushing that allows you to go from the left structure to the right is shown here:



In (d), it is the traditional "carbonyl" carbon–oxygen double bond that is the better form. It contains more bonds and has no charge separation.

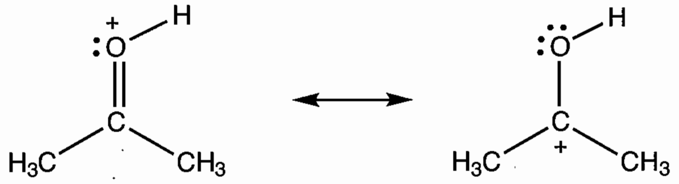
(d)



The carbon on the resonance structure on the right does not have an octet of electrons.

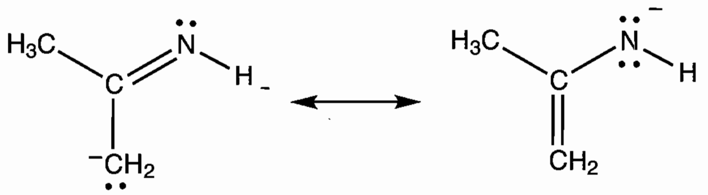
Problem 1.22

(a)



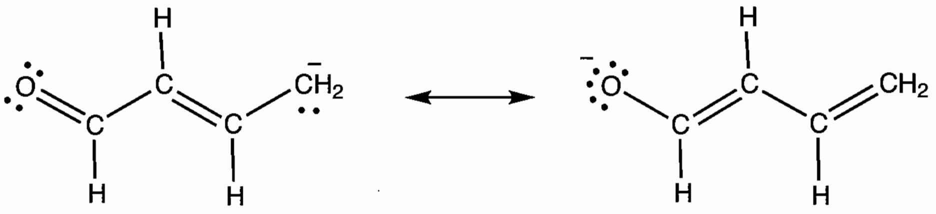
This structure contributes more because there is one more bond. The carbons and oxygen all have an octet!

(b)



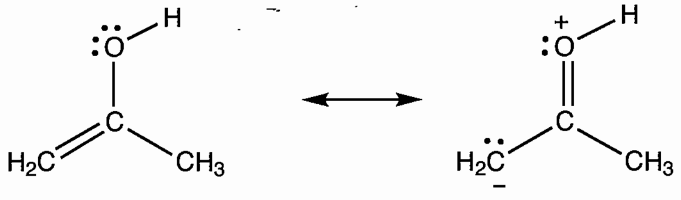
This structure contributes more because the negative charge is on the more electronegative atom.

(c)



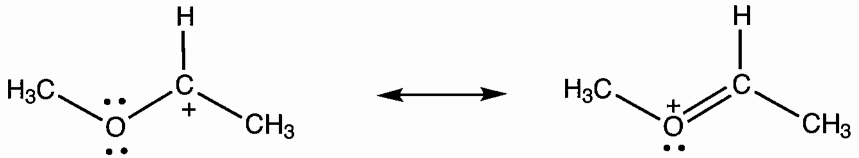
This structure contributes more because the negative charge is on the more electronegative atom.

(d)



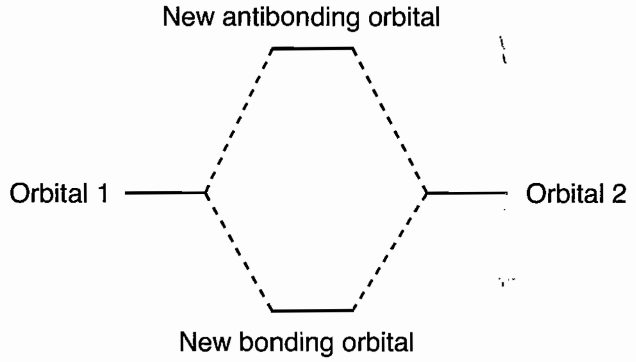
This structure contributes more because it minimizes the charge and because it gives more electrons to the more electronegative oxygen.

(e)



This structure contributes more because there is one more bond. The carbons and oxygen all have an octet!

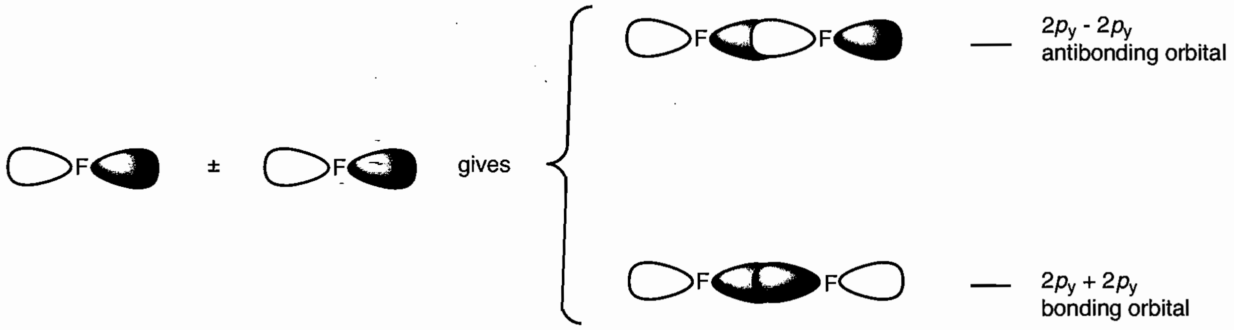
Many of the problems in this chapter require simple combinations of orbitals to produce new orbitals, and then the placement of electrons in the orbitals. The key thing to remember is that orbitals can interact in both constructive and destructive ways; $H_{1s} + H_{1s} = \Phi_B$ and $H_{1s} - H_{1s} = \Phi_A$ are prototypal examples discussed in the chapter. The interaction of orbitals is often shown in a graphical way:



Each orbital can hold a total of two electrons. Remember that placing single electrons with parallel spins in different orbitals of equal energy gives a lower energy species than the one made by placing two electrons with paired (opposite) spins in a single orbital. We move from fairly simple examples to quite sophisticated systems in these problems, but the principles remain the same. Notice the complete absence of mathematics.

Problem 1.23 The simplest molecule is "H_2 minus something." The H_2 molecule contains only two protons and two electrons. As loss of a proton doesn't leave a molecule behind, that "something" can only be an electron. The simplest molecule must be H_2^+. Another electron cannot be lost to give something even simpler because H_2^{2+} is not a molecule. In H_2^{2+}, there would be no electrons to bind the two nuclei.

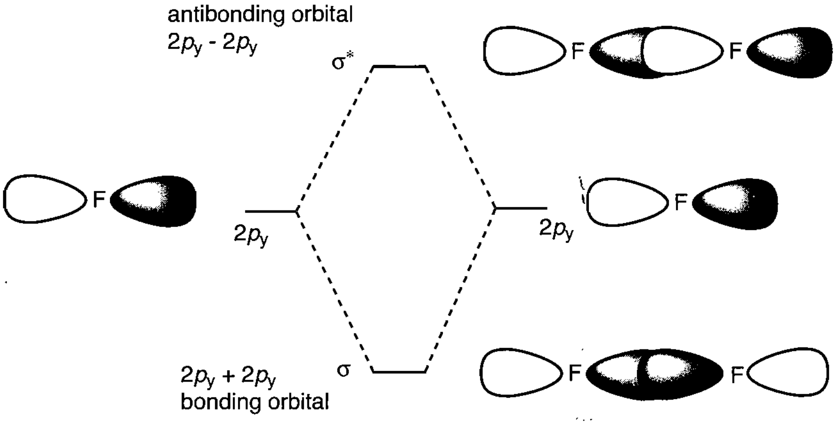
Problem 1.25



Mixing two *p* orbitals that are lined up head-to-head gives two molecular orbitals (MOs). These new MOs are σ and σ^*.

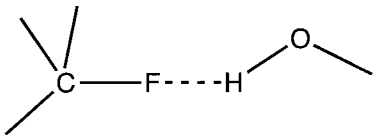
(continued)

Problem 1.25 *(continued)*

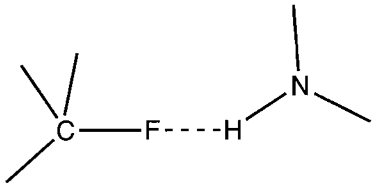


This energy diagram shows the mixing of two equal-energy $2p_y$ fluorine orbitals to obtain bonding and antibonding σ orbitals in F_2.

Problem 1.28 Fluorine is able to participate in hydrogen bonding (H-bonding). Although the strength of such interactions is theoretically calculated to be 2.38 kcal/mol, the actual observation of R—F----H—O—H is rare.



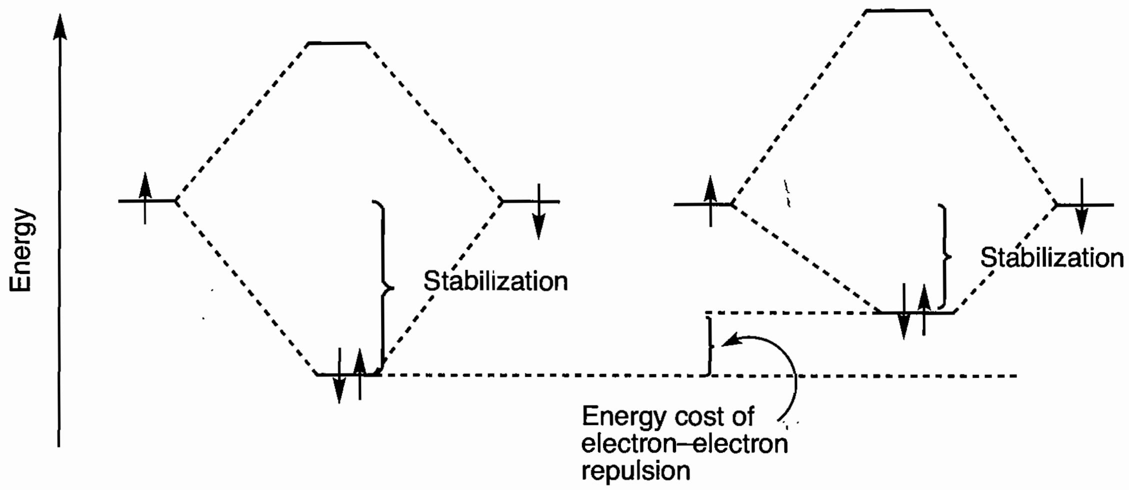
or



Hydrogen bonding might occur between a fluorine in R—F and an O—H or N—H hydrogen.

In addition, the C—F bond is much more polar than the C—H bond. This polarity can influence the way a fluorinated molecule interacts with other molecules. The ability of a molecule to bind with an enzyme, for example, can be altered as a result of a C—F bond.

Problem 1.29 In making this estimate, we divided the known bond strength of H_2 by 2. The supposition was that if two electrons in the bonding orbital are stabilized by 104 kcal/mol, one electron should be stabilized by 52 kcal/mol. However, we neglected to worry about the repulsive forces between two electrons in the same orbital. The energy of H_2 is *raised* by the repulsive forces between two negatively charged electrons occupying the same orbital. When an electron is removed to form H_2^+, these repulsive forces disappear!

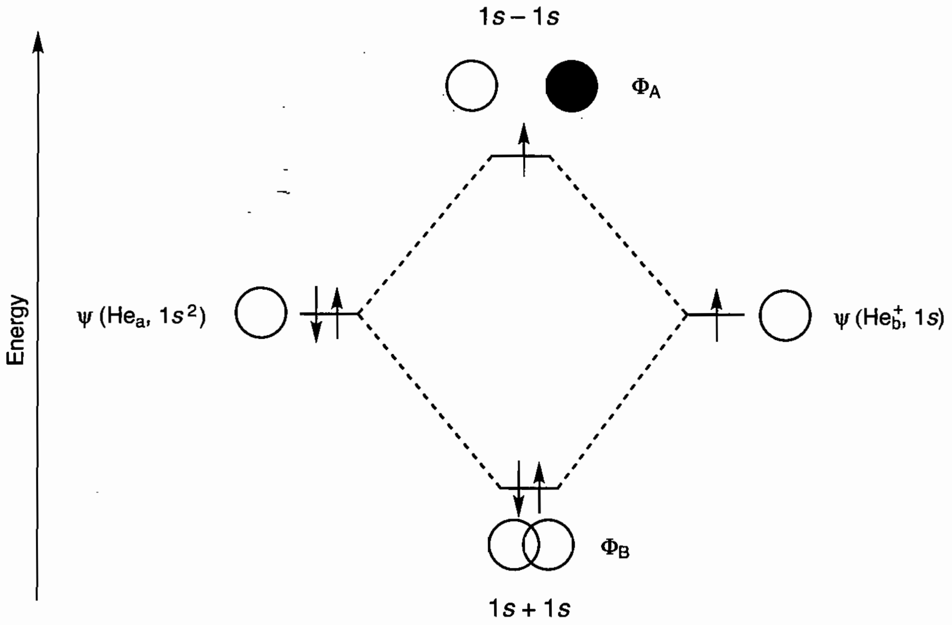


This diagram does not consider electron–electron repulsion

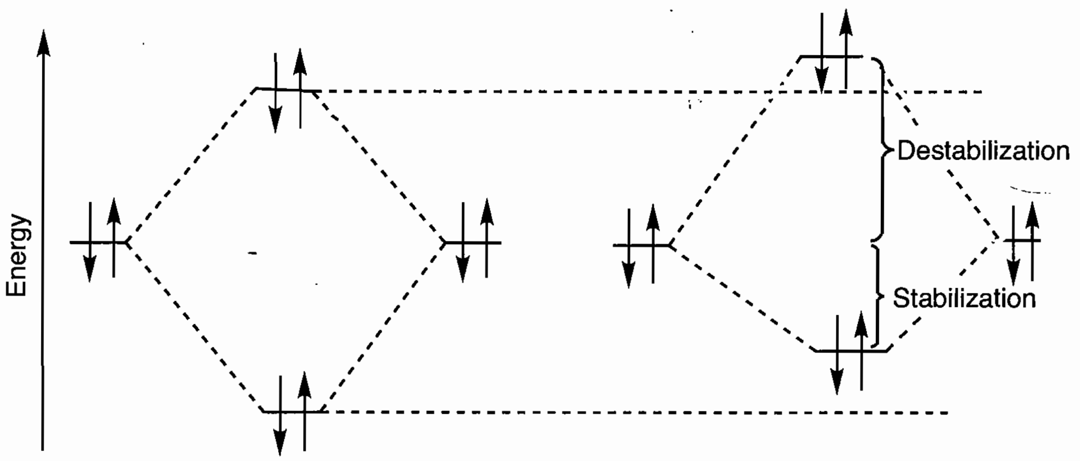
The effect of electron–electron repulsion is to raise the energy of filled orbitals

Look at it backward. If one electron in the bonding molecular orbital is stabilized by 64 kcal/mol, two electrons will be stabilized by 128 kcal/mol. However, these two electrons will repel each other, a somewhat destabilizing factor, and the real bond energy is only 104 kcal/mol.

Problem 1.30 The diagram for He_2^+ can easily be derived from the diagram in Figure 1.48 by removal of one electron. *Remember*: Construction of molecular orbitals from atomic orbitals does not depend on the number of electrons. The electrons are placed in the appropriate orbitals later. In this case, we first build the molecular orbitals of He_2 from two He 1*s* orbitals. In Figure 1.48, we put in four electrons to construct He_2. In this problem, you need only put in three electrons to make He_2^+.



Problem 1.32 The energy of an electron in an orbital depends on both stabilizing and destabilizing forces. Whenever two electrons occupy an orbital, electron–electron repulsion is a destabilizing factor and raises the energy of the electrons in that orbital. An electron in a filled bonding orbital is moved higher in energy, closer to the energy of its constituent atomic orbitals. An electron in a filled antibonding orbital is also increased in energy but moves away from the energy of its constituent atomic orbitals. The net result is that an electron in a filled bonding molecular orbital is stabilized less than an electron in a filled antibonding molecular orbital is destabilized.



Here there is no consideration of electron–electron repulsion; destabilization and stabilization are equal

The effect of electron–electron repulsion is to raise the energy of electrons in filled orbitals; now destabilization is greater than stabilization

Problem 1.33

(a) H^+ $H:^-$ $\longrightarrow$ $H{-}H$

Acid Base Product

(b) H^+ $^-:\ddot{\underset{\cdot\cdot}{O}}H$ $\longrightarrow$ $H{-}OH$

Acid Base Product

(c) H_3C^+ $^-:CH_3$ $\longrightarrow$ $H_3C{-}CH_3$

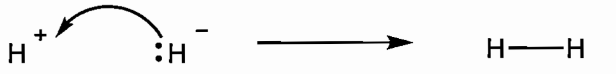
Acid Base Product

(d) H_3C^+ $:NH_3$ $\longrightarrow$ $H_3C{-}\overset{+}{N}H_3$

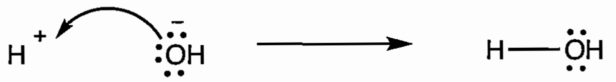
Acid Base Product

Problem 1.34 The most important aspect of electron pushing is to start where the electrons are and show where they go.

(a)



(b)



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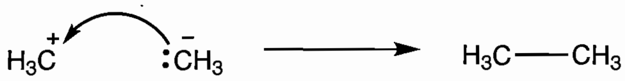

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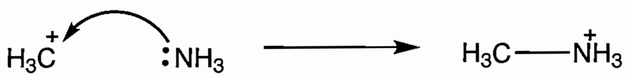
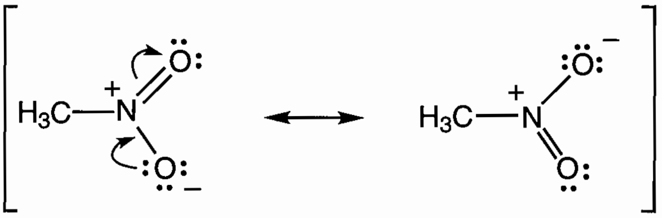


Additional Problem Answers

Problems 1.35, 1.36

(a)



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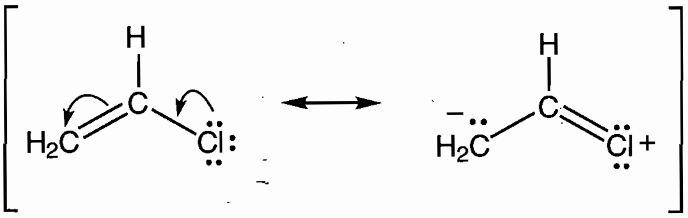

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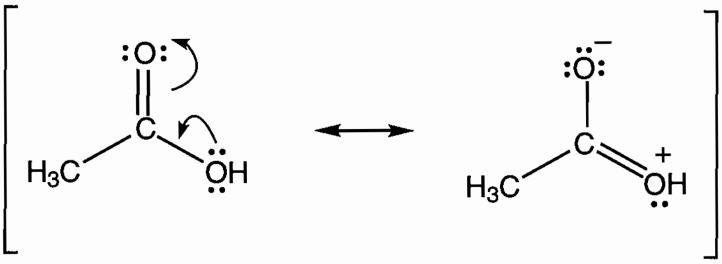

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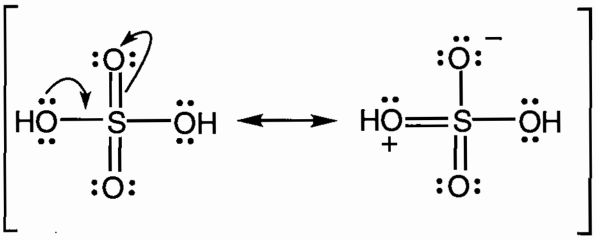
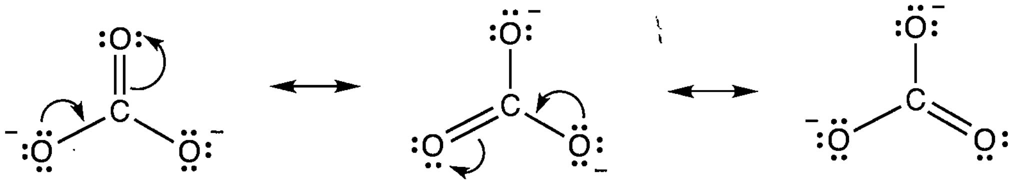
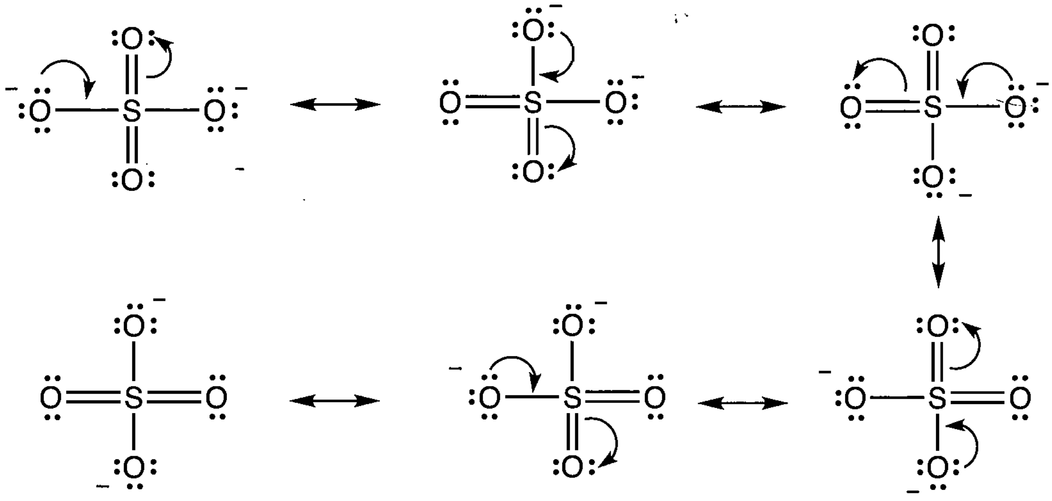


Problem 1.37 In these answers, the arrows shown will always produce the resonance form immediately to the right or below. That is, these answers are to be read left to right or top to bottom. Notice the extensive use of the double-headed resonance arrow.

(a) Carbonate

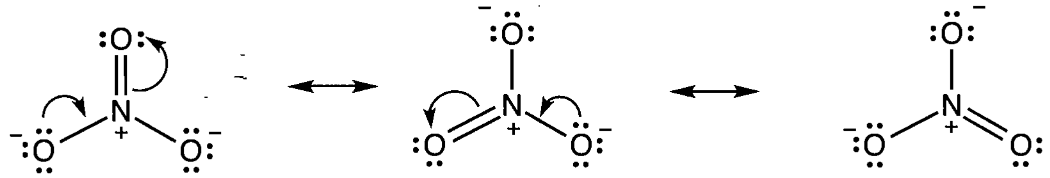


(b) Sulfate

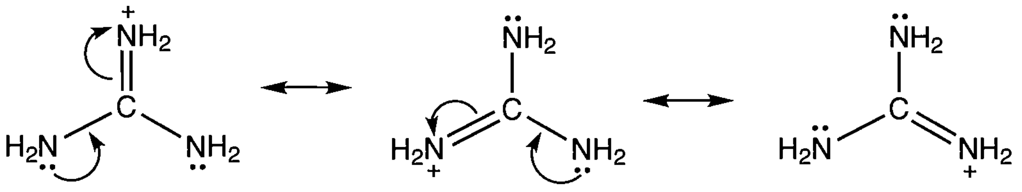


There are also resonance forms in which sulfur bears a positive charge and three oxygen atoms are negative. Can you draw these?

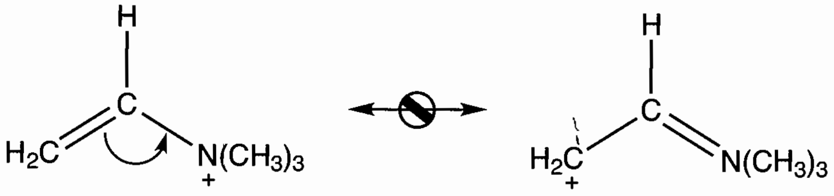
(c) Nitrate



(d) Guanidinium



(e) Vinyl ammonium

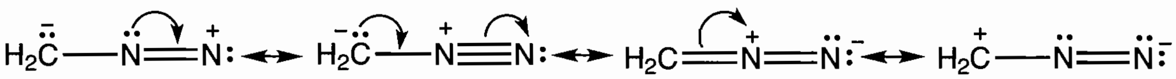


No resonance

There are no important resonance forms for this species. There is no pair of electrons on nitrogen, and five bonds cannot be formed to nitrogen. Once again, it is tempting to "push the arrow," but in this case it is best to resist that temptation. There is no empty orbital on nitrogen to receive the electrons we are trying to push.

Problem 1.38 In drawing resonance forms for these molecules, it is sometimes hard to know when to stop, as less and less stable structures are produced. We have perhaps gone too far on occasion. Can you see which forms are likely to be especially unstable and, therefore, minor contributors?

(a)



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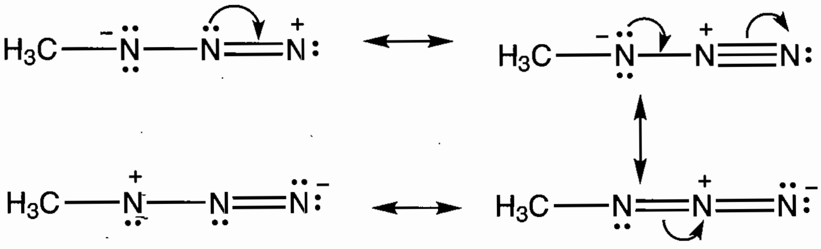
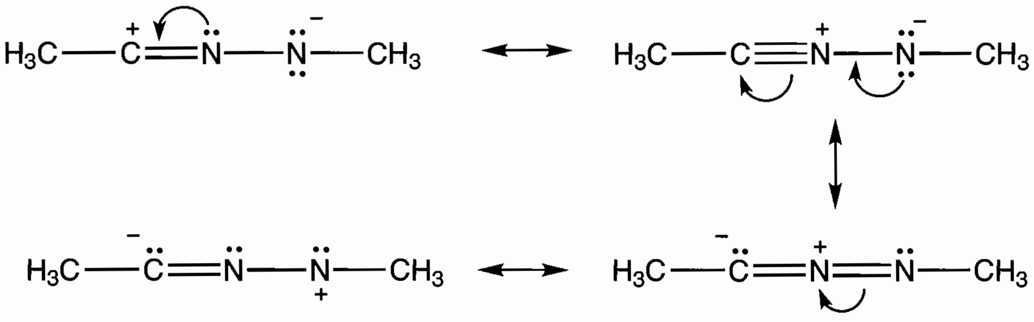


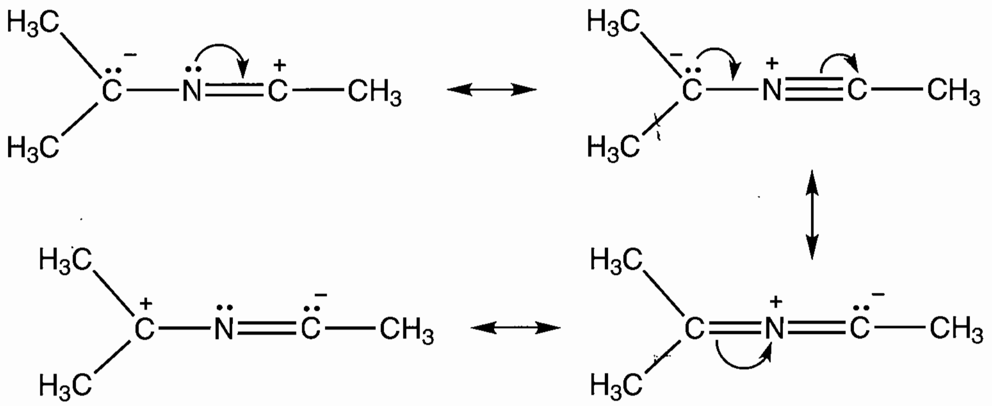
(c)



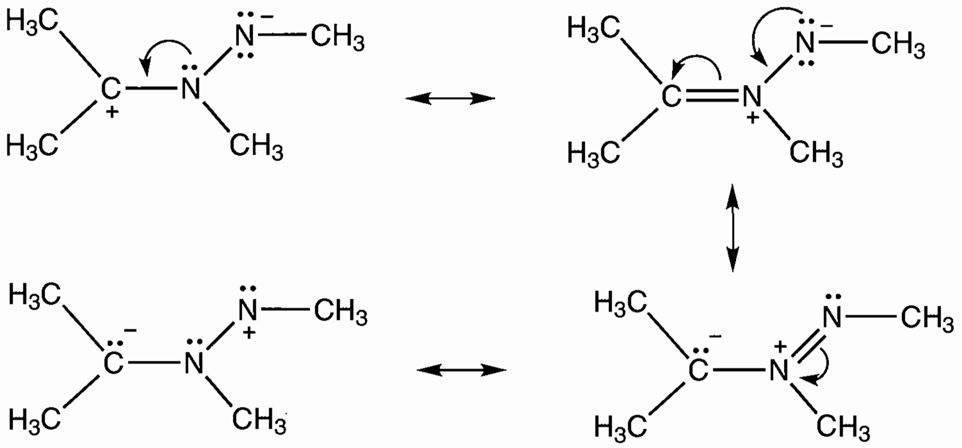
(continued)

Problem 1.38 *(continued)*

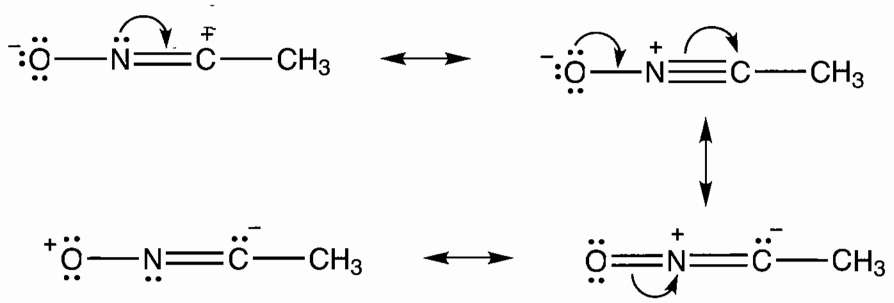
(d)



(e)

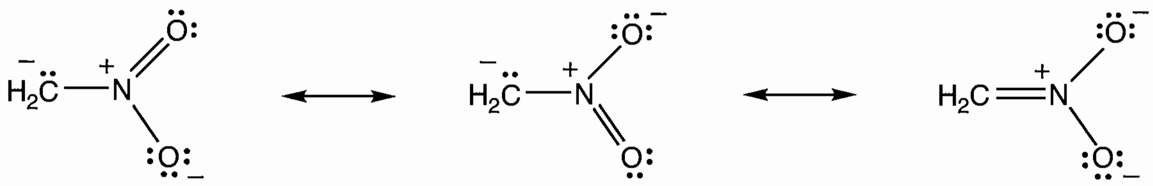


(f)

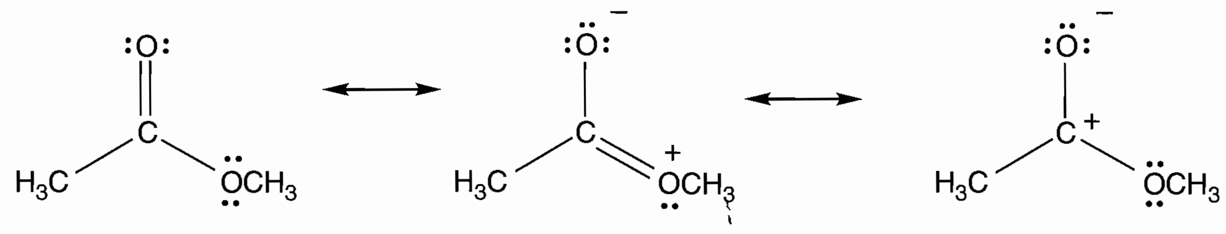


Problem 1.39

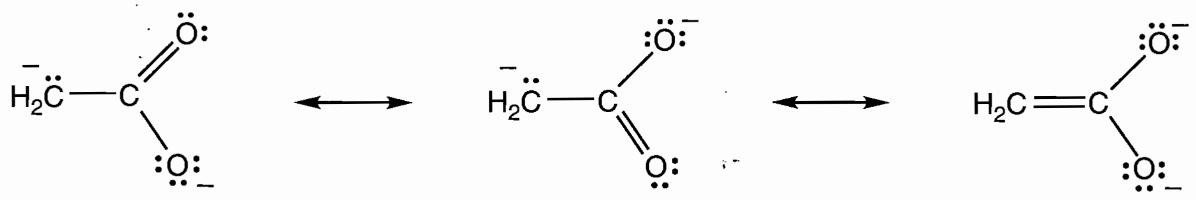
(a)



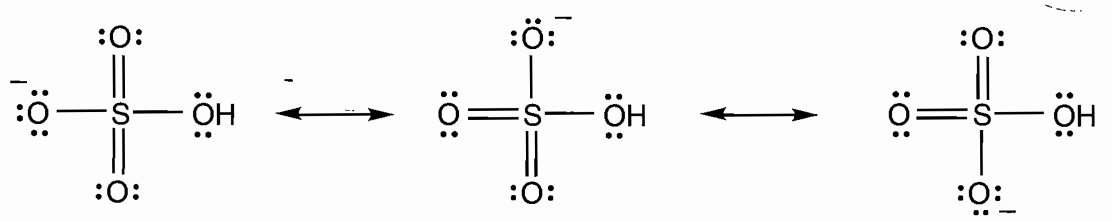
(b)



(c)

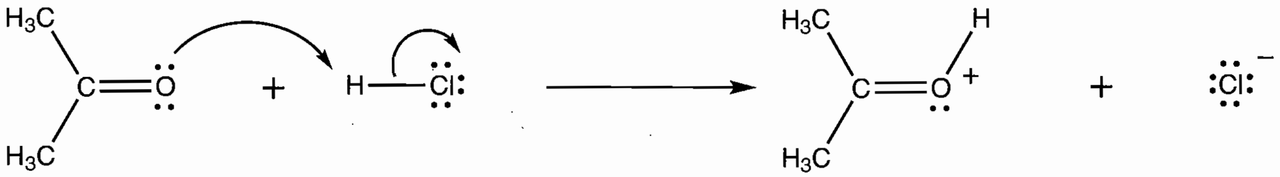


(d)

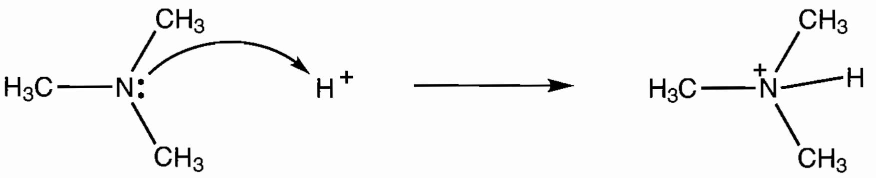


Problem 1.40

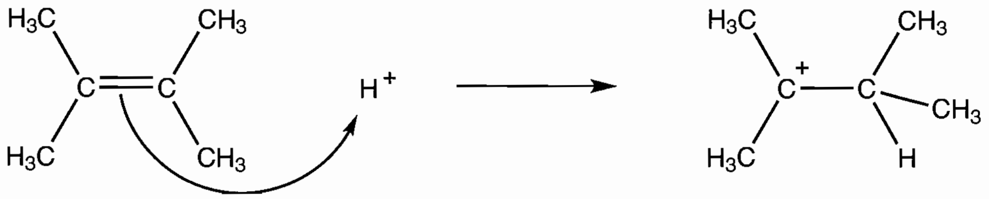
(a) The oxygen is the nucleophile and the proton of H—Cl is the electrophile in this reaction. Electrons go from the oxygen lone pair to the sigma antibond of the H—Cl, and the electrons in the sigma bond between the hydrogen and the chlorine go to the chlorine to make the relatively stable chloride ion.



(b) The nitrogen is the nucleophile, and the proton is the electrophile. Electrons go from the nitrogen lone pair to the proton.



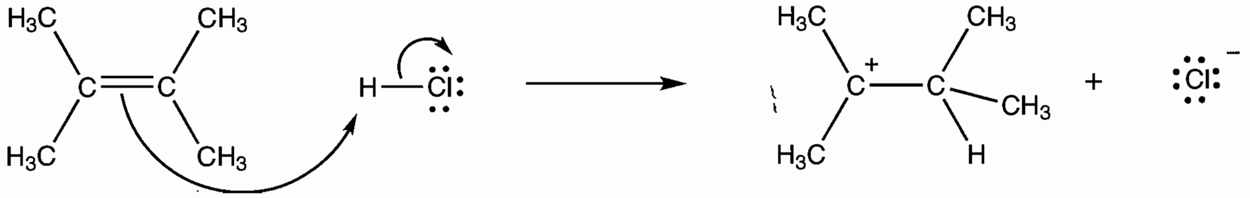
(c) The arrow needs to show the electrons going from the double bond, the nucleophile, all the way to the proton, the electrophile



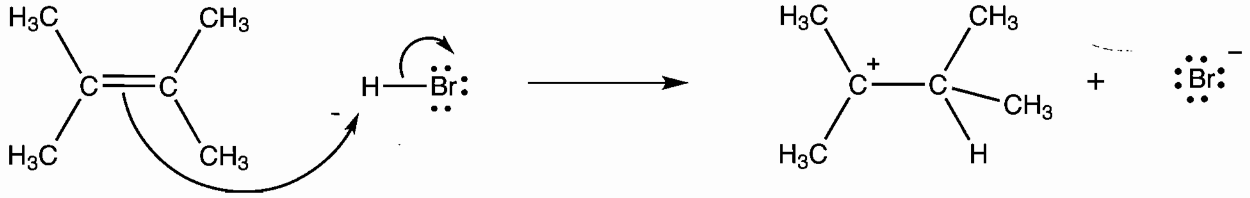
(continued)

Problem 1.40 *(continued)*

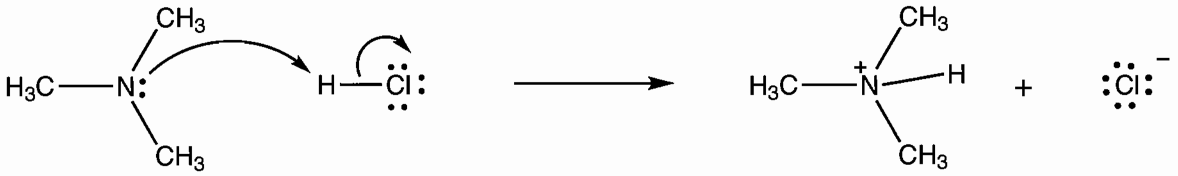
(d) The electrophile is the proton of the H—Cl. But we can't have hydrogen with two bonds. So we must show the electrons of the sigma bond in H—Cl going to the chlorine.



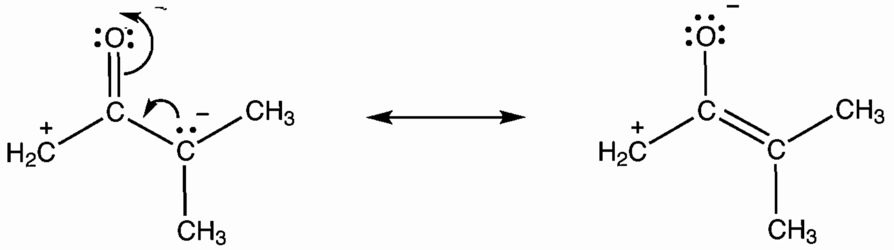
(e) The electrons in the double bond will not go to the sigma bond of the H—Br. Electrons won't make a bond with other electrons. The proper representation will have the electrons go to an electrophile, which is the H of H—Br in this case. You know that H—Br is a strong acid. It is a source of H^+.



(f) The only error in this problem is the arrow drawn from the chlorine lone pair. As the nucleophile, the nitrogen in this case, attacks the electrophile, the H of H—Cl in this case, the sigma bond of H—Cl must break. Hydrogen can't have two bonds.

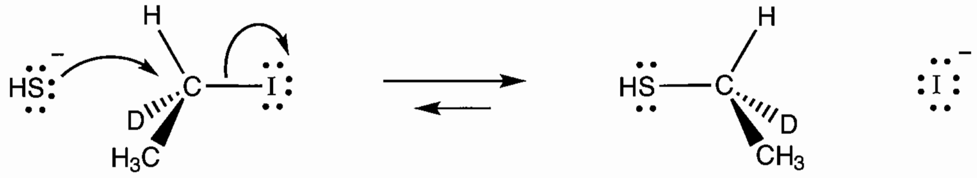


(g) Notice that this process involves resonance, not a reaction between a nucleophile and an electrophile. We are only moving electrons. The arrow pushing can't stop where the carbon has five bonds. Carbon will not have five bonds because that means 10 electrons around the atom, which violates the octet rule. Carbon cannot handle five bonds. So the movement of electrons must continue up to the oxygen.

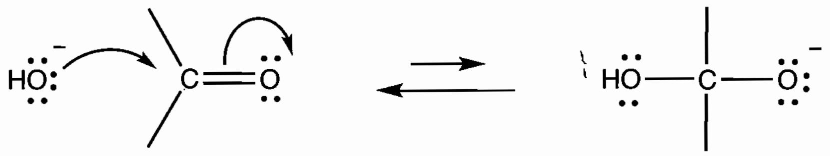


Problem 1.41

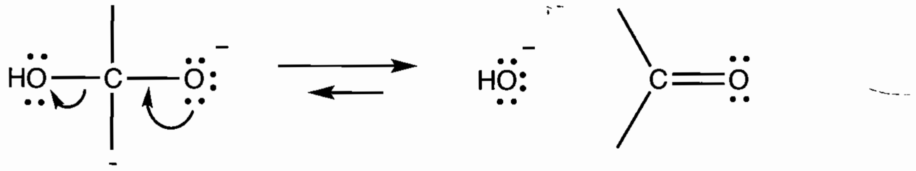
(a) Sulfide is an excellent nucleophile, and the C—I bond is weak. The nucleophile attacks the sigma antibond of the C—I. We will learn about this reaction in Chapter 7.



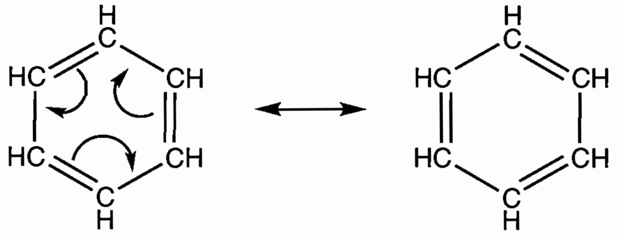
(b) Hydroxide is a nucleophile, and the carbon of a C═O bond is an electrophile. It is the antibonding orbital associated with the π bond that the nucleophile adds into. We will learn about this reaction in Chapter 16.



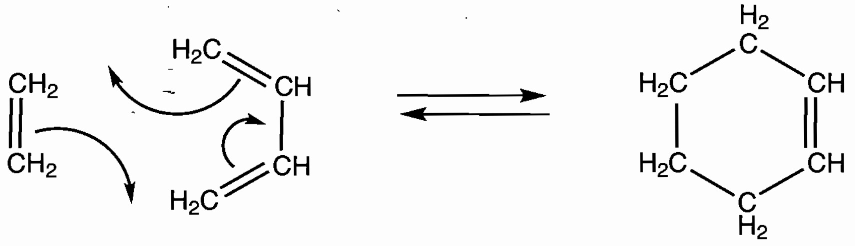
(c) The reverse reaction of the previous problem is favored in this equilibrium. The carbon–oxygen double bond is stronger than a carbon with two C–O bonds.



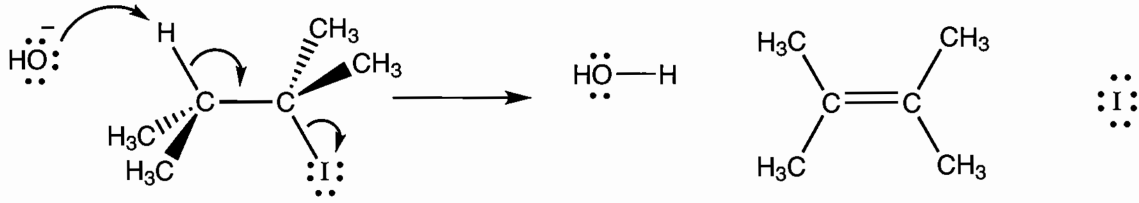
(d) This example involves resonance, not a nucleophile–electrophile reaction. These are resonance structures. Notice that no atoms are moved.



(e) This is a reaction that makes two new sigma bonds in one step. We will learn about it in Chapter 13.

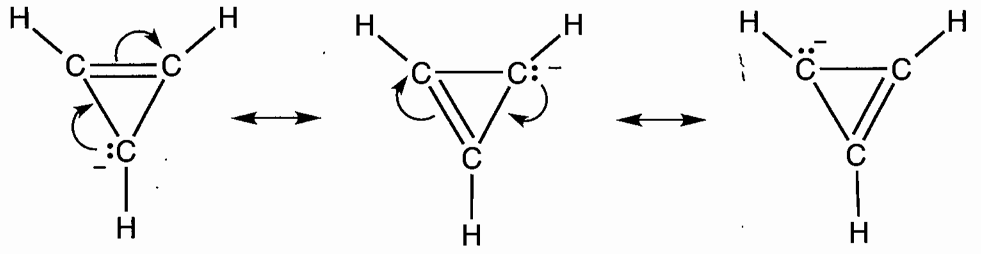


(f) Hydroxide is a nucleophile, and it deprotonates the starting molecule, as the electron pushing illustrates. We will learn about this reaction in Chapter 8.

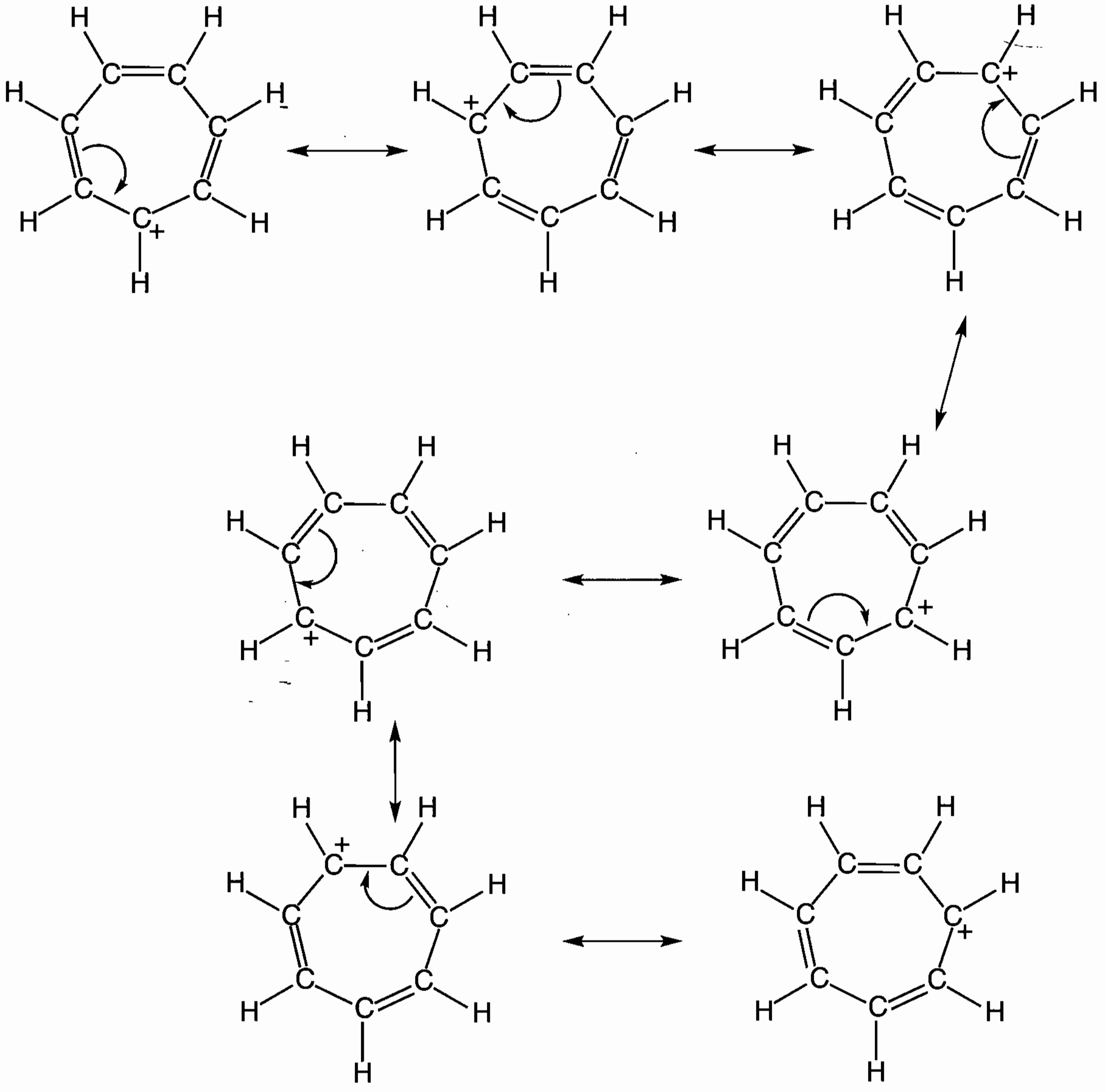


Problem 1.42

(a)

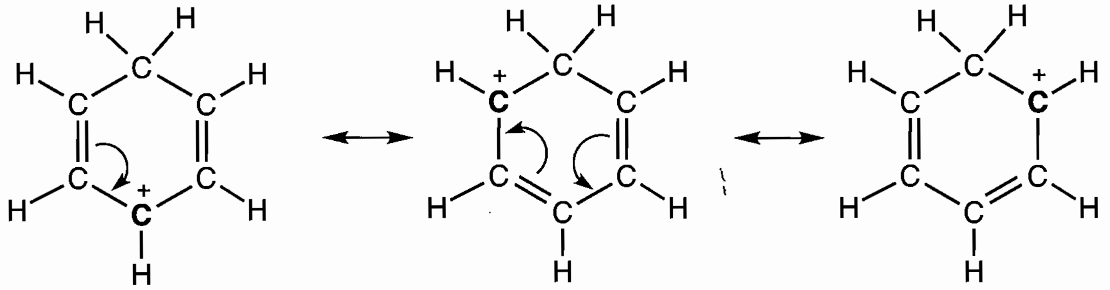


(b)



In parts (a) and (b), all ring atoms share the charge. This sets you up for part (c), in which they do not.

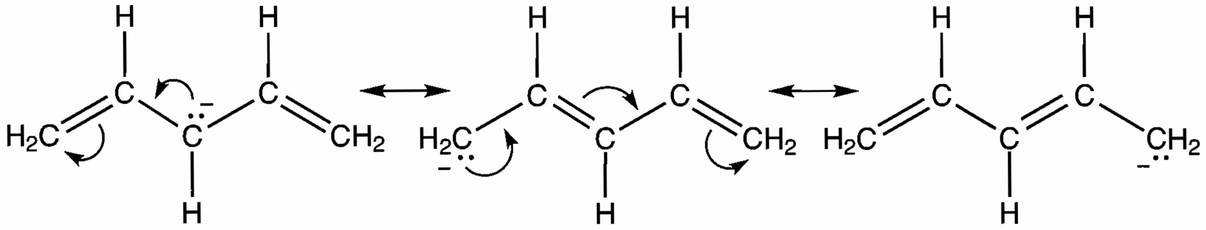
(c)



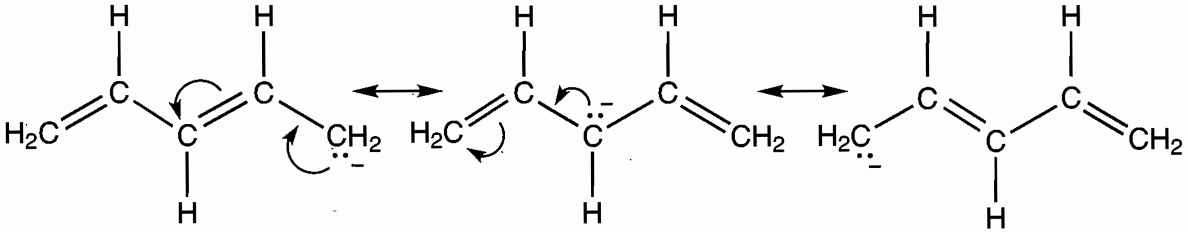
Notice the difference between (a) and (b) of this question and (c). In the first two molecules, every carbon helps share the charge. In (c), in which a CH_2 group interrupts the connectivity of $2p$ orbitals, only three carbons share the charge. We will talk more about such molecules in the future, but note now the difference between these two kinds of system. In cyclic molecules in which every ring atom has a p orbital, each atom shares the charge. In systems in which there is an insulator (an atom or atoms without a p orbital), not every ring atom will share the charge.

Problem 1.43

(a)

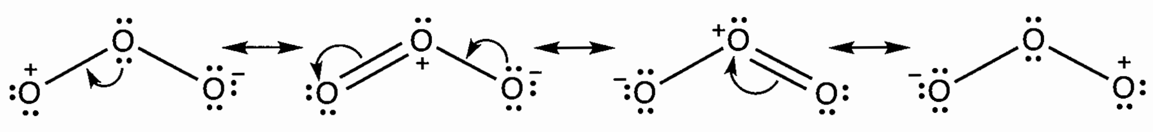


(b)

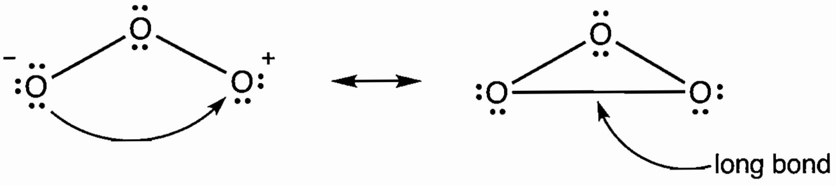


Now look carefully at these "two" species. They are exactly the same! Each has exactly the same set of three resonance contributors. Tricky, tricky, tricky.

Problem 1.44



The neutral resonance form can be produced this way:



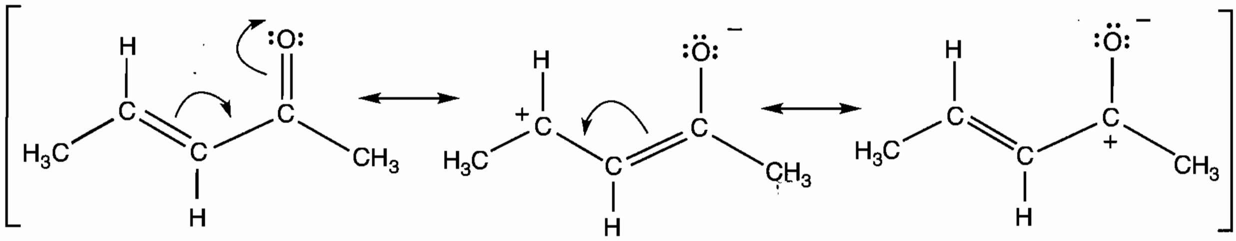
(continued)

Problem 1.44 *(continued)*

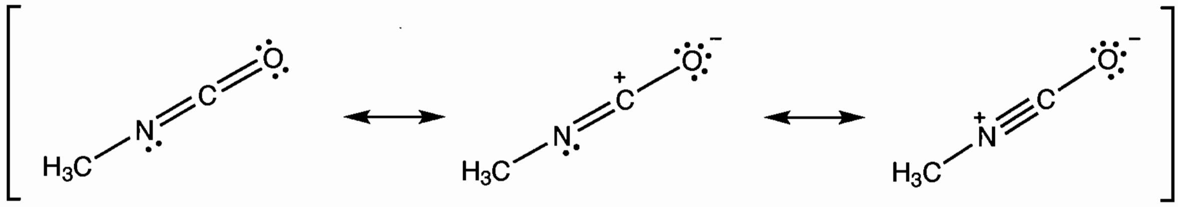
The cyclic, "no charge" resonance form *is* a resonance form, but it is not a very good one. *Remember*: No atoms may be moved in drawing resonance forms—only electrons. Resonance forms are different *electronic* structures. The long bond in the cyclic form is not a strong bond because the two oxygen atoms are very far apart.

Problem 1.45

(a)



(b) This molecule is actually linear. We will learn why in Chapter 2.

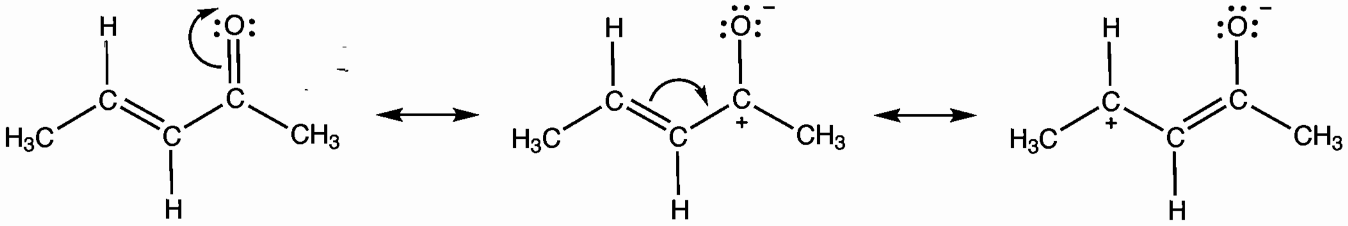


Problem 1.46

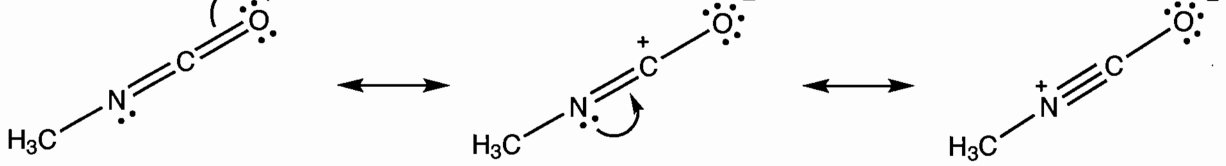
See Problem 1.45 answers that already show the electron pushing. It will always be a good idea to use the electron pushing to come up with your resonance structures. So when you are asked to draw a resonance structure, you should automatically use electron pushing to figure it out.

Often there are multiple ways to show the electron pushing. Here are equally valid options for electron pushing to get resonance structures for the molecules in Problem 1.45.

(a)



(b) This molecule will be linear because the nitrogen (and the carbon between the nitrogen and oxygen) are *sp* hybridized.



Problem 1.47 Structure (b) violates the rules of valence (there are five bonds to neutral nitrogen) and thus is not a resonance contributor.

Problem 1.48 These molecules all look alike, but a bit of electron counting shows that the charges on the noncarbon atom are different.

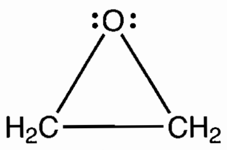
(a) For oxygen, the atomic number is 8, which means that there are eight positive charges in the nucleus. The oxygen atom in the three-membered ring has a total of eight electrons: two 1*s* electrons (never shown), four nonbonding electrons, and a share in two bonds for an additional two electrons. This oxygen is neutral. For $_8O$, 2 (1*s*) + 4 (nonbonding) + 2 (shared) = 8 electrons.

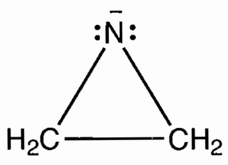
The other electron counts are as follows:

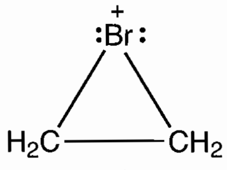
(b) For $_7N$, 2 (1*s*) + 4 (nonbonding) + 2 (shared) = 8 electrons, so N is net 1^-.

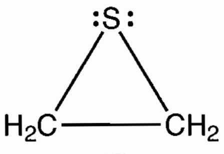
(c) For $_{35}Br$, the calculation is tougher. Bromine is in the same column as fluorine, $_9F$, and will have the same number of valence electrons. There are 28 "core" electrons ($n = 1, 2, 3$ levels, 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 3*d*), leaving 7 valence electrons. This bromine atom has 4 nonbonding and 2 shared electrons for a total of 6, and a grand total of 28 + 6 = 34. The Br is net 1^+.

(d) For $_{16}S$, there are 2 (1*s*) + 2 (2*s*) + 6 (2*p*) + 4 (nonbonding) + 2 (shared) = 16 electrons. This S is neutral. Notice that atoms in the same column of the periodic table are similar. For example, both oxygen and sulfur are neutral.


(a)

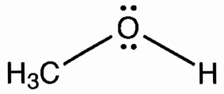

(b)


(c)


(d)

Problem 1.49 This problem reinforces the notion that atoms in the same column of the periodic table with the same number of electron dots in their Lewis structure will have the same charge. If you count for oxygen across the first three structures, you get

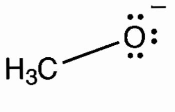
(a)



$_8O$ 2 (1*s*)
4 (nonbonding)
2 (shared)
8 total

O neutral

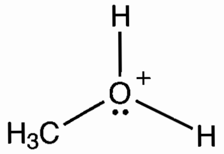
(b)



$_8O$ 2 (1*s*)
6 (nonbonding)
1 (shared)
9 total

O negative

(c)



$_8O$ 2 (1*s*)
2 (nonbonding)
3 (shared)
7 total

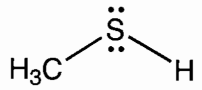
O positive

(continued)

Problem 1.49 *(continued)*

The charge determination for sulfur comes out the same:

(d)

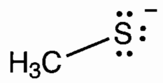


$_{16}$S 2 (1*s*)
2 (2*s*)
6 (2*p*)
4 (nonbonding)
2 (shared)

16 total

S neutral

(e)

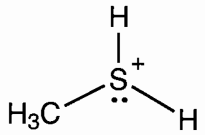


$_{16}$S 2 (1*s*)
2 (2*s*)
6 (2*p*)
6 (nonbonding)
1 (shared)

17 total

S negative

(f)



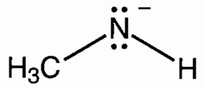
$_{16}$S 2 (1*s*)
2 (2*s*)
6 (2*p*)
2 (nonbonding)
3 (shared)

15 total

S positive

Similarly, nitrogen and phosphorus atoms in the same column of the periodic table are also identically charged in identical bonding situations.

(g)

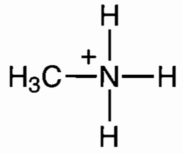


$_7$N 2 (1*s*)
4 (nonbonding)
2 (shared)

8 total

N negative

(h)

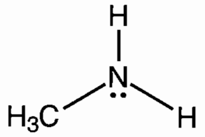


$_7$N 2 (1*s*)
0 (nonbonding)
4 (shared)

6 total

N positive

(i)

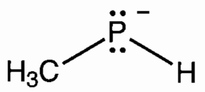


$_7$N 2 (1*s*)
2 (nonbonding)
3 (shared)

7 total

N neutral

(j)

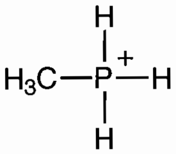


$_{15}$P 2 (1*s*)
2 (2*s*)
6 (2*p*)
4 (nonbonding)
2 (shared)

16 total

P negative

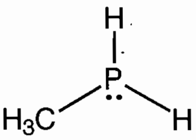
(k)



$_{15}$P
2 (1*s*)
2 (2*s*)
6 (2*p*)
0 (nonbonding)
4 (shared)
14 total

P positive

(l)

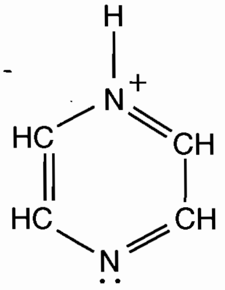


$_{15}$P
2 (1*s*)
2 (2*s*)
6 (2*p*)
2 (nonbonding)
3 (shared)
15 total

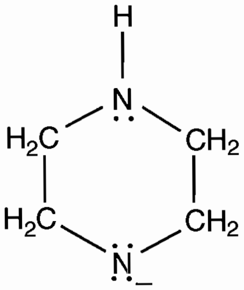
P neutral

Problem 1.50

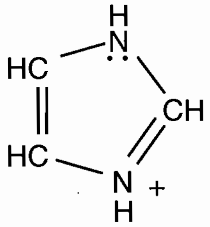
(a)



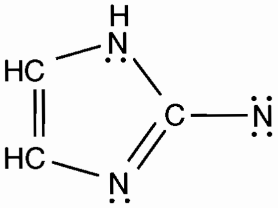
(b)



(c)

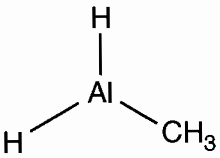


(d)

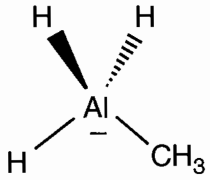


Problem 1.51

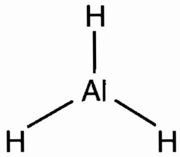
(a)



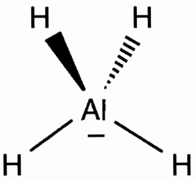
(b)



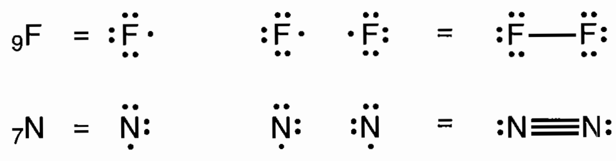
(c)



(d)



Problem 1.52 Start by drawing Lewis dot structures for the atoms. For fluorine ($_9$F), there will be seven electrons available for bonding (nine less the two 1*s* electrons), and for nitrogen ($_7$N), there will be five (seven less the two 1*s* electrons). For F_2, where there is a single bond between the two atoms, there will be six electrons left over. For N_2, where there is a triple bond between the atoms, there will be only a single pair of electrons left on each nitrogen.



Problem 1.53 As shown in the chapter, the ground state of carbon is $1s^2\ 2s^2\ 2p_x\ 2p_y$. There are many possible excited states, including $1s^2\ 2s^2\ 2p_x^{\ 2}$ and $1s^2\ 2s\ 2p_x\ 2p_y\ 2p_z$. In these species, two electrons have been brought closer together than is optimal, or one electron has been promoted to a higher energy orbital.

Problem 1.54 For these ions, we first figure out the configuration of the neutral atom. Then we add or remove electrons as necessary to accommodate the charge.

$_{11}\mathrm{Na} = 1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\,2}\, 2p_z^{\,2}\, 3s$
… so $_{11}\mathrm{Na}^+$ with one fewer electron will be

$1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\,2}\, 2p_z^{\,2}$

$_9\mathrm{F} = 1s^2, 2s^2, 2p_x^{\,2}, 2p_y^{\,2}, 2p_z$
… so $_9\mathrm{F}^-$ with one more electron will be

$1s^2, 2s^2, 2p_x^{\,2}, 2p_y^{\,2}, 2p_z^{\,2}$

$_{20}\mathrm{Ca} = 1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\,2}\, 2p_z^{\,2}\, 3s^2\, 3p_x^{\,2}\, 3p_y^{\,2}\, 3p_z^{\,2}\, 4s^2$
… so $_{20}\mathrm{Ca}^{2+}$ with two fewer electrons must be

$1s^2, 2s^2, 2p_x^{\,2}, 2p_y^{\,2}, 2p_z^{\,2}, 3s^2, 3p_x^{\,2}, 3p_y^{\,2}, 3p_z^{\,2}$

Problem 1.55

$_{19}\mathrm{K} = 1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\,2}\, 2p_z^{\,2}\, 3s^2\, 3p_x^{\,2}\, 3p_y^{\,2}\, 3p_z^{\,2}\, 4s = [\mathrm{Ar}]\, 4s$
$_{20}\mathrm{Ca} = [\mathrm{Ar}]4s^2$
$_{21}\mathrm{Sc} = [\mathrm{Ar}]4s^2 3d$
$_{22}\mathrm{Ti} = [\mathrm{Ar}]4s^2\, 3d^2$
$_{23}\mathrm{V} = [\mathrm{Ar}]4s^2\, 3d^3$
$_{24}\mathrm{Cr} = [\mathrm{Ar}]4s^2\, 3d^4$ (in fact, $_{24}\mathrm{Cr}$ is $[\mathrm{Ar}]4s\, 3d^5$)
$_{25}\mathrm{Mn} = [\mathrm{Ar}]4s^2\, 3d^5$
$_{26}\mathrm{Fe} = [\mathrm{Ar}]4s^2\, 3d^6$
$_{27}\mathrm{Co} = [\mathrm{Ar}]4s^2\, 3d^7$
$_{28}\mathrm{Ni} = [\mathrm{Ar}]4s^2\, 3d^8$
$_{29}\mathrm{Cu} = [\mathrm{Ar}]4s^2\, 3d^9$ (in fact, $_{29}\mathrm{Cu}$ is $[\mathrm{Ar}]4s\, 3d^{10}$)
$_{30}\mathrm{Zn} = [\mathrm{Ar}]4s^2\, 3d^{10}$
$_{31}\mathrm{Ga} = [\mathrm{Ar}]4s^2\, 3d^{10}\, 4p_x$
$_{32}\mathrm{Ge} = [\mathrm{Ar}]4s^2\, 3d^{10}\, 4p_x\, 4p_y$
$_{33}\mathrm{As} = [\mathrm{Ar}]4s^2\, 3d^{10}\, 4p_x\, 4p_y\, 4p_z$
$_{34}\mathrm{Se} = [\mathrm{Ar}]4s^2\, 3d^{10}\, 4p_x^{\,2}\, 4p_y\, 4p_z$
$_{35}\mathrm{Br} = [\mathrm{Ar}]4s^2\, 3d^{10}\, 4p_x^{\,2}\, 4p_y^{\,2}\, 4p_z$
$_{36}\mathrm{Kr} = [\mathrm{Ar}]4s^2\, 3d^{10}\, 4p_x^{\,2}\, 4p_y^{\,2}\, 4p_z^{\,2}$

Problem 1.56

$_{14}\mathrm{Si} = 1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\,2}\, 2p_z^{\,2}\, 3s^2\, 3p_x^{\uparrow}\, 3p_y^{\uparrow}$
$_{15}\mathrm{P} = 1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\,2}\, 2p_z^{\,2}\, 3s^2\, 3p_x^{\uparrow}\, 3p_y^{\uparrow}\, 3p_z^{\uparrow}$
$_{16}\mathrm{S} = 1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\,2}\, 2p_z^{\,2}\, 3s^2\, 3p_x^{\uparrow\downarrow}\, 3p_y^{\uparrow}\, 3p_z^{\uparrow}$

Hund's rule states that for orbitals of equal energy, such as the three $3p$ orbitals, the electronic configuration with the greatest number of parallel spins will be the lowest in energy. Electrons with parallel spins (same spin quantum number s) cannot occupy the same orbital and are therefore kept apart, minimizing electron–electron repulsion. We faced the same problem in determining the spin state of a carbon atom. Here $_6\mathrm{C} = 1s^2 2s^2 2p_x^{\uparrow} 2p_y^{\uparrow}$ is preferred to $1s^2 2s^2 2p_x^{\,2}$ or $1s^2 2s^2 2p_x^{\downarrow} 2p_y^{\uparrow}$.

Problem 1.57 In oxygen, the last two electrons fill the $2p_y$ and $2p_z$ orbitals and have unpaired spins (Hund's rule). In this case, the ESR machine will find two unpaired spins.

$_8\mathrm{O} = 1s^2\, 2s^2\, 2p_x^{\,2}\, 2p_y^{\uparrow}\, 2p_z^{\uparrow}$

In O$^+$, there will be one fewer electron, and the ESR instrument will still find the three unpaired electrons in the $2p_x$, $2p_y$, and $2p_z$ orbitals.

${}_8O^+ = 1s^2\, 2s^2\, 2p_x{}^{\uparrow}\, 2p_y{}^{\uparrow}\, 2p_z{}^{\uparrow}$

In O^{2-}, there will be two more electrons than in neutral O. The electronic configuration will be ${}_8O^{2-} = 1s^2, 2s^2, 2p_x{}^{\uparrow\downarrow}, 2p_y{}^{\uparrow\downarrow}, 2p_z{}^{\uparrow\downarrow}$ and the ESR instrument will see no unpaired electrons.

In neutral neon (${}_{10}$Ne), there are 10 electrons, so in ${}_{10}$Ne$^+$, there will be only 9. The electronic configuration will be ${}_{10}Ne^+ = 1s^2, 2s^2, 2p_x{}^{\uparrow\downarrow}, 2p_y{}^{\uparrow\downarrow}\, 2p_z{}^{\uparrow}$. Once again, the ESR instrument will find a single unpaired electron.

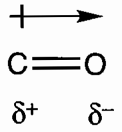
Fluoride, F$^-$, has the electronic configuration of Ne. All electrons are paired, and the ESR instrument will seek in vain for an unpaired spin.

${}_9F^- = 1s^2, 2s^2, 2p_x{}^{\uparrow\downarrow}, 2p_y{}^{\uparrow\downarrow}\, 2p_z{}^{\uparrow\downarrow}$

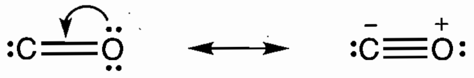
Problem 1.58 Both carbon and oxygen are neutral.

${}_6$C	${}_8$O
2 (1*s*) 2 (shared) 2 (nonbonding)	2 (1*s*) 2 (shared) 4 (nonbonding)
6 total	8 total
C is neutral	O is neutral

As oxygen is more electronegative than carbon, the dipole will be



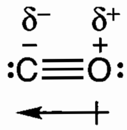
The second Lewis structure is



In the new Lewis structure, the carbon is negative and the oxygen positive:

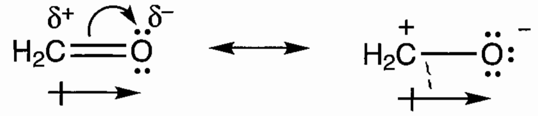
${}_6$C	${}_8$O
2 (1*s*) 3 (shared) 2 (nonbonding)	2 (1*s*) 3 (shared) 2 (nonbonding)
7 total	7 total
C is negative	O is positive

So, to the extent that this second resonance form is important, the dipole will be in the opposite direction:

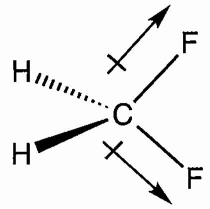


The dipoles in the two Lewis structures (two resonance forms) will tend to cancel each other out. The result is a very small observed dipole.

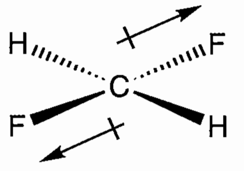
Problem 1.59 This molecule also has two important resonance forms, but the dipole is in the same direction in each and will reinforce. Formaldehyde will have a larger dipole moment than carbon monoxide.



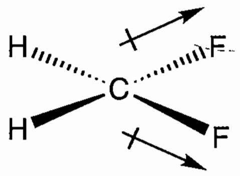
Problem 1.60 Structure **B** will have no dipole moment, as the dipoles cancel. Therefore, the observation of a dipole moment for CH_2F_2 eliminates **B** as a possibility. However, in planar structure **C**, the dipoles reinforce. This molecule will have a dipole moment and cannot be distinguished from **A** on this basis.



A



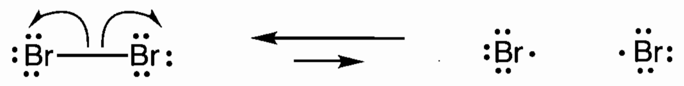
B



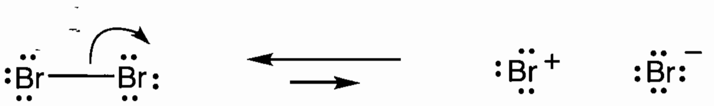
C

Problem 1.61

Homolytic cleavage



Heterolytic cleavage



Problem 1.62 It all starts normally enough, so *n* must increase monotonically. The 1*s* shell fills with two electrons so $s = \pm 1/2$. Lithium (Li) and beryllium (Be) are normal as the 2*s* shell fills. However, there seem to be no 2*p* orbitals. So *l* must not be the same as in our universe. In the new universe, $_5B$ is similar to $_1H$ and $_3Li$, and $_6C$ is similar to $_2He$ and $_4Be$. The 3*s* shell must be filling with these two atoms.

$_1H = 1s$
$_2He = 1s^2$
$_3Li = 1s^2, 2s$
$_4Be = 1s^2, 2s^2$

(as no 2*p* orbitals are available in this universe, start to fill the 3*s* shell in boron)

$_5B = 1s^2, 2s^2, 3s$
$_6C = 1s^2, 2s^2, 3s^2$

Now we find six atoms filling $_7$N through $_{12}$Mg. These must be the three 3*p* orbitals.

$_7N = 1s^2, 2s^2, 3s^2, 3p$
$_8O = 1s^2, 2s^2, 3s^2, 3p^2$
$_9F = 1s^2, 2s^2, 3s^2, 3p^3$
$_{10}Ne = 1s^2, 2s^2, 3s^2, 3p^4$
$_{11}Na = 1s^2, 2s^2, 3s^2, 3p^5$
$_{12}Mg = 1s^2, 2s^2, 3s^2, 3p^6$

Apparently, l in this universe has the value $l = 0, 1, 2, 3 \ldots (n - 2)$.
So, when $n = 1, l = 0, n = 2, l = 0$ (no 2*p* orbitals), $n = 3, l = 1, m_l = -1 \ldots 0 \ldots +1, s = \pm 1/2$.

Now the 4*s* shell must fill.

$_{13}Al = 1s^2, 2s^2, 3s^2, 3p^6, 4s$
$_{14}Si = 1s^2, 2s^2, 3s^2, 3p^6, 4s^2$

Now the 4*p* orbitals fill to complete the periodic table, as shown below.

$_{15}P = 1s^2\ 2s^2\ 3s^2\ 3p^6\ 4s^2\ 4p$
$_{16}S = 1s^2\ 2s^2\ 3s^2\ 3p^6\ 4s^2\ 4p^2$
$_{17}Cl = 1s^2\ 2s^2\ 3s^2\ 3p^6\ 4s^2\ 4p^3$
$_{18}Ar = 1s^2\ 2s^2\ 3s^2\ 3p^6\ 4s^2\ 4p^4$
$_{19}K = 1s^2\ 2s^2\ 3s^2\ 3p^6\ 4s^2\ 4p^5$
$_{20}Ca = 1s^2\ 2s^2\ 3s^2\ 3p^6\ 4s^2\ 4p^6$

Problem 1.63

(a)

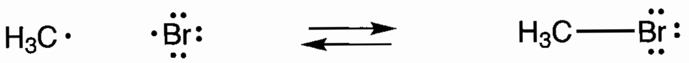
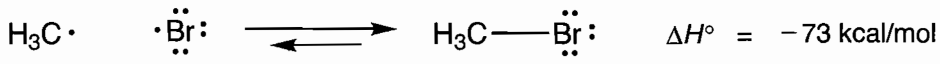
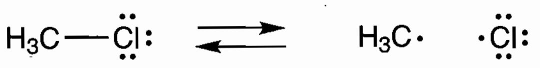


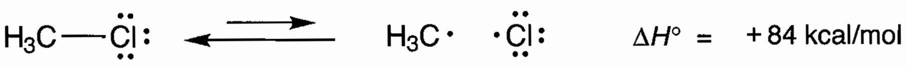
Table 1.10 gives the bond energy of the carbon–bromine bond, 73 kcal/mol. This reaction involves pure bond making, an exothermic process. The reaction would be written



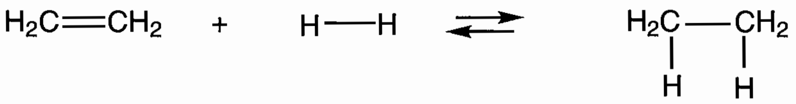
(b)



By contrast, this reaction involves only the breaking of the carbon–chlorine bond. This reaction is endothermic by about 84 kcal/mol. The reaction would be written



(c)



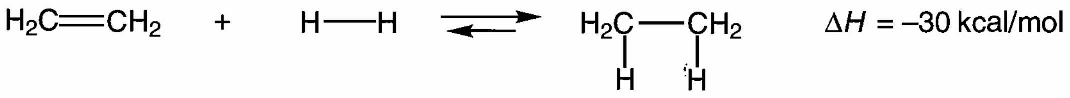
This reaction is more complicated than those of parts (a) and (b). Bonds are both made and broken. Assume that the four carbon–hydrogen bonds in the starting material are exactly balanced by the four carbon–hydrogen bonds in the product.

(continued)

Problem 1.63 *(continued)*

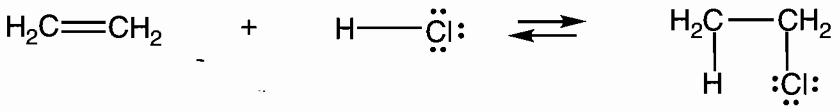
Bonds broken in starting material (kcal/mol)		Bonds made in product (kcal/mol)	
π $H_2C{=}CH_2$	66	two C—H	200
H—H	104		
	170		

This reaction is exothermic by 30 kcal/mol (200 – 170 = 30). The reaction is written



$$H_2C{=}CH_2 + H{-}H \rightleftharpoons H_2\underset{H}{C}{-}\underset{H}{C}H_2 \qquad \Delta H = -30\ \text{kcal/mol}$$

(d)

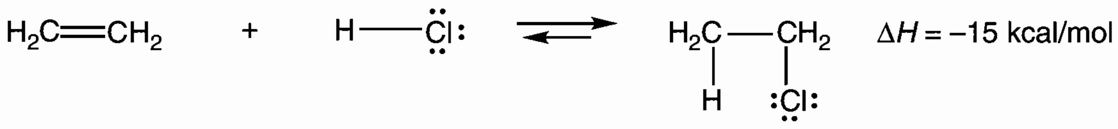


$$H_2C{=}CH_2 + H{-}\ddot{\underset{..}{Cl}}: \rightleftharpoons H_2\underset{H}{C}{-}\underset{:\ddot{Cl}:}{C}H_2$$

Bonds are both broken and made in this reaction.

Bonds broken in starting material (kcal/mol)		Bonds made in product (kcal/mol)	
π $H_2C{=}CH_2$	66	C—H	100
H—Cl	103	C—Cl	84
	169		184

This reaction is exothermic by about 15 kcal/mol (184 – 169 = 15). The reaction is written

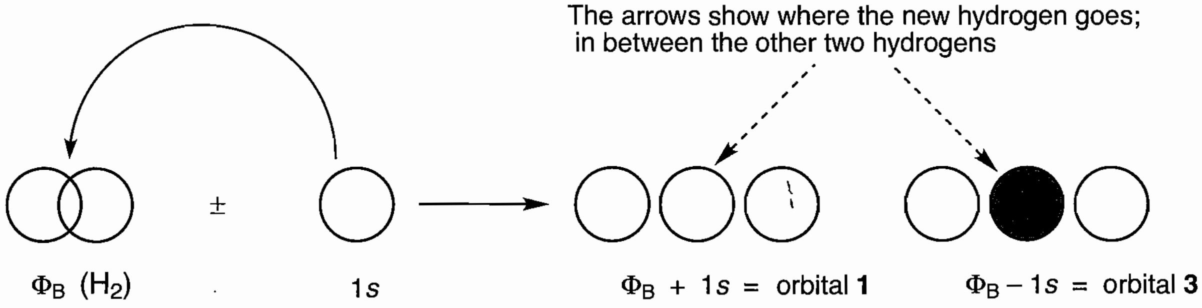


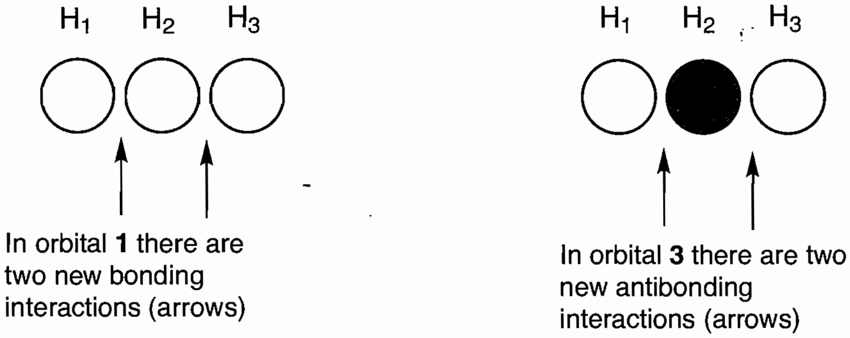
$$H_2C{=}CH_2 + H{-}\ddot{\underset{..}{Cl}}: \rightleftharpoons H_2\underset{H}{C}{-}\underset{:\ddot{Cl}:}{C}H_2 \qquad \Delta H = -15\ \text{kcal/mol}$$

Problem 1.64

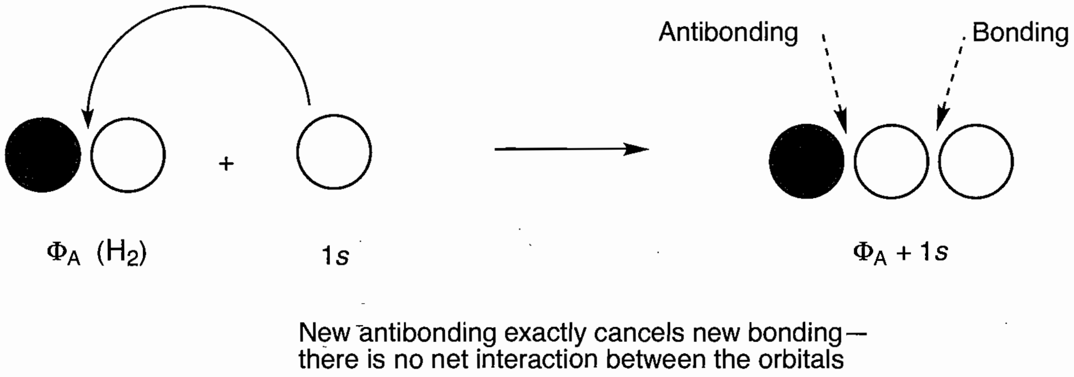
(a) As there are three orbitals going into our calculation, there must be three coming out. The H_3 molecule will have three molecular orbitals.

(b) First of all, remember that the problem tells us how to construct H_3. Place the new H in between the two hydrogens of H—H. The interaction of Φ_B with 1*s* will yield two new molecular orbitals, 1 and **3**.

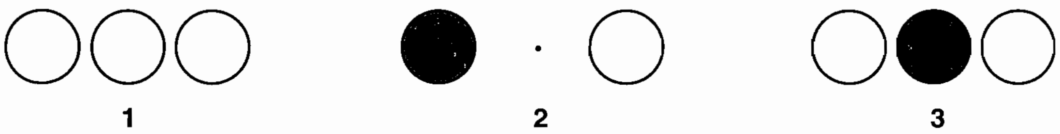




However, Φ_A will not interact with a hydrogen 1s orbital placed between the two hydrogens; this is a net-zero interaction, as the new bonding interaction is exactly canceled by the new antibond.



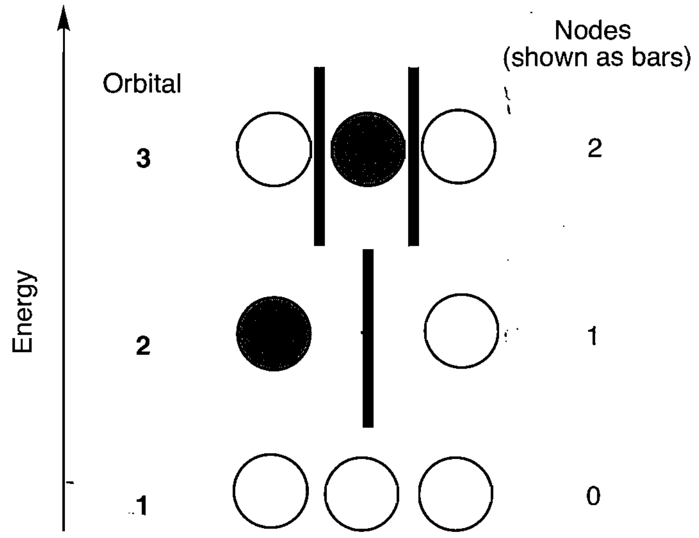
So, the three orbitals for HHH are **1** and **3** and the old Φ_A of H_2, modified only by the moving apart of the two hydrogens. Let's call this one **2**. The center dot shows the position of the middle hydrogen. The sign of the wave function at this point is zero.



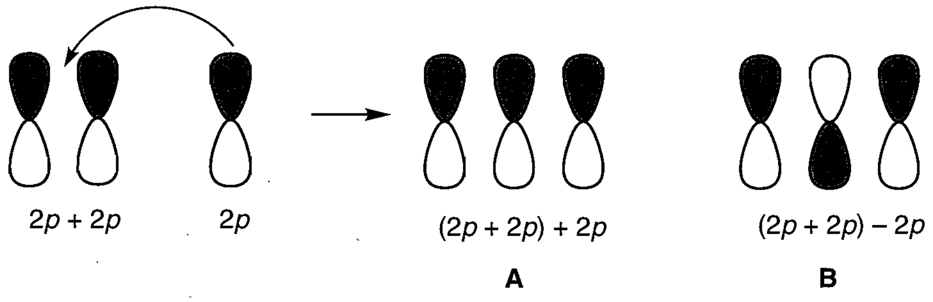
(continued)

Problem 1.64 *(continued)*

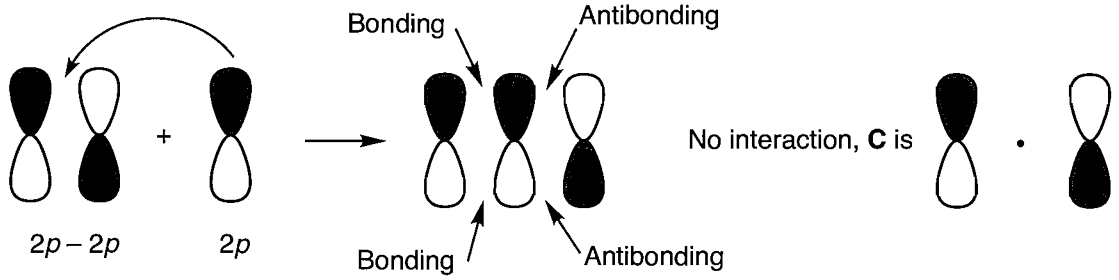
(c) You can easily order these new orbitals by simply counting the nodes.



Problem 1.65 The situation is directly parallel to the formation of HHH, made in Problem 1.64. Once again, there will be three molecular orbitals. Two new orbitals, **A** and **B**, are formed by the interaction of a single 2*p* orbital with (2*p* + 2*p*).

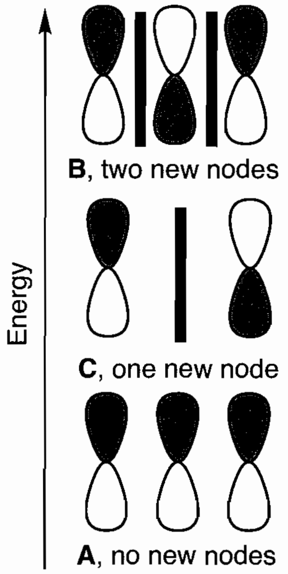


The third orbital, **C**, comes from (2*p* – 2*p*), which does not interact with a 2*p* orbital placed in the middle. Once again, this is a net-zero situation as the bonding and antibonding interactions exactly cancel.



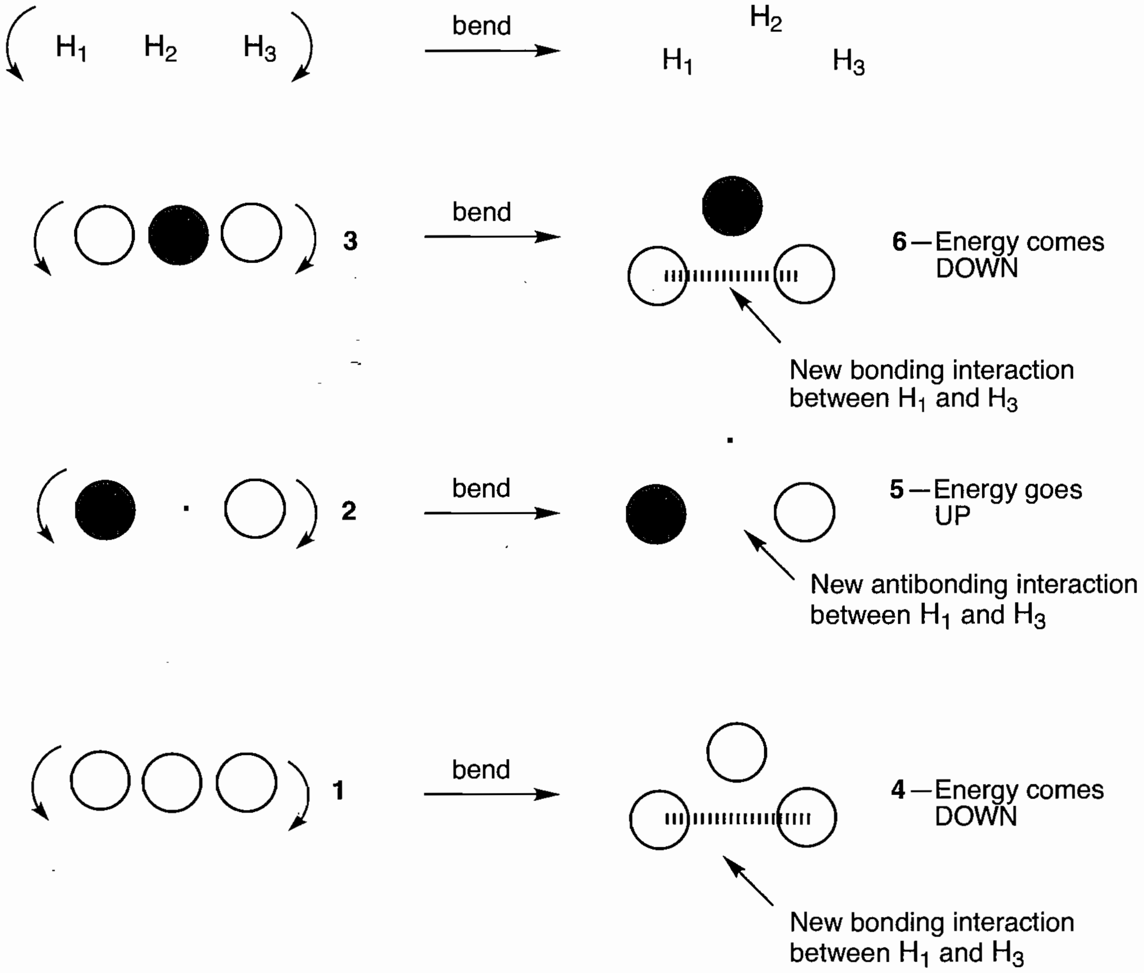
The dot in **C** simply marks the position of the central atom.

The new orbitals **A**, **B**, and **C** can be ordered by counting nodes:



Problem 1.66

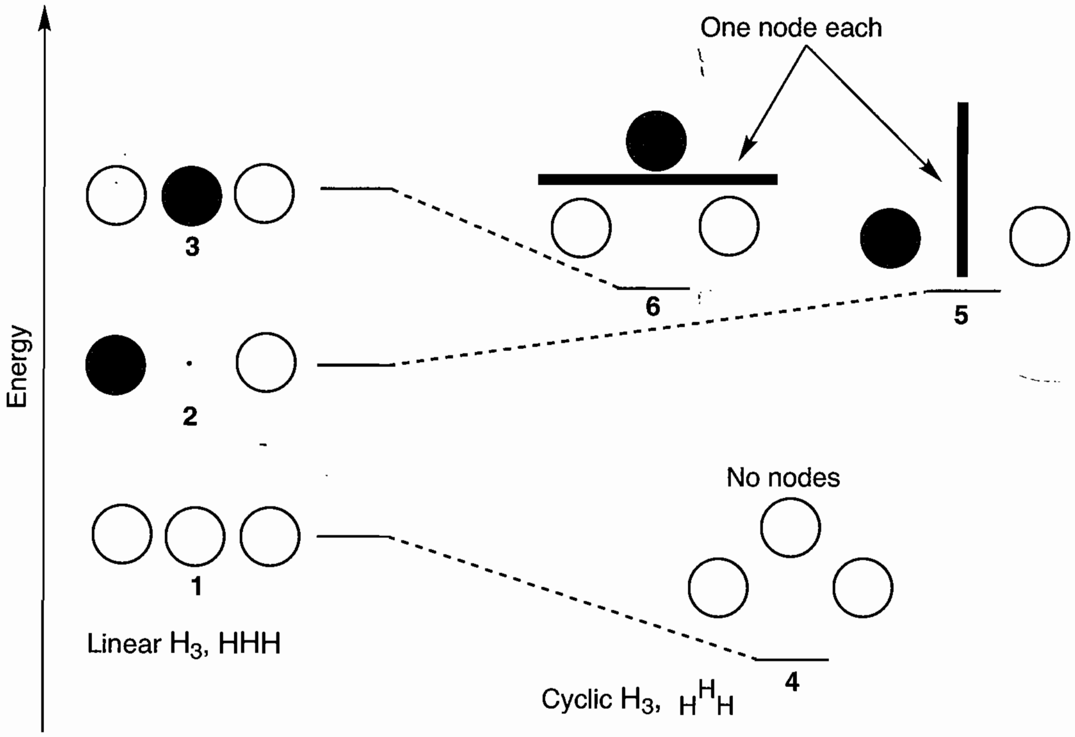
(a) All you need to do is to bend the orbitals for HHH into a triangle to generate the molecular orbitals for the triangular H_3. The direction of energy change is determined by noting whether a new bonding or antibonding interaction is created.



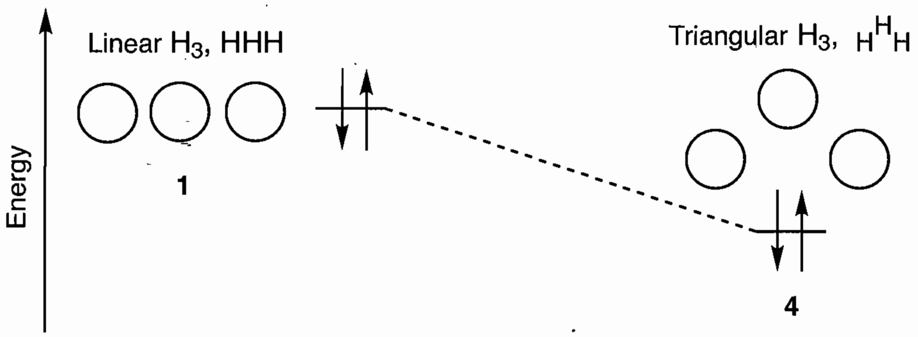
(continued)

Problem 1.66 *(continued)*

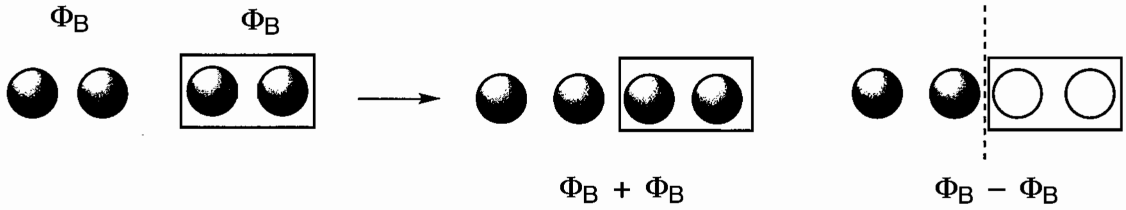
(b) Apply what the answer to (a) tells us. This answer shows how the energies of **1**, **2**, and **3** will change as bending occurs to make **4**, **5**, and **6**. Notice that orbitals **5** and **6**, each with one node (shown as a bar in the figure), are placed at the same energy.

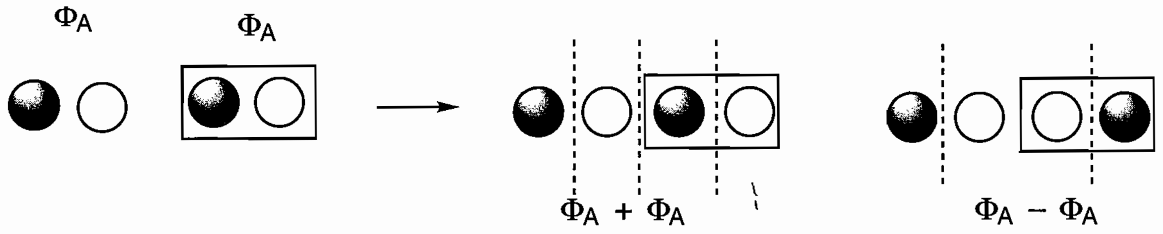


(c) In any H_3^+ molecule, there will be two electrons. In neutral H_3, there are three electrons, one from each hydrogen, and H_3^+ will have one fewer. So, only the lowest molecular orbital will be occupied. As the diagram for part (b) shows, this orbital is lower for triangular H_3 than for linear H_3. The bent species will be more stable than the linear molecule.

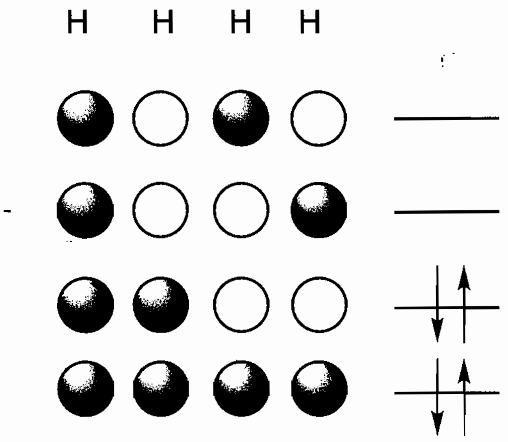


Problem 1.67 We take combinations of $\Phi_B \pm \Phi_B$ and $\Phi_A \pm \Phi_A$ placed end to end to generate four new molecular orbitals. Nodes are shown as dashed lines.

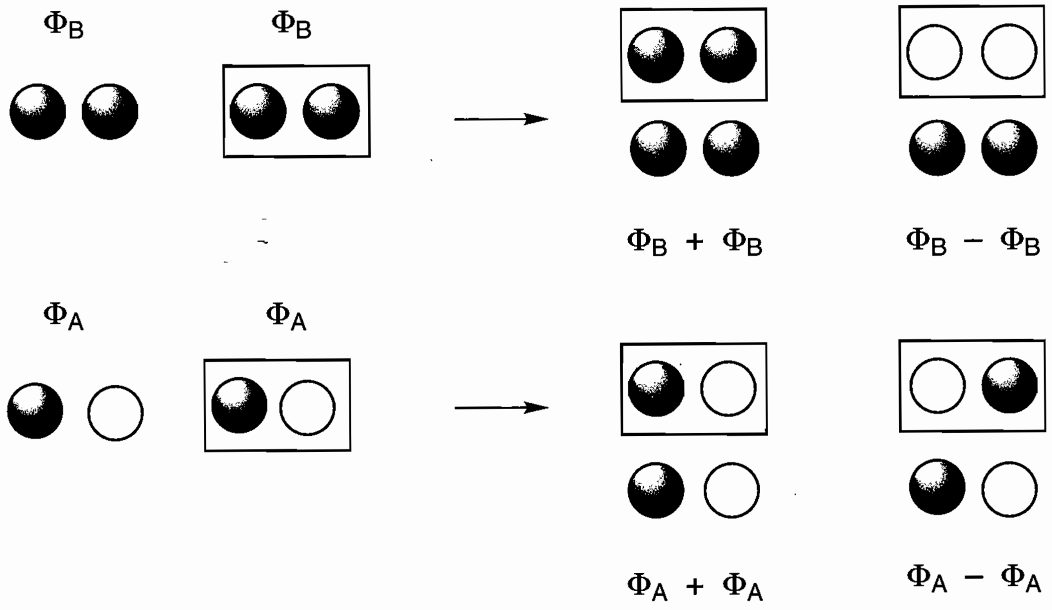




Counting nodes leads to the following order. The four electrons are placed as shown:



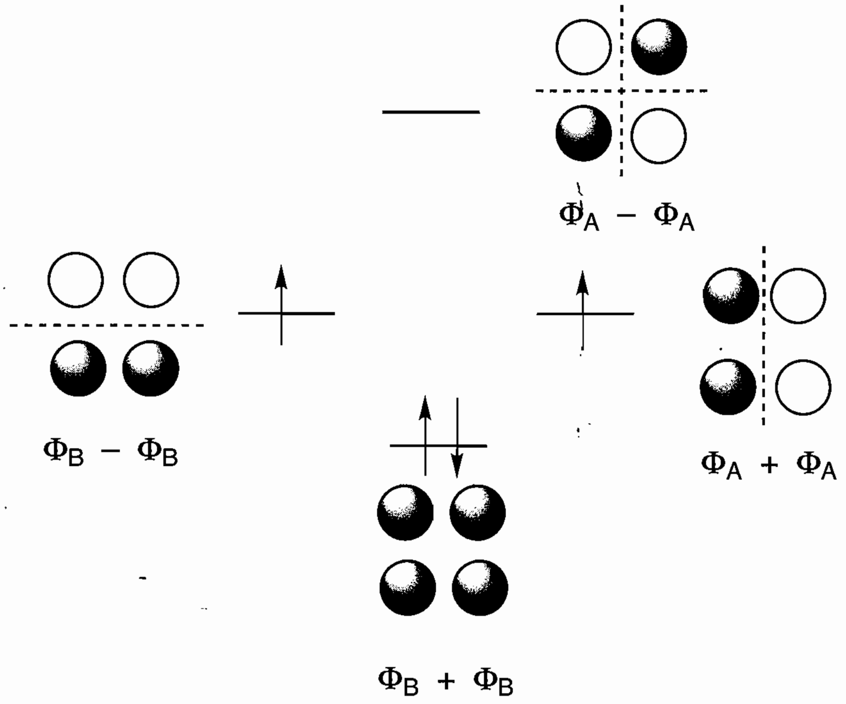
Problem 1.68 Here are the interactions:



One new orbital has zero nodes, two have one node, and one has two nodes. The order will be as shown. For neutral, square H_4, there will be four electrons placed as shown. Note the parallel spins in the singly occupied orbitals. Nodes are shown as dashed lines.

(continued)

Problem 1.68 *(continued)*



Problem 1.69 The carbon–bromine bond breaks in the first step. We can consider the two ways that bond could break: a homolytic cleavage to give a carbon radical and a bromine radical or a heterolytic cleavage to give a carbocation and a bromide ion. It is not easy to tell the difference just by seeing the bond breaking. However, there is a clue in the reaction drawn out on the right side of the screen. The product is a bromide ion. This observation tells you that the cleavage was heterolytic. It is also helpful to observe the HOMO track. Notice that the highest occupied orbital ends up on the bromine as the bond breaks. A homolytic cleavage would show electrons on both the carbon (the carbon radical) and the bromine (the bromine radical). The heterolytic cleavage has all the electron density going to the bromide, as shown in the animation.

Problem 1.70 A heterolytic cleavage gives charged species: ions. These charged ions would be stabilized by a polar solvent. A polar solvent would have more impact on such a heterolytic cleavage.

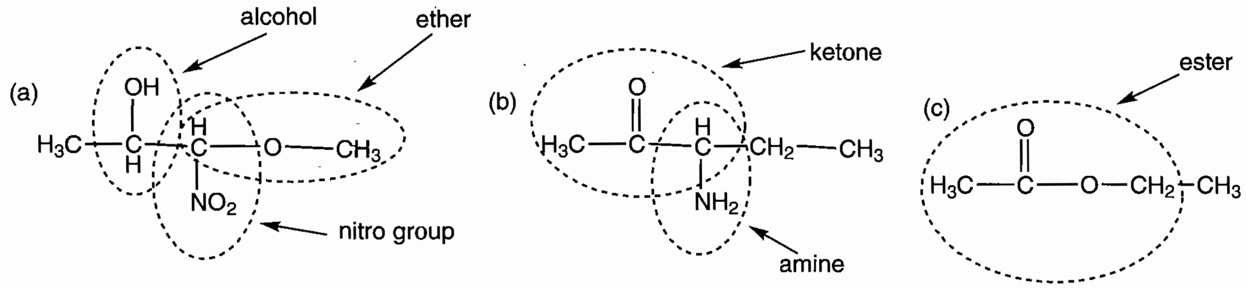
Problem 1.71 One can see from the selected picture that the calculated area for the π bond electrons is above and below the plane of the carbon atoms. This orbital is where the electrons in the π bond are located. They are not between the carbon atoms. It makes sense to conclude that π bond electrons are not as tightly held as electrons in σ bonds, which *are* between the atoms.

2

Alkanes

This set of problems provides practice in using the various hybridization schemes developed in this chapter. The major theme of the chapter is structure, and the specific focus is on the structure of alkanes. Special attention is paid to writing and naming isomeric alkanes and to using Newman projections to help us to visualize molecules in three dimensions. Practice in using the various coded two-dimensional representations of three-dimensional molecules is provided, and ring compounds are introduced.

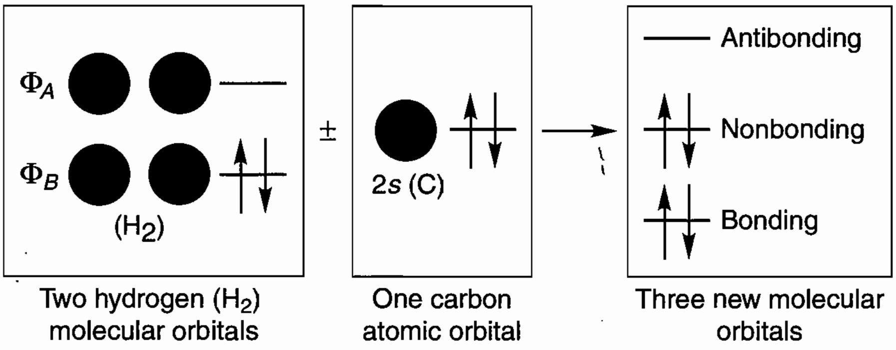
Problem 2.1



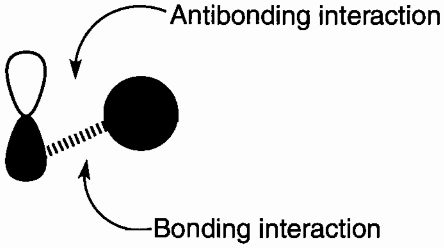
Problem 2.2 This problem asks you to consider the molecular orbital system made up of overlapping 1*s*, 2*s*, and 1*s* orbitals containing four electrons. Where are these four electrons? *Three* overlapping atomic orbitals will produce *three* molecular orbitals. That is all we really need to notice in this problem. There is plenty of room for four electrons. One of the three new orbitals is bonding, one nonbonding, and one antibonding. The four electrons will occupy the lowest two molecular orbitals. There is no violation of the Pauli principle here, as shown on the next page.

(continued)

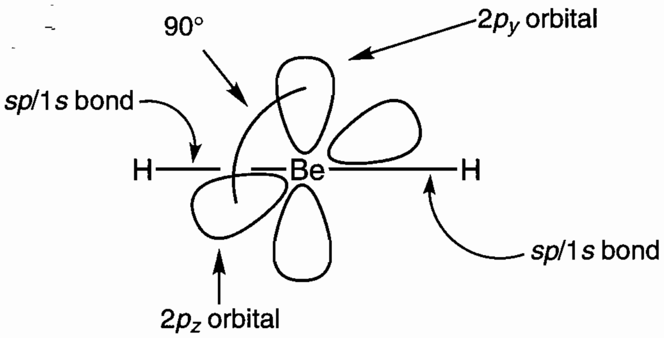
Problem 2.2 *(continued)*



Problem 2.3 As the bonding and antibonding interactions exactly cancel, there is *no* net interaction between the orbitals. In this orientation, a $2p$ and an s orbital do not interact; they are orthogonal.

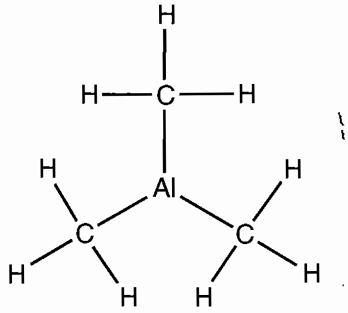


Problem 2.4 In BeH_2, the empty $2p_y$ and $2p_z$ orbitals are oriented at 90° to each other and to the pair of sp hybrid orbitals.

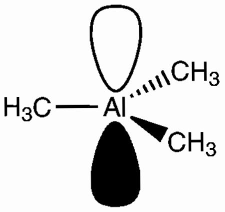


Problem 2.6 Trimethyl means that there are three methyl (CH_3) groups. Aluminum (like boron) has three valence electrons. So it is the central atom, and it can have a bond to each of the carbons of the three methyl groups. Those bonds will be at maximum distance from each other, which will give the planar arrangement with 120° angles for the C—Al—C bonds.

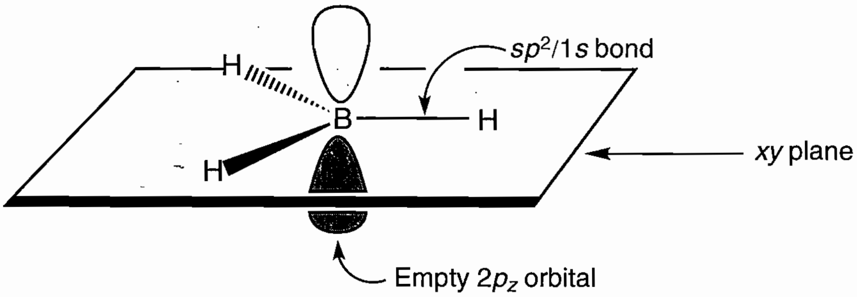
Lewis structure:



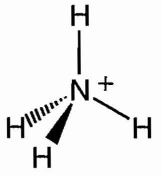
Aluminum is in the third row, and in trimethylaluminum, it only sees three electrons as its own (one electron from each bond to carbon belongs to the aluminum). So the aluminum is neutral, and it will be sp^2 hybridized. It will have an empty $3p$ orbital.



Problem 2.7 The unused empty $2p_z$ orbital on boron extends above and below the xy plane of the three boron–hydrogen bonds.



Problem 2.8 Nitrogen is attached to four atoms—the four hydrogens. Thus, we need four hybrid orbitals. These sp^3 hybrids are constructed from nitrogen's $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. The nitrogen is sp^3 hybridized and tetrahedral in shape.



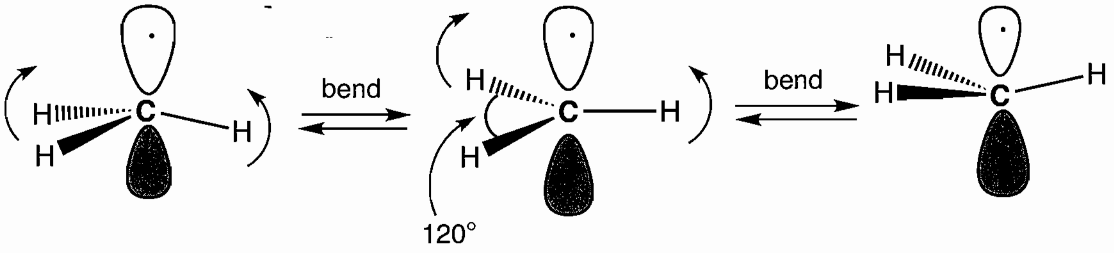
Problem 2.9

CH_2F_2 CH_2Cl_2 CH_2Br_2 CH_2I_2
CH_2ClF CH_2BrF CH_2FI
CH_2BrCl CH_2BrI
CH_2ICl

Problem 2.10

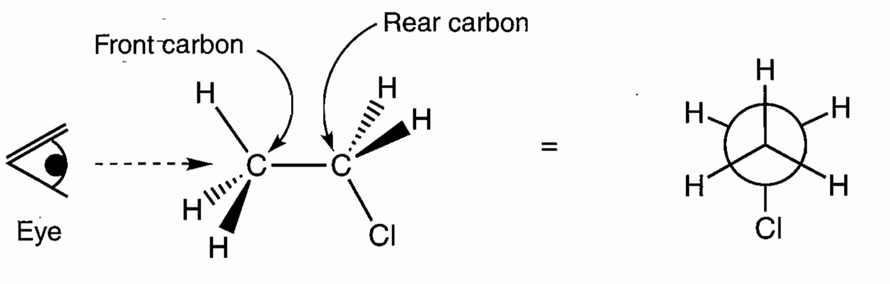
CH_2F_2 CH_2Cl_2 CH_2FCl
CHF_3 $CHCl_3$ CHF_2Cl $CHFCl_2$
CF_4 CCl_4 CF_3Cl CF_2Cl_2 $CFCl_3$

Problem 2.11 Exactly halfway between the two pyramids, the molecule must be flat, and therefore the carbon atom is sp^2 hybridized. One pyramidal molecule cannot pass to the other without going through a planar form, **A**.

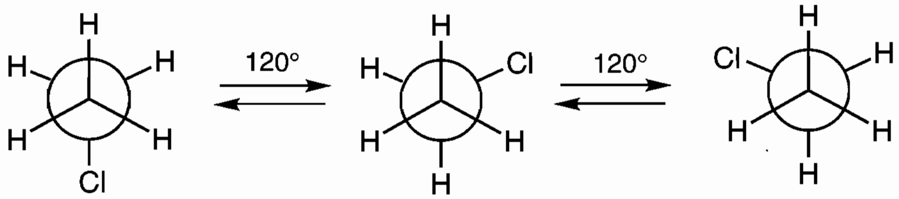


Pyramid Planar, sp^2 hybridized form, "**A**" Pyramid

Problem 2.12 Look down the carbon–carbon bond of ethyl chloride (CH_3—CH_2—Cl) with the methyl group in front. You see three carbon–hydrogen bonds attached to the front carbon. In the rear you see the carbon represented as a circle attached to two hydrogens and a chlorine. There are three staggered forms of equal energy.

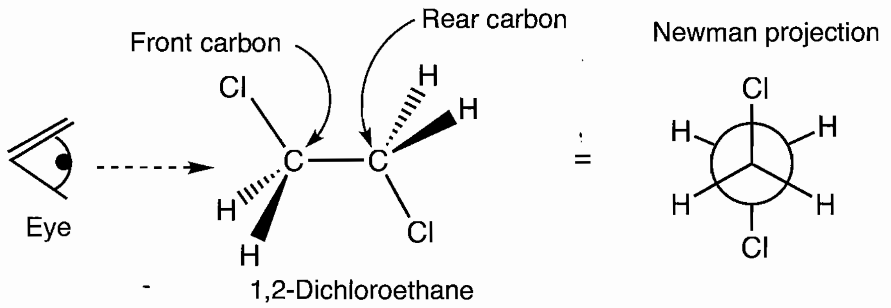


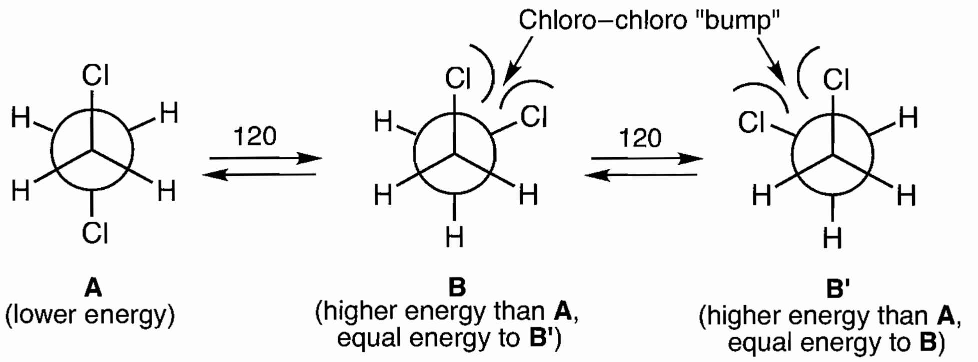
Ethyl chloride Newman projection



The three equivalent forms are interconverted by 120° rotations about the carbon–carbon bond.

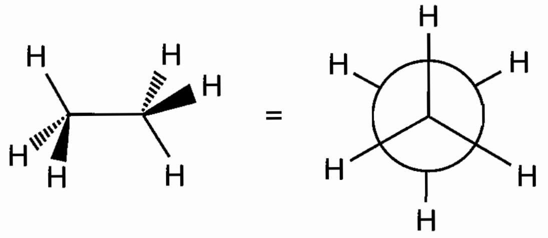
The second compound, 1,2-dichloroethane ($Cl—CH_2—CH_2—Cl$), is more complicated. As you look down the central carbon–carbon bond, you see in front a carbon attached to two hydrogens and a chlorine. In back, the carbon represented as a circle is also attached to two hydrogens and a chlorine. There are three forms interconverted by rotation, **A**, **B**, and **B′**. Forms **B** and **B′** are of equal energy, but **A** is different. As **A** keeps the two relatively large chlorine groups as far apart as possible, it is lower in energy than **B** or **B′**.



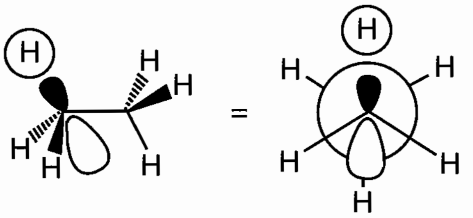


Problem 2.14

(a)



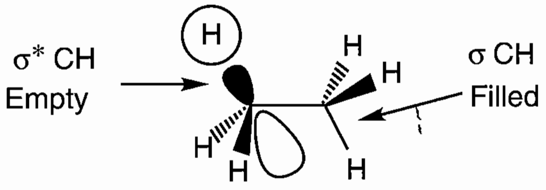
(b)



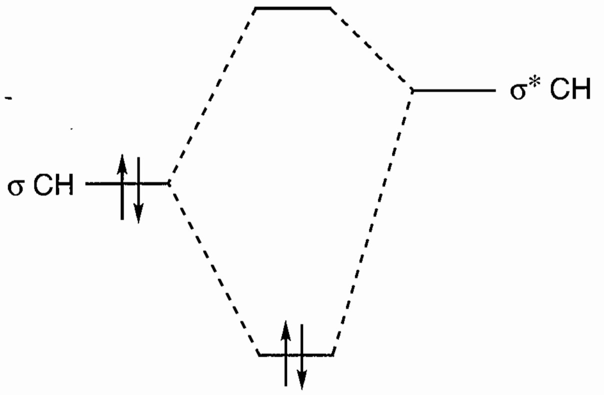
(continued)

Problem 2.14 *(continued)*

(c)

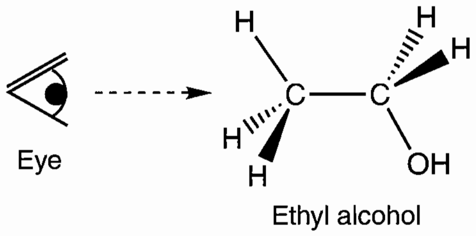


(d) The filled–empty interaction is between σ CH on one carbon and σ* CH on the other. There are six of these bonding orbital-antibonding orbital overlapping interactions in the staggered conformation of ethane. There are none in the eclipsed conformation.

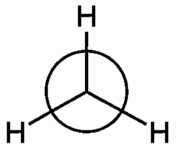


Problem 2.15 A transition state was first encountered in Problem 2.11 (p. 67). The planar form separating the two pyramidal forms of the methyl radical is a transition state. Transition states are often shown in brackets, [TS].

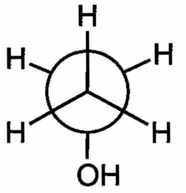
Problem 2.16 Start by drawing a "stick" or "sawhorse" figure for staggered ethyl alcohol.



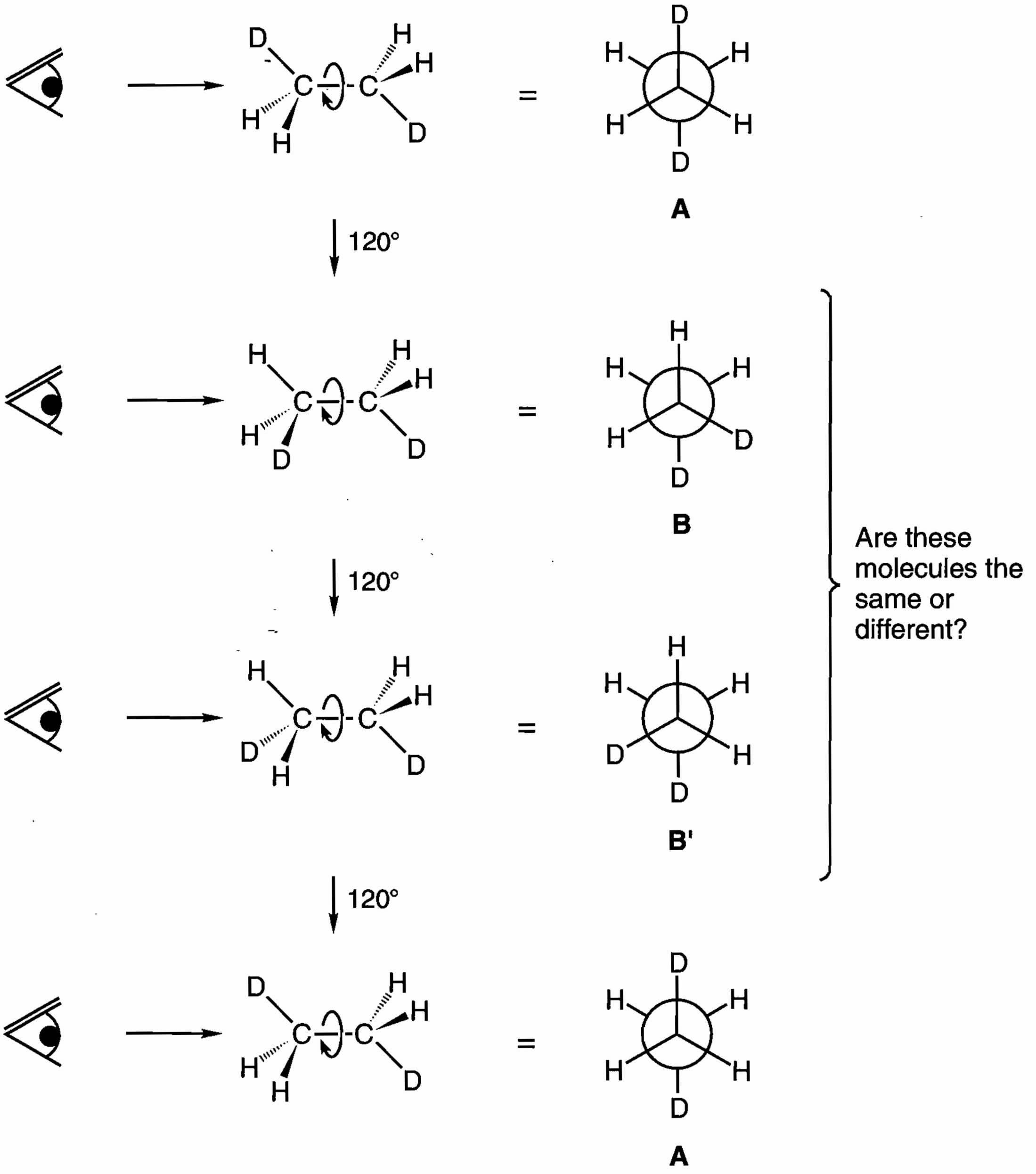
Next, convert this figure into a Newman projection. What do we see on the front carbon? Three hydrogens. In this projection, they appear at 120° angles.



Next, add the substituents on the back carbon, two hydrogens and an OH. Now we have our Newman projection.



Problem 2.17 This problem can be reduced to: How many isomers of 1,2-dideuterioethane are possible? This problem is actually much tougher than it looks. Part of it is easy, but there is a hidden, and quite subtle, difficulty. By far the easiest way to attack this problem is to use Newman projections. Sight down the carbon–carbon bond and examine all possible staggered conformations.



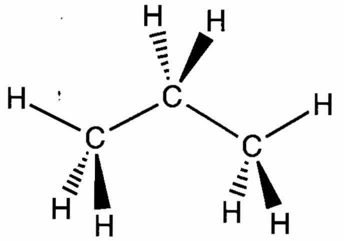
(continued)

Problem 2.17 *(continued)*

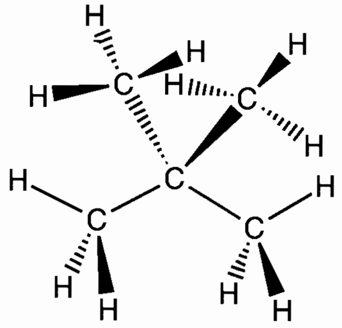
The first 120° rotation takes us from **A** to **B**, and the two are clearly different. A second 120° rotation generates **B′**, and a third 120° rotation takes us back to **A** as a 360° rotation is completed. The hard part of this problem is ferreting out the relationship between **B** and **B′**. Are they the same or not? At this point, this problem is very tough to do without models. Your models will show you that **B** and **B′** are not the same. There are three different possible staggered forms of 1,2-dideuterioethane. Just how **B** and **B′** differ is an interesting question, and we will deal with it extensively in Chapter 4.

Problem 2.18

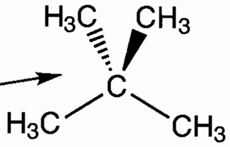
$(Me)_2CH_2$ = propane = $EtCH_3$
= $CH_3CH_2CH_3$ = EtMe = MeEt



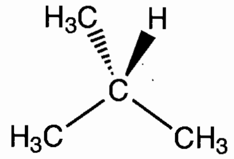
$(CH_3)_4C$ =



Such a complicated structure! We need a simplification...



$(CH_3)_3CH$ =



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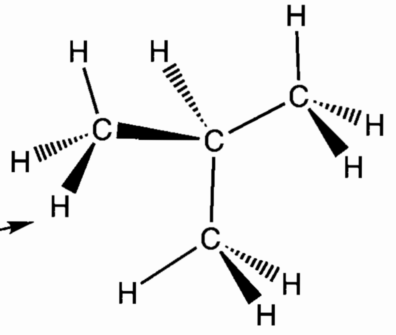
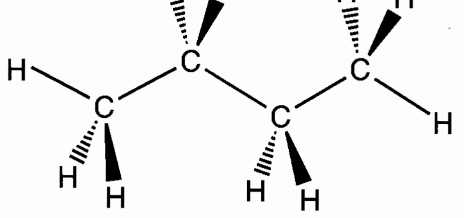
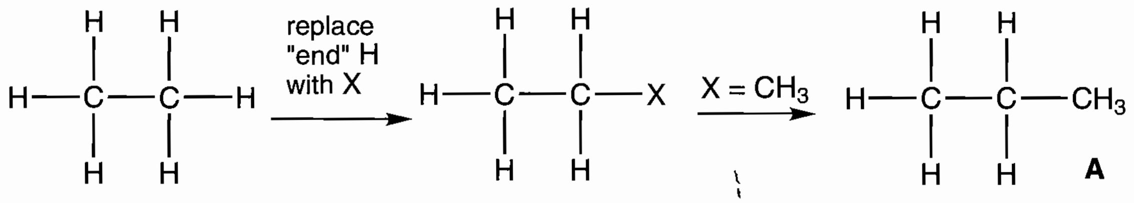


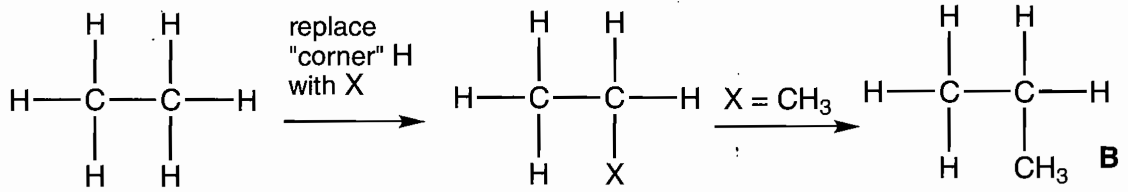
A simpler view of this complex structure

$(Et)_2$ = butane =

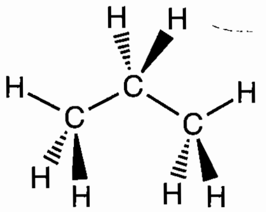


Problem 2.19 Your models will serve you better than words here. Replacement of the "end" hydrogen to give **A** and the "corner" hydrogen to give **B** leads to the same thing. The C—C—C right angle apparent in structure **B** is not real. The take-home lesson here is, *Always Remember*: Organic molecules are three-dimensional. Never trust the two-dimensional surface.

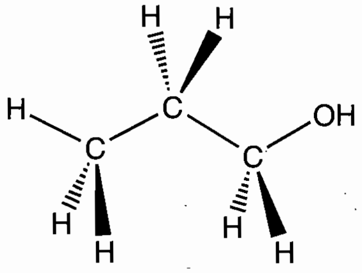




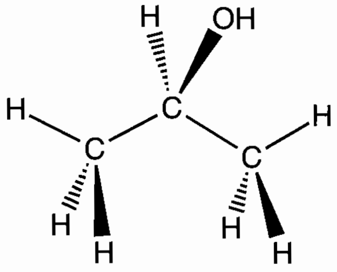
Both **A** and **B** are in fact the same, $CH_3CH_2CH_3$, propane =



Problem 2.20 The only trick here is to remember to keep all carbon–hydrogen and carbon–hydroxyl bonds staggered.

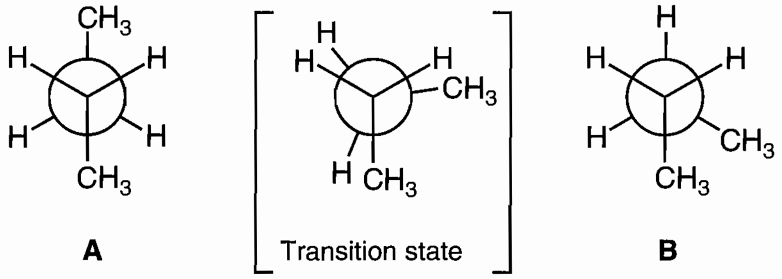


CH_3–CH_2–CH_2—OH



CH_3–CH(OH)–CH_3

Problem 2.21 In this problem you need to calculate the amount of destabilization caused by C—CH_3/C—H and C—CH_3/C—CH_3 interactions. Each C—H/C—H eclipsed interaction costs about 1.0 kcal/mol (p. 71). The transition state for the interconversion of **A** and **B** is an eclipsed form. In the figure, it is reached through a 60° clockwise rotation of the rear carbon. A second 60° clockwise rotation takes us to **B**.

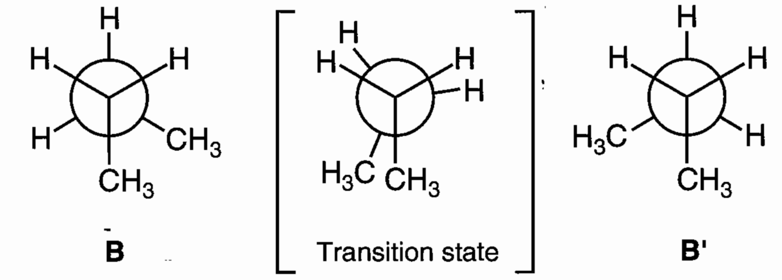


(continued)

Problem 2.21 *(continued)*

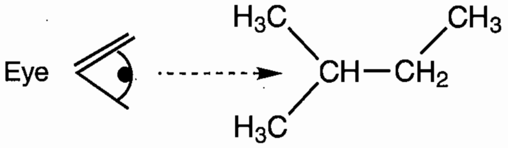
In the transition state, there are one eclipsed C—H/C—H interaction and two eclipsed C—H/C—CH_3 interactions. We know that the transition state lies 3.4 kcal/mol above **A** (Fig. 2.33). The C—H/C—H interaction costs 1.0 kcal/mol, and so the two C—H/C—CH_3 interactions must produce the remaining 2.4 kcal/mol. Each one must cause about 1.2 kcal/mol destabilization.

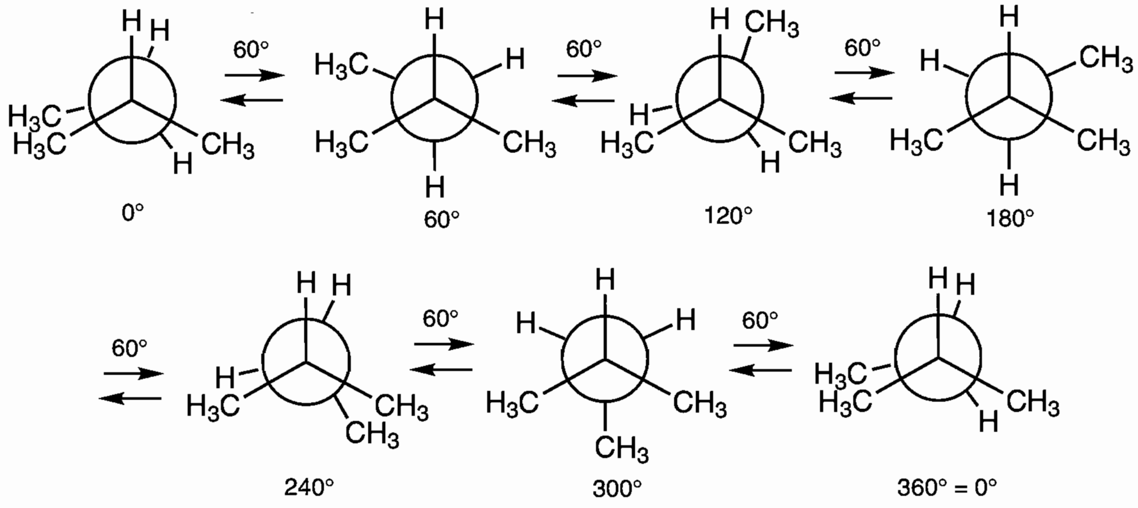
Figure 2.33 shows that the transition state for the interconversion of **B** and **B′** lies 3.8 + 0.6 = 4.4 kcal/mol above **A**. The transition state for this conversion is shown.



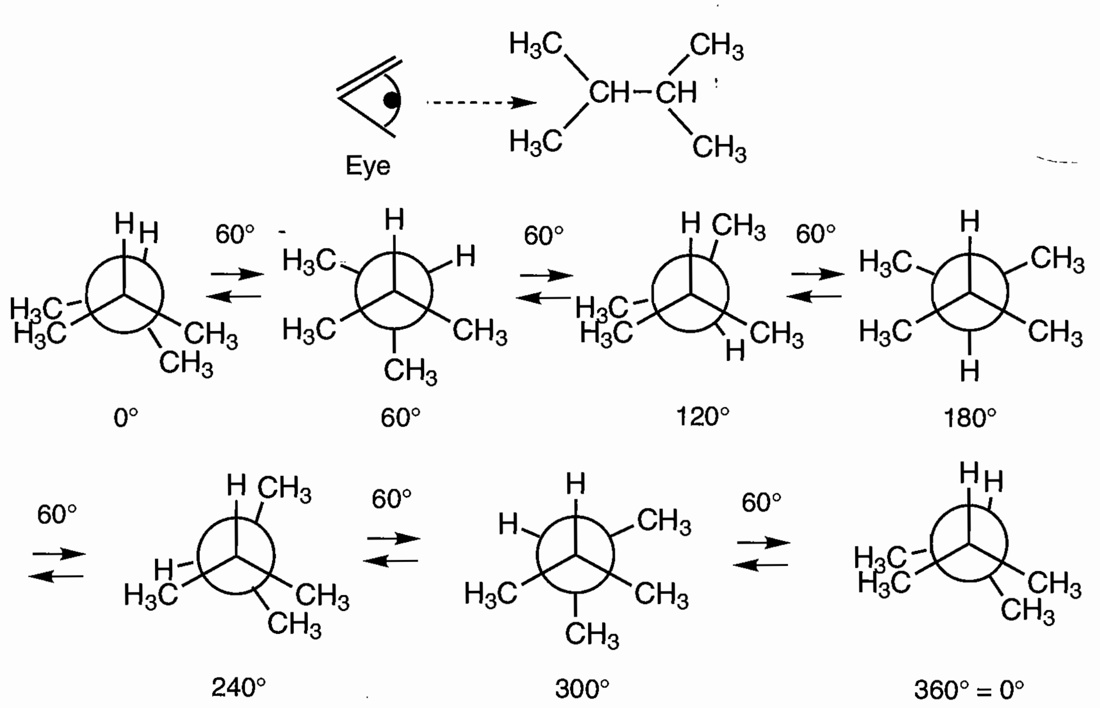
Each of the two eclipsed C—H/C—H interactions costs 1.0 kcal/mol, so the single C—CH_3/C—CH_3 eclipsing interaction must cause the remaining 2.4 kcal/mol destabilization.

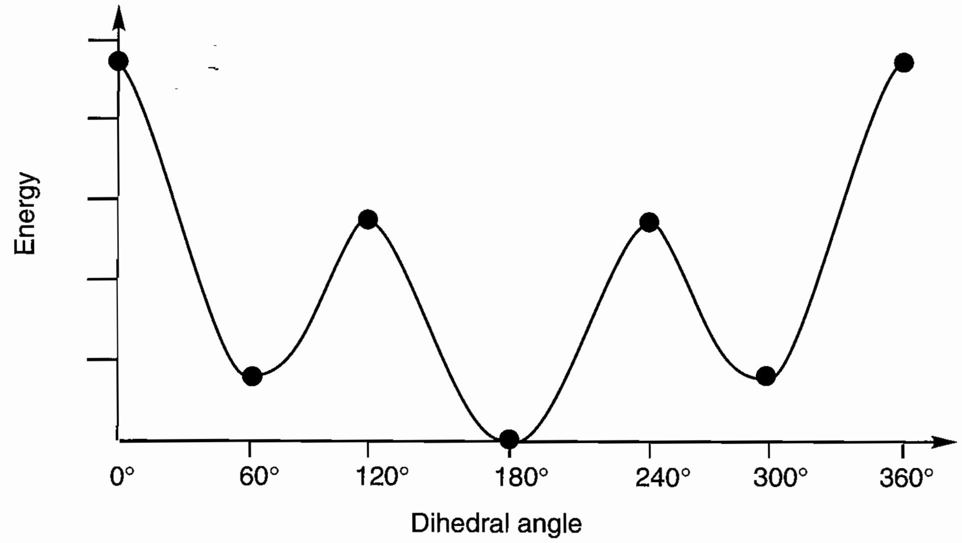
Problem 2.22 For the first molecule, the Newman projection is constructed as usual. The front carbon bears two methyl groups and a hydrogen, and the rear carbon, shown as a circle, two hydrogens and one methyl group. Start at 0° with an eclipsed form and then proceed by 60° rotations of the rear carbon to generate the other Newman projections.



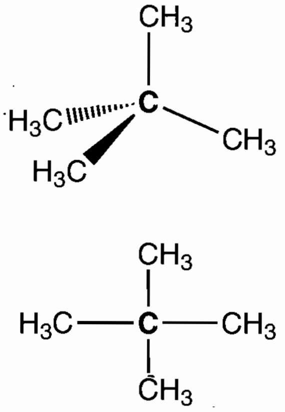


The second molecule is more symmetrical, as both carbons bear two methyl groups and a single hydrogen. The 0° and 360° forms are identical and contain two methyl–methyl eclipsed interactions. These will be the highest energy conformations. A 60° rotation leads to a staggered molecule with three methyl–methyl gauche interactions. The 120° and 240° transition states have one methyl–methyl eclipsed interaction and two methyl–hydrogen eclipsed interactions and will be lower in energy than the 0° and 360° conformations. Lowest energy of all is the 180° form, which contains only two methyl–methyl gauche interactions. The graph shows the relative energies.

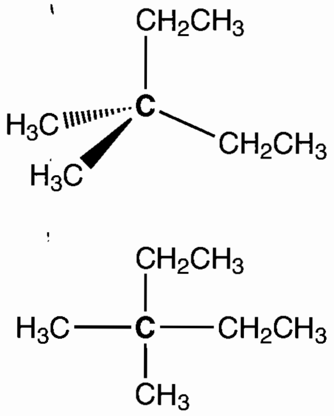




Problem 2.23 Any compound containing a carbon attached to four other carbons contains a “quaternary” carbon. The quaternary carbon is shown in boldface type in the figure.

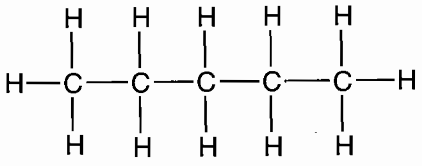


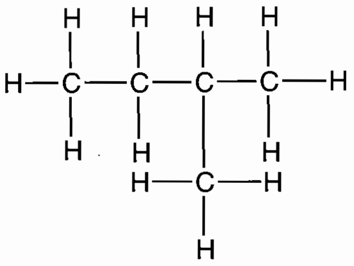
2,2-Dimethylpropane
(neopentane)

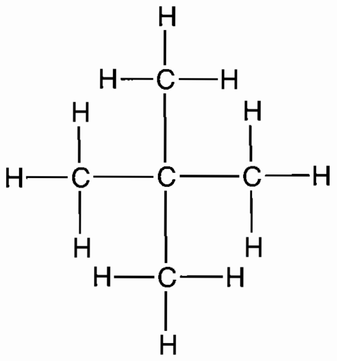


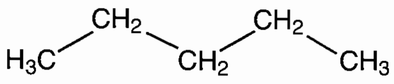
3,3-Dimethylpentane

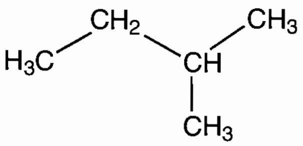
Problem 2.24

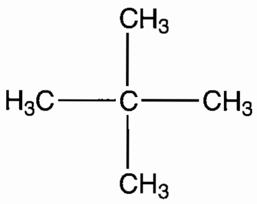






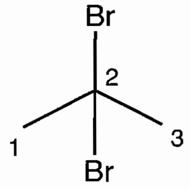






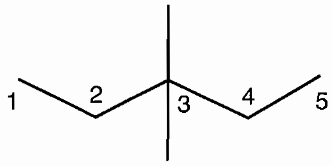
Problem 2.25

(a)



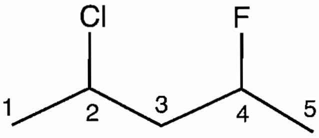
2,2-Dibromopropane

(b)



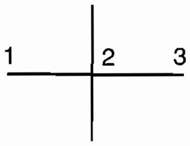
3,3-Dimethylpentane
not 2-Ethyl-2-methylbutane

(c)



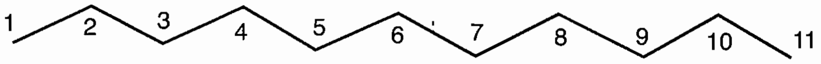
2-Chloro-4-fluoropentane
not 2-Fluoro-4-chloropentane

(d)



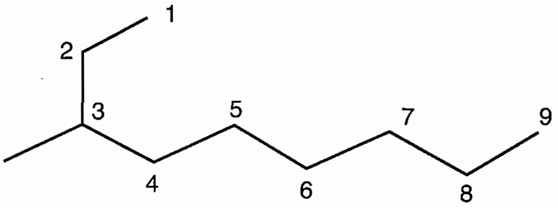
2,2-Dimethylpropane
(neopentane)

(e)



Undecane

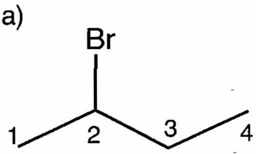
(f)



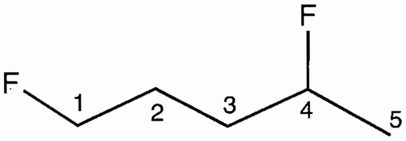
3-Methylnonane
not 2-Ethyloctane

Problem 2.26

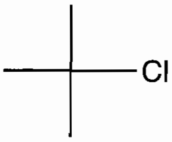
(a)



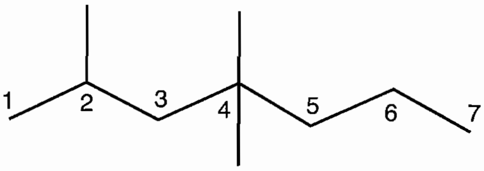
(d)



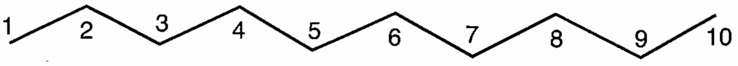
(c)



(e)

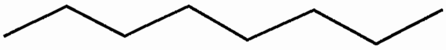


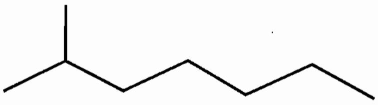
(b)

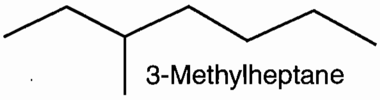


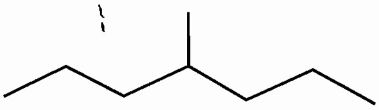
Problem 2.27 4-ethyl-5-isobutyldecane; 5-(*sec*-butyl)-4-ethyldecane.

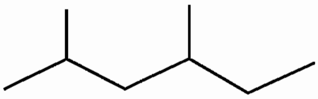
Problem 2.28 Here we use only the most schematic representations for the molecules.

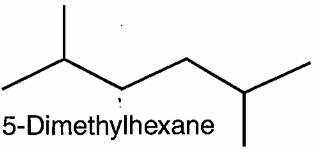

Octane

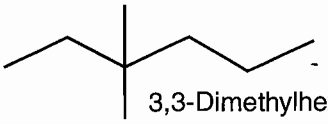

2-Methylheptane

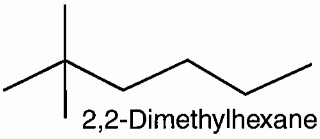

3-Methylheptane

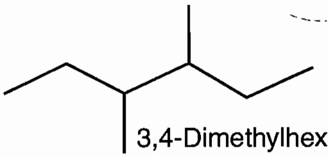

4-Methylheptane

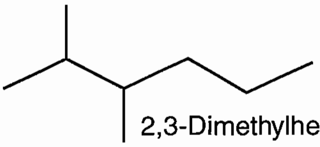

2,4-Dimethylhexane

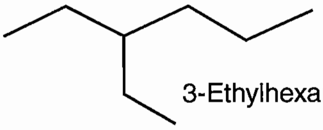

2,5-Dimethylhexane

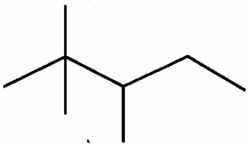

3,3-Dimethylhexane

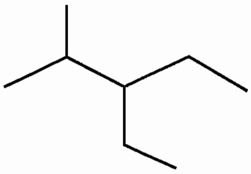

2,2-Dimethylhexane

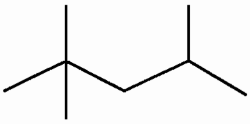

3,4-Dimethylhexane

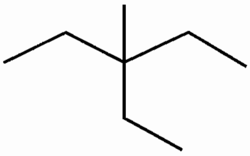

2,3-Dimethylhexane

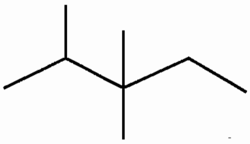

3-Ethylhexane

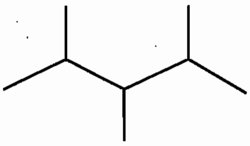

2,2,3-Trimethylpentane

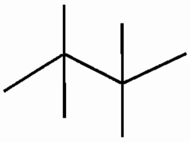

3-Ethyl-2-methylpentane


2,2,4-Trimethylpentane

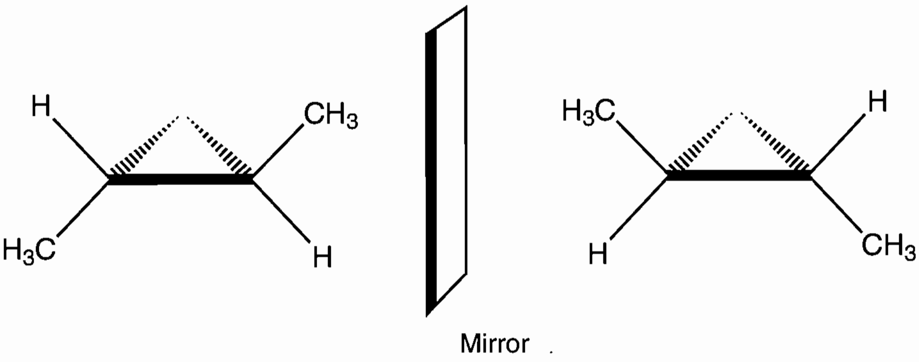

3-Ethyl-3-methylpentane


2,3,3-Trimethylpentane

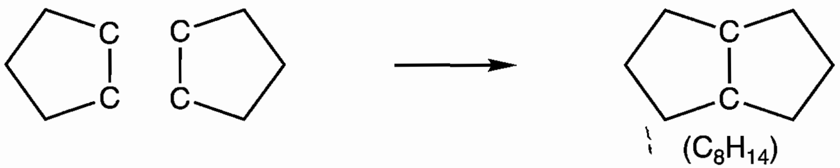

2,3,4-Trimethylpentane


2,2,3,3-Tetramethylbutane

Problem 2.29 This problem looks forward to Chapters 4 and 5. There really are two isomers of *trans*-1,2-dimethylcyclopropane. No number of translational or rotational operations will suffice to change one mirror image into the other. These two isomers are related in the same way that your right and left hands are. By all means, use your models to be certain of this answer.

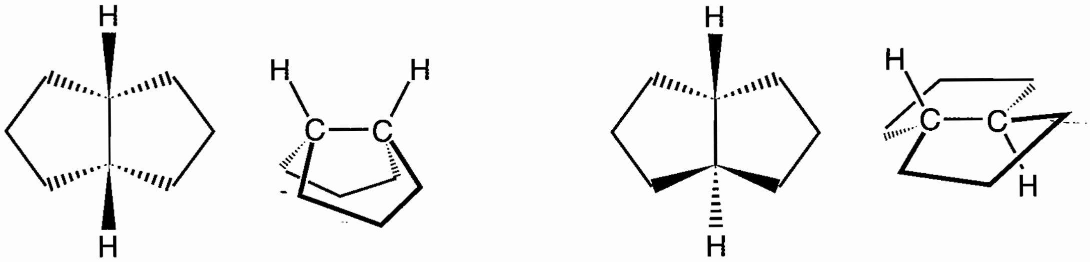


Problem 2.32 The two rings share two carbons in the following way:



(C_8H_{14})
The two rings share two carbons

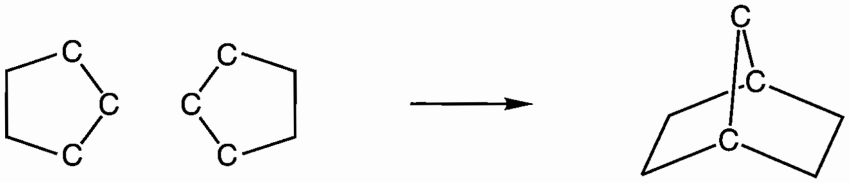
But the problem points out that there are two of these compounds. Remember that rings have sides. There are cis and trans forms for this molecule (p. 88). The two rings can be fused together in a cis or trans fashion.



cis Form

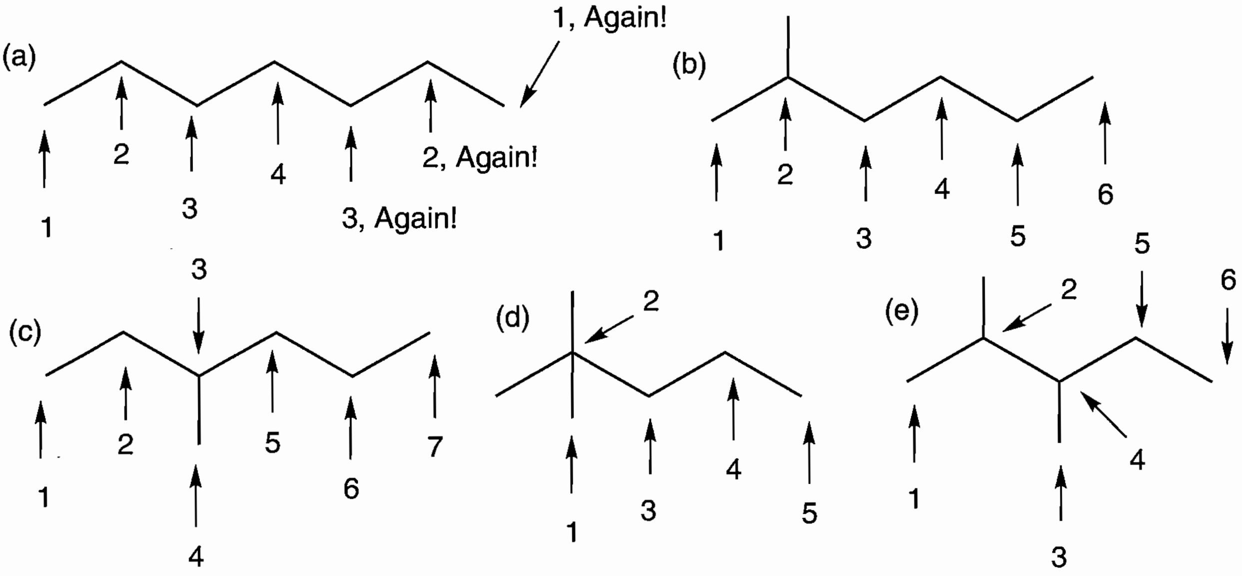
trans Form

Problem 2.33 Finally, we come to C_7H_{12}, in which the two rings share three carbons. A "cage" structure results.



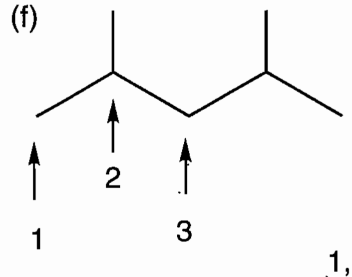
(C_7H_{12})
Now three carbons are shared

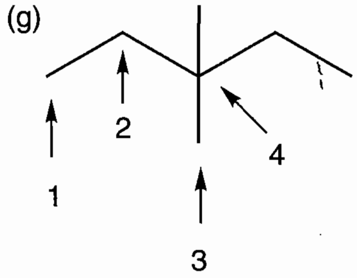
Problem 2.34 The arrows and numbers show the different carbons. Be careful of symmetry! The only way to make a "real" mistake (as opposed to just overlooking some carbon) is to miss the symmetry of the situation and find too many "different" carbons.

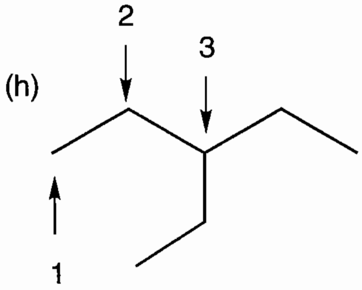


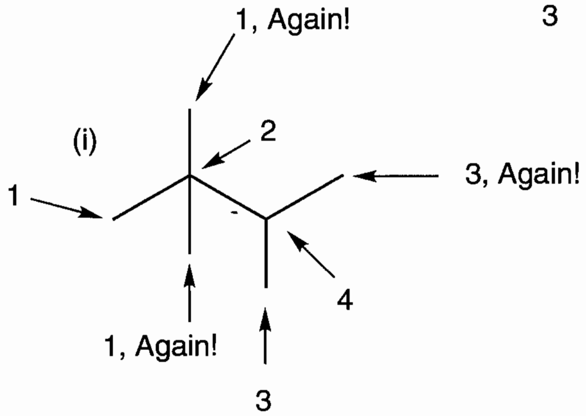
(continued)

Problem 2.34 *(continued)*



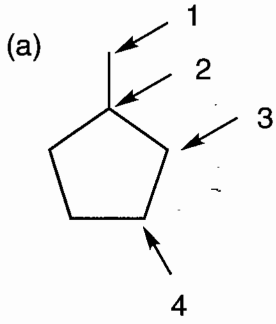


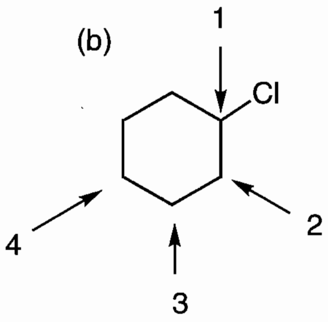


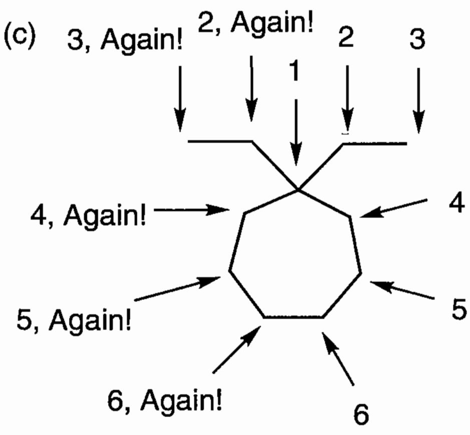


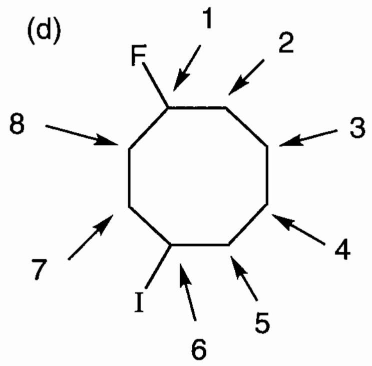
Beware of the two-dimensional page! The "repeats" are shown in the first and last examples, (a) and (i). When in doubt, make a model.

Problem 2.35 Here is more practice in seeing symmetry and not finding too many "different" carbons. In the third example (c), the repeats are pointed out. In the last example (d), all eight carbons are different. Would this still be true if the iodine were replaced with a fluorine?



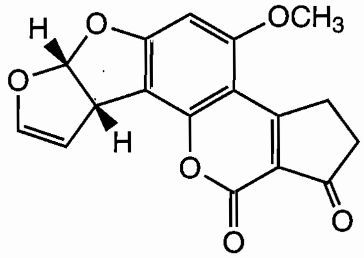


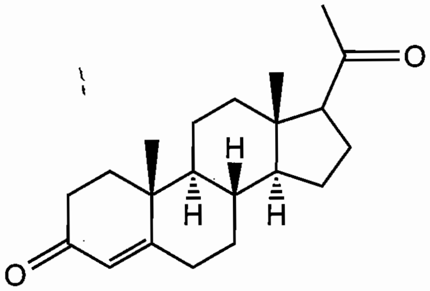




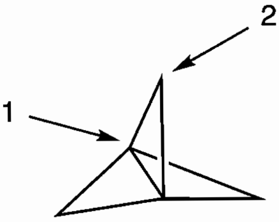
Here they are all different

Problem 2.36





All carbons are different in both these molecules—there are 17 in the first and 21 in the second.

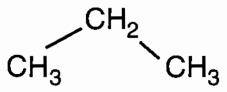


Here there is quite another situation—very high symmetry is present, and there are only two different carbons.

Problem 2.37 In propane, the methylene (CH_2) hydrogens are different from the six equivalent methyl hydrogens, so there will be two signals.

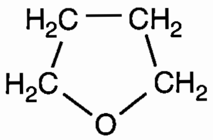
Tetrahydrofuran will show two signals in the ^{1}H NMR spectrum, one for the four equivalent hydrogens on the carbons adjacent to oxygen, and one for the four hydrogens on the carbons remote from the oxygen atom.

Remember that integration is relative, a ratio, not an absolute count of hydrogens.



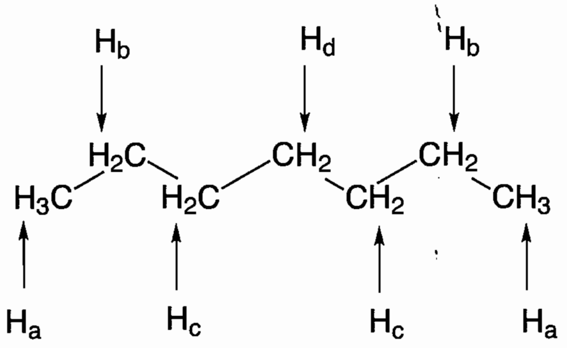
$CH_3CH_2CH_3$

3:1

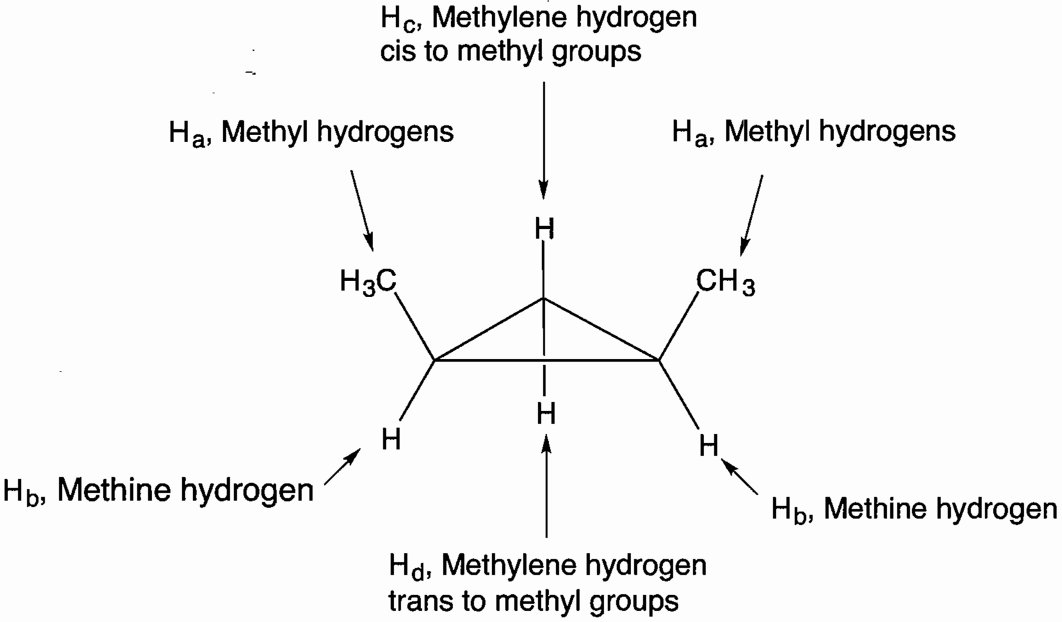


1:1

Problem 2.38 Heptane will show four signals in the ratio 6:4:4:2 = 3:2:2:1 (H_a:H_b:H_c:H_d).

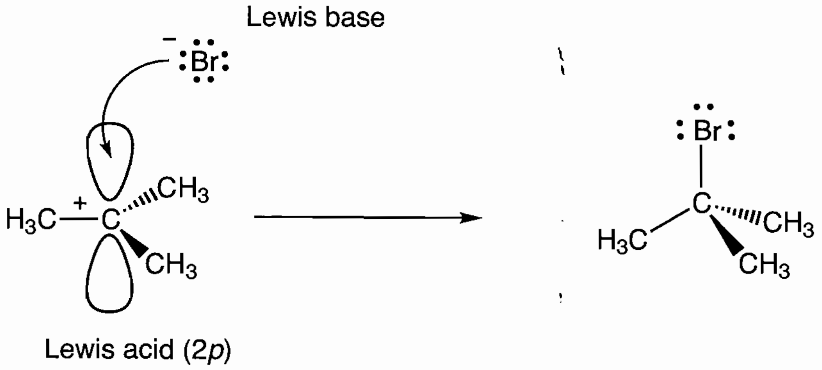


Problem 2.39 As advertised, this question takes some careful three-dimensional (3-D) viewing. It is tempting to say that there are only three different kinds of hydrogen: the six methyl hydrogens, the two methines (CH), and the methylene group (CH_2). But that analysis ignores the fact that rings have sides—the hydrogen cis to the methyl groups is not exactly the same as the hydrogen trans to the methyl groups. A look in 3-D should make it all clear. There are, in fact, four different hydrogens in *cis*-1,2-dimethylcyclopropane: H_a, H_b, H_c, and H_d.

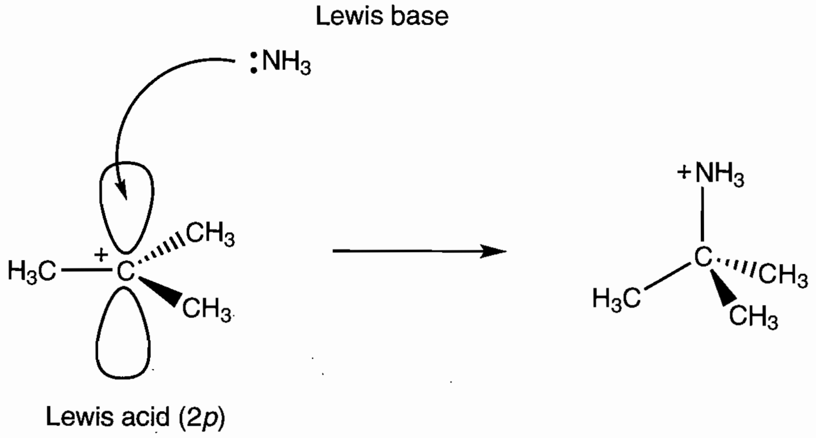


Problem 2.40

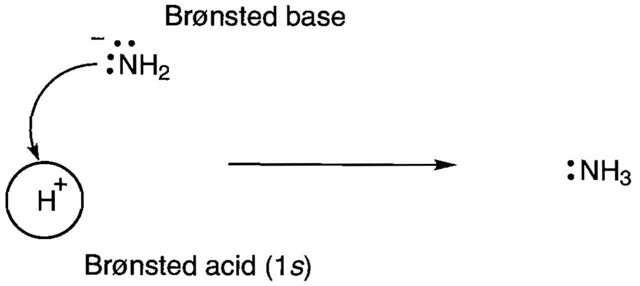
(a)



(b)



(c)



Additional Problem Answers

Problem 2.41

(a) 4-Fluoro-9-iodo-2,3-dimethylundecane

(b) 1,1,3-Trichloro-3,5-diethylcyclohexane

(c) 2,4-Dibromo-3-ethyl-2-methylpentane

(d) 5-Bromo-3-ethyl-2,2-dimethylheptane

(e) 2-Chloro-1-fluoro-3-methylcyclopentane

(f) 2,3,3-Trimethylpentane

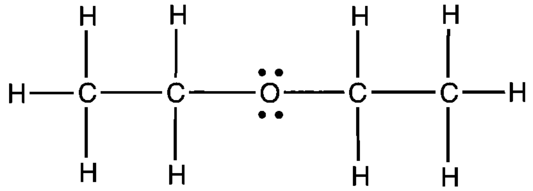
(g) 1,1-Dichloro-1-cyclobutylbutane

(h) 4,4-Diethyloctane

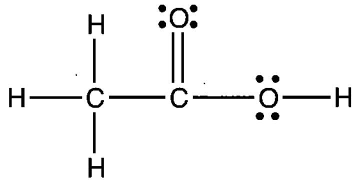
(i) 2-Bromo-3-methylhexane

Problem 2.42

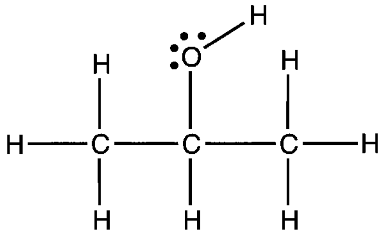
Et_2O is an ether:



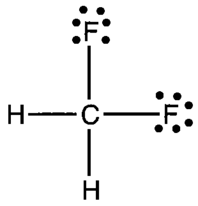
CH_3CO_2H is a carboxylic acid:



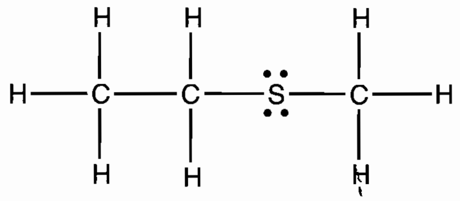
$CH_3CHOHCH_3$ is an alcohol:



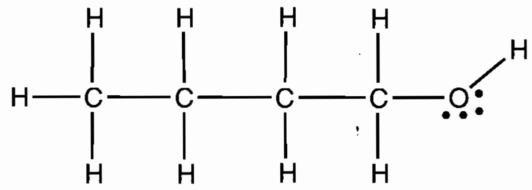
CH_2F_2 is an alkyl halide:



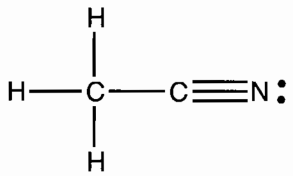
$CH_3CH_2SCH_3$ is a thioether:



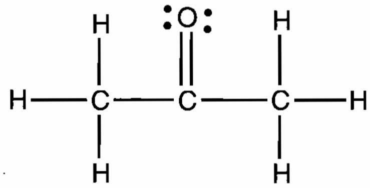
$CH_3(CH_2)_3OH$ is an alcohol:



MeCN is a nitrile:

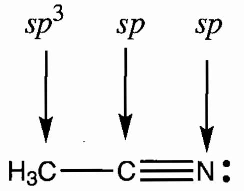


$(CH_3)_2CO$ is a ketone:

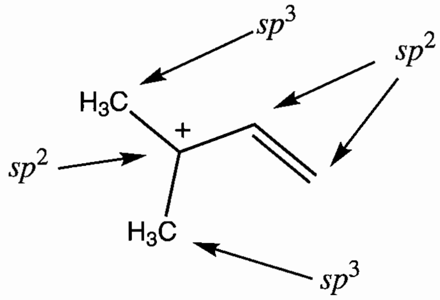


Problem 2.43

(a)



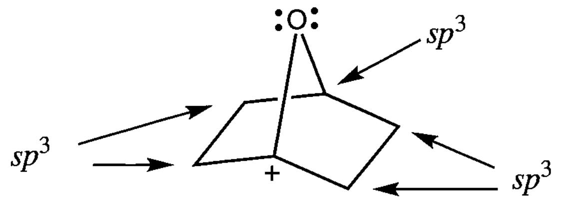
(c)

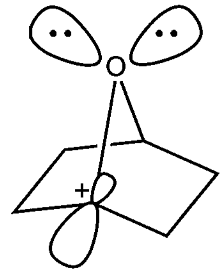


(b) This problem needs some explanation. All the carbons are sp^3. We expect the carbocation to be sp^2, but in this molecule the carbocation cannot adopt the planar geometry that is required for sp^2. Were you supposed to know that? Maybe, maybe not. But if you made a model of this structure, then you would have noticed. The structure on the right shows the empty orbital of the carbocation and the orbitals that the oxygen lone pairs occupy. Notice that the oxygen is also sp^3.

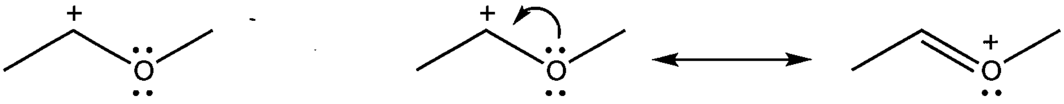
(continued)

Problem 2.43 *(continued)*





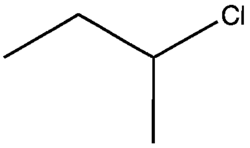
That's not all that is unique about this molecule. An oxygen with its lone pairs is normally described as sp^3 hybridized. But an oxygen next to a carbocation can stabilize the carbocation by resonance. In order to do that, the oxygen must use a p orbital. Consider the ether shown below. You can draw a resonance structure using one of the lone pairs of electrons from the oxygen. By doing this, you are saying that the lone pair is in a p orbital.



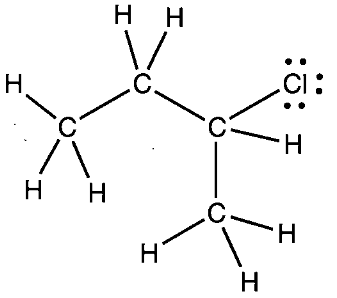
Now go back to the bicyclic ether shown above. Notice that the oxygen lone pairs are not able to line up with the empty orbital of the cation. There is no resonance between the oxygen and the carbocation in this case.

Problem 2.44

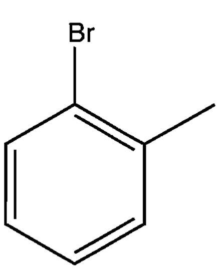
(a)



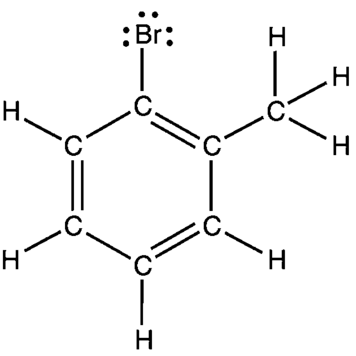
is



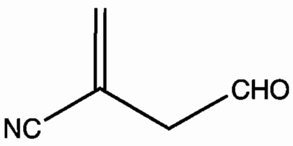
(b)



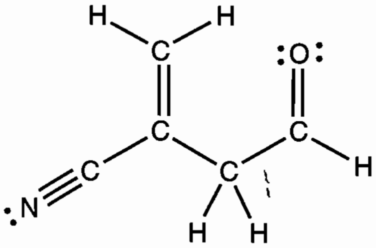
is



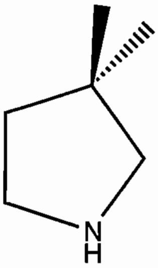
(c)



is



(d)



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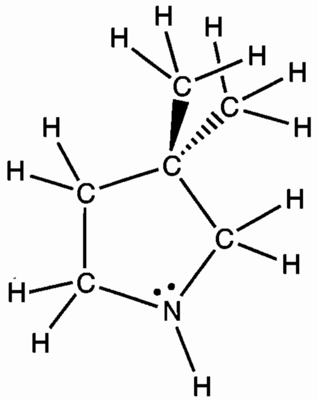
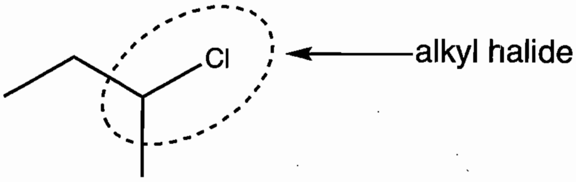
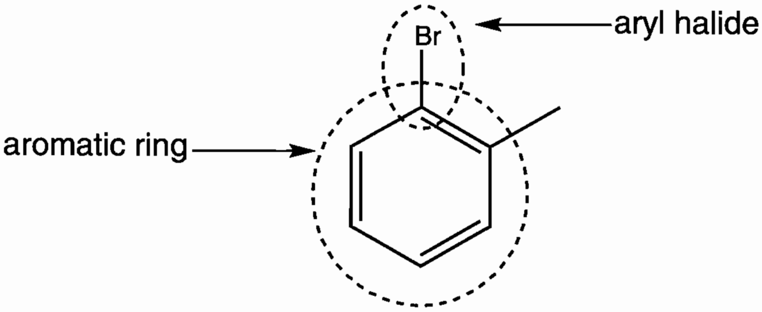


Problem 2.45

(a)



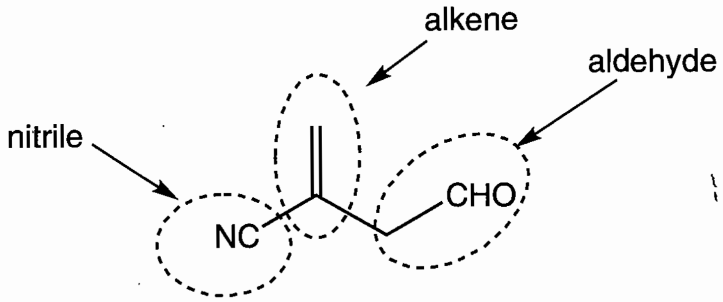
(b)



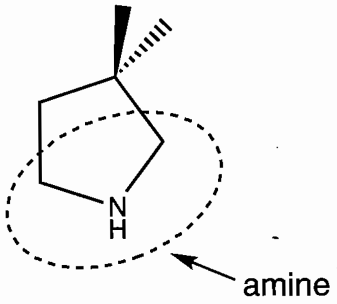
(continued)

Problem 2.45 *(continued)*

(c)

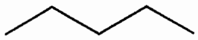


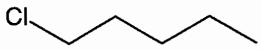
(d)



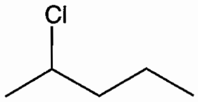
Problem 2.46

From pentane,

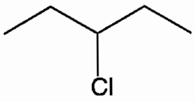




1-Chloropentane

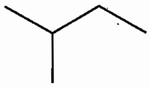


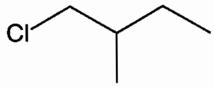
2-Chloropentane



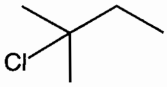
3-Chloropentane

From 2-methylbutane,

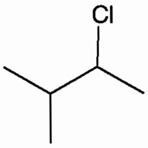




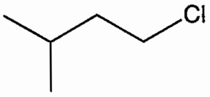
1-Chloro-2-methylbutane



2-Chloro-2-methylbutane

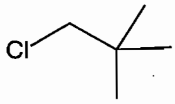


2-Chloro-3-methylpentane



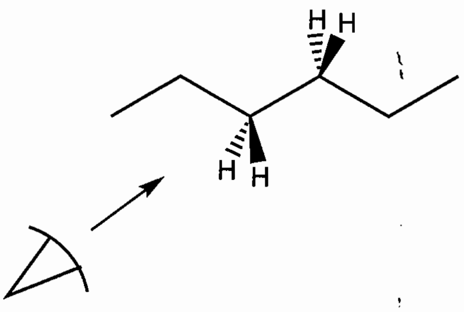
1-Chloro-3-methylbutane

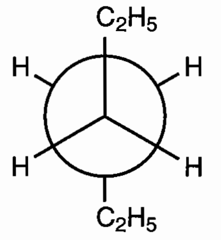
From 2,2-dimethylpropane,



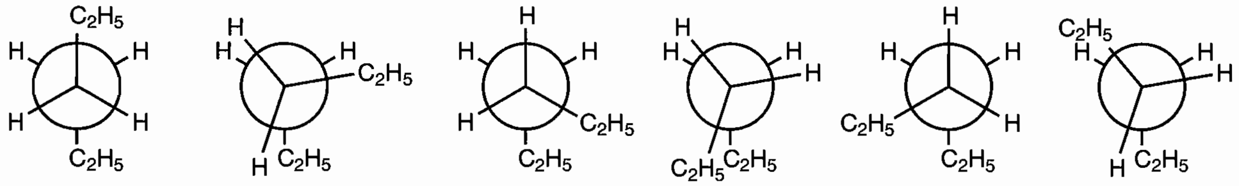
1-Chloro-2,2-dimethylpropane

Problem 2.47 First draw the line structure for hexane. Now find the C(3)—C(4) bond and draw in any hydrogens that are on those carbons. Use wedges and dashes to make your drawings. Now look down that bond in either direction. Represent what you see on a Newman projection.



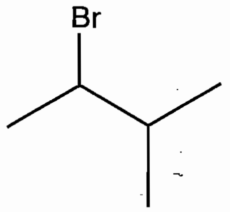


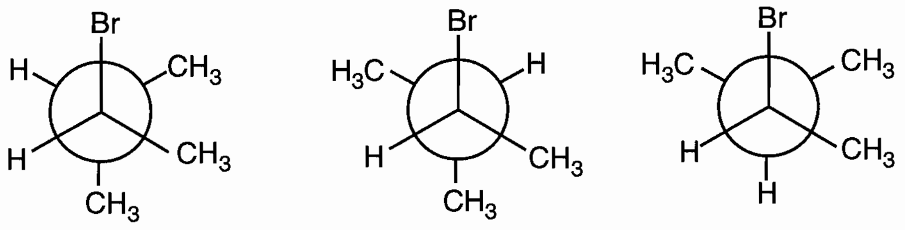
Now draw the conformational isomers (conformers) that are obtained when you rotate the front carbon in a clockwise fashion. You could rotate the back carbon if you prefer.



staggered anti — eclipsed — staggered gauche — eclipsed — staggered gauche — eclipsed

Problem 2.48

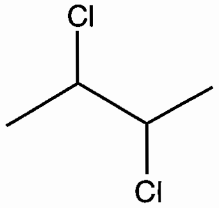




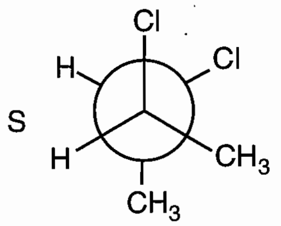
The first Newman projection has one bromo–methyl gauche and two methyl–methyl gauche interactions. The second Newman projection has one bromo–methyl gauche and one methyl–methyl gauche interaction. The third Newman projection has two bromo–methyl gauche and one methyl–methyl gauche interactions. Regardless of whether the bromo–methyl or methyl–methyl interaction causes more strain, the second projection has the lowest total strain.

The bromo group is much larger than a methyl group, but its space is made up of electrons, not atoms as in the methyl group. The bromo–methyl gauche interaction actually causes less strain than a methyl–methyl gauche interaction.

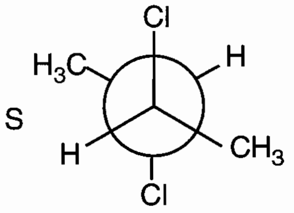
Problem 2.49



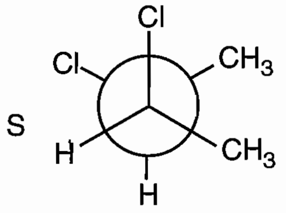
S = Staggered
E = Eclipsed



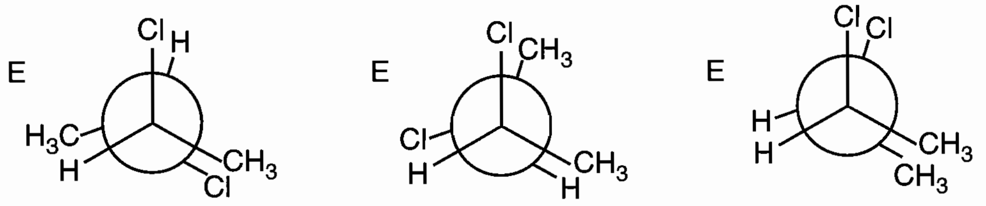
Gauche:
Cl-Cl
Cl-CH_3
CH_3-CH_3



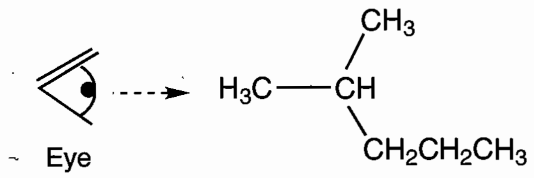
Gauche:
2 Cl-CH_3



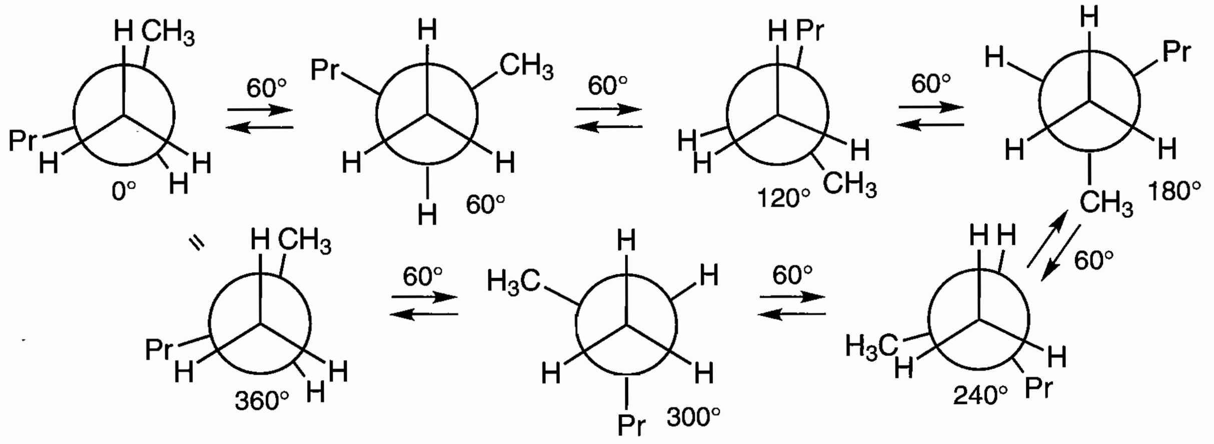
Gauche:
Cl-Cl
Cl-CH_3
CH_3-CH_3



Problem 2.50 Look down the C(1)—C(2) bond of 2-methylpentane with the methyl group in front.

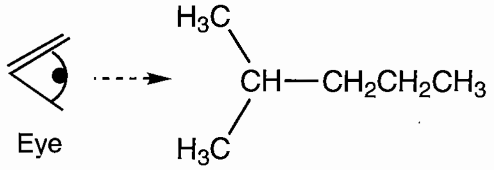


On the front carbon you see three hydrogens. On the rear carbon you see one hydrogen, a methyl group, and a propyl (Pr) group. Start at 0°, an eclipsed form, and then proceed by 60° rotations of the rear carbon.

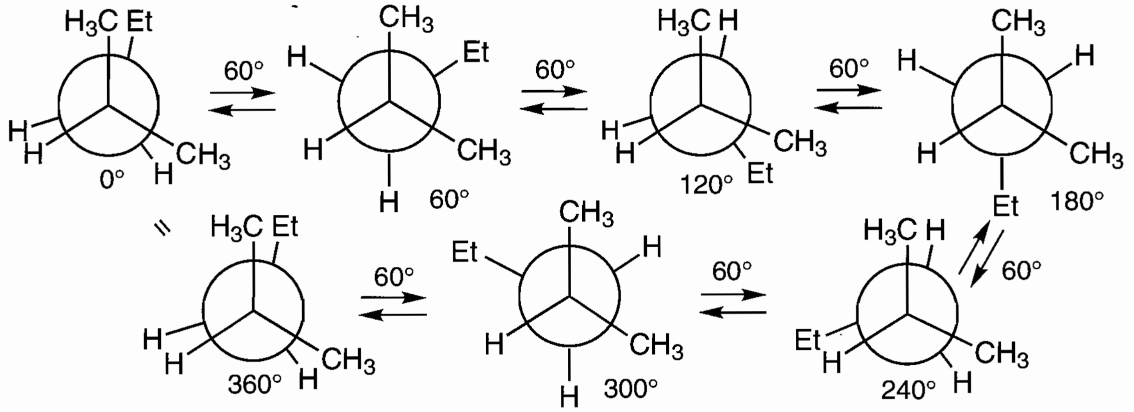


The three eclipsed conformations (0°, 120°, and 240°) are equi-energetic. These will be the highest energy conformations as they contain eclipsed methyl–hydrogen, propyl–hydrogen, and hydrogen–hydrogen interactions. The three staggered conformations (60°, 180°, and 300°) are also of equal energy. They will be lower in energy than the eclipsed conformation, as they contain only gauche, not eclipsed, interactions.

Now look down the C(2)—C(3) bond of 2-methylpentane with the methine (CH) carbon in front.

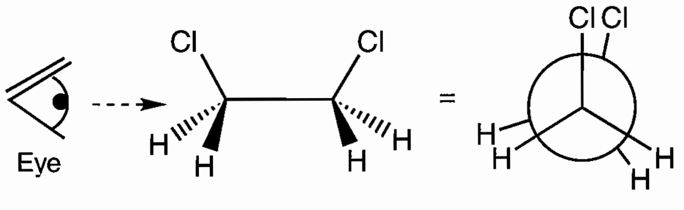


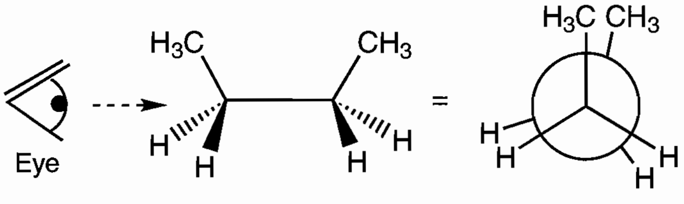
On the front carbon you see two methyl groups and a hydrogen. On the rear carbon you see two attached hydrogens and an ethyl (Et) group. Again, start at 0° with an eclipsed form and proceed by 60° rotations of the rear carbon.



The situation is more complex from this view. The eclipsed conformations (0°, 120°, and 240°) are still energy maxima. The 0° and 120° conformations each contain a methyl–ethyl, a methyl–hydrogen, and a hydrogen–hydrogen eclipsed interaction and are equi-energetic. These are probably higher in energy than the eclipsed 240° form, which contains two methyl–hydrogen and one ethyl–hydrogen interactions. The staggered conformations (60°, 180°, and 300°) represent energy minima. The 180° and 300° conformations, which contain one methyl–ethyl gauche interaction, are equi-energetic and are lower in energy than the 60° conformation in which there are two methyl–ethyl gauche interactions.

Problem 2.51 Start by drawing the two conformations. If size were all that mattered, the two would surely be very close in energy.

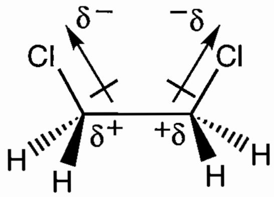


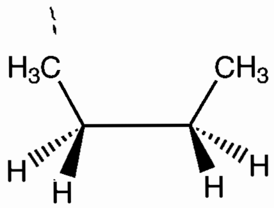


(continued)

Problem 2.51 *(continued)*

However, the carbon–chlorine bond is much more polar than a carbon–methyl bond. Note that in the eclipsed form of 1,2-dichloroethane shown, the two C—Cl dipoles are lined up. This molecule will be strongly destabilized through charge–charge opposition.

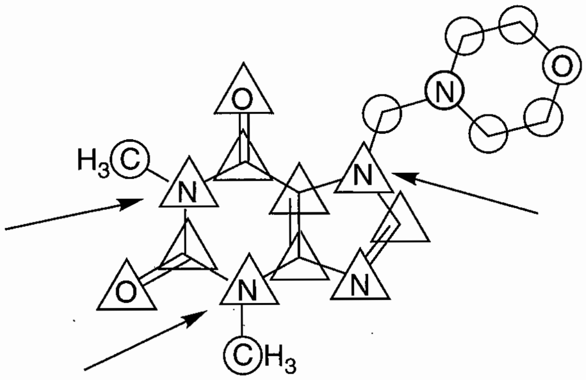


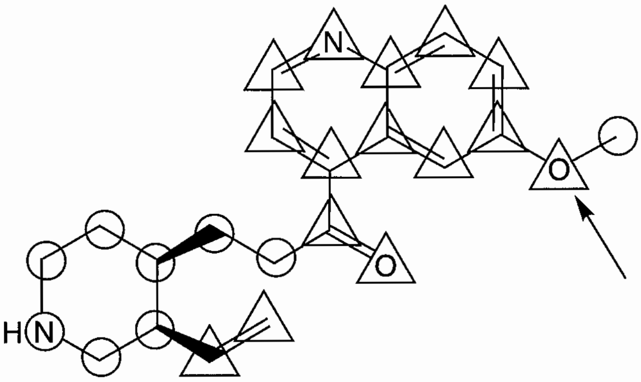


Problem 2.52 Trivalent carbon requires three bonds, so sp^2 hybridization is necessary. Divalent carbon requires only two bonds, so sp hybridization is appropriate.

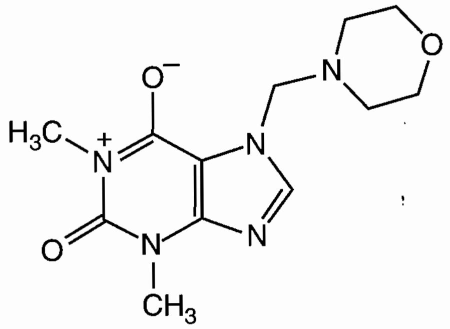
(a) sp^2 (b) sp^3 (c) sp^3 (d) sp (e) sp^2 (f) sp^3

Problem 2.53





There are three nitrogens in Xanturil (the ones with arrows pointed at them) and one oxygen in Viquidil (with an arrow) that you might have decided were sp^3 rather than sp^2. Each of these atoms is sp^2 because they have a lone pair that can participate in resonance. It would be good practice to draw the resonance structures that show the reason for the sp^2 hybridization. A drawing of one of the resonance structures responsible for the sp^2 hybridization is shown. There are no sp hybridized atoms.



Problem 2.54 Extrapolate from the boiling points of dodecane ($C_{12}H_{26}$, bp 216.3 °C) and eicosane ($C_{20}H_{42}$, bp 343°C). So, 343 – 216.3 = 126.7. The compound C_{15} is three-eighths of the way from C_{12} to C_{20}, so we take three-eighths of 126.7 = 47.5. The boiling point of C_{15} should be the boiling point of C_{12} plus this number, 216.3 + 47.5 = 263.8 °C. This procedure works reasonably well, as the real value is found to be 270.6 °C.

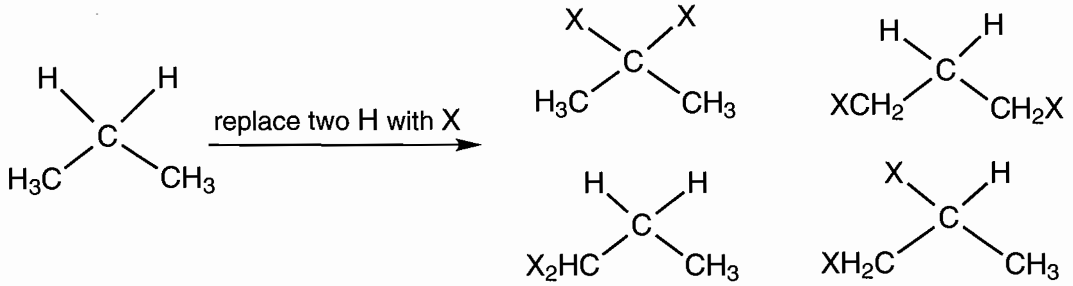
Problem 2.55 As noted in Section 2.13 (p. 90), symmetry is important in determining melting points. Highly symmetrical molecules pack well into crystal lattices, and more energy is required to break up the lattice than for molecules that do not pack so well. Thus, the highly symmetrical neopentane melts 113 °C higher than pentane. However, branched-chain hydrocarbons without high symmetry tend to have lower melting points than straight-chain hydrocarbons because the branching interferes with regular packing in the crystal. Accordingly, isopentane melts 30 °C lower than pentane.

Problem 2.56

(a) Ethane yields only two compounds. You can either replace two hydrogens on one carbon or one hydrogen on each carbon. Those are the only possibilities.

$$H_3C{-}CH_3 \xrightarrow{\text{replace two H with X}} H_3C{-}CHX_2 \quad \text{and} \quad XH_2C{-}CH_2X$$

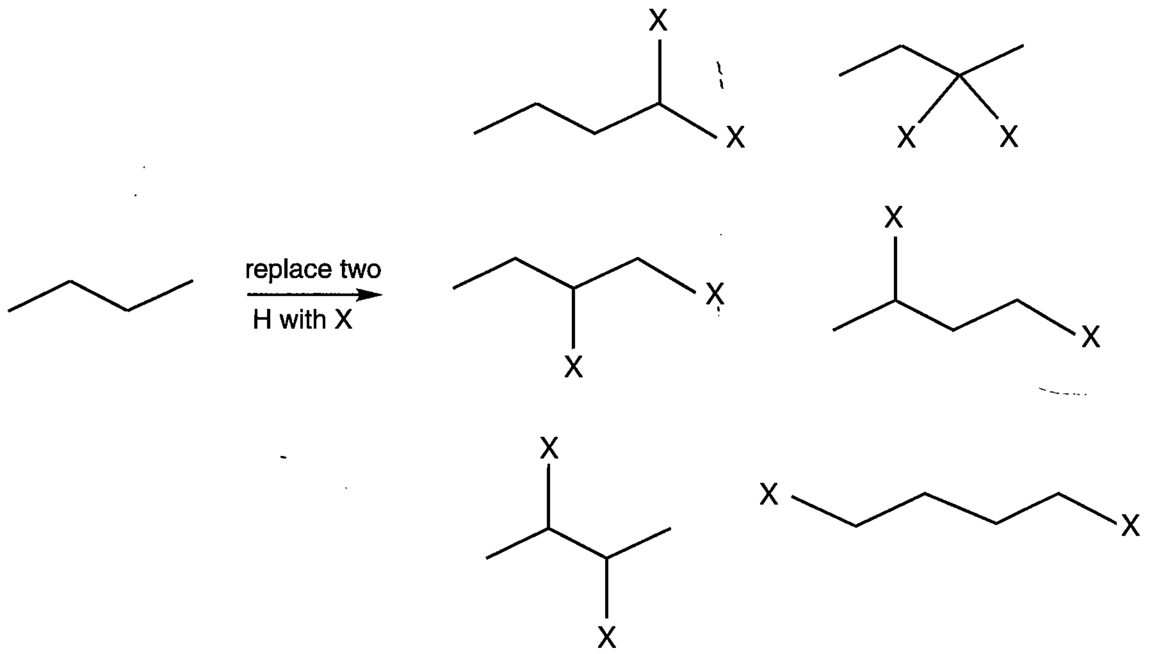
(b) Propane yields four compounds:



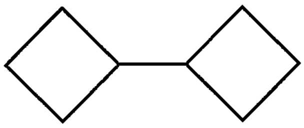
(continued)

Problem 2.56 *(continued)*

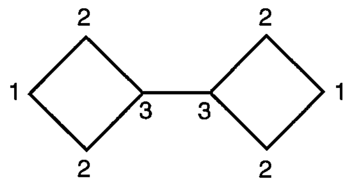
(c) Butane yields six new compounds. Notice the changing code level in the representations of these compounds.



Problem 2.57 The eight-carbon molecule that has only two cyclobutanes and no ethyl or methyl groups must be the structure shown below.

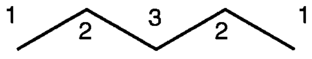


This molecule has a horizontal plane of symmetry and a vertical plane of symmetry. So there are only three different carbons in the structure, as shown.

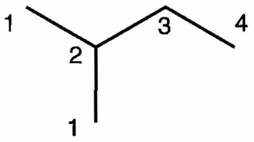


Problem 2.58

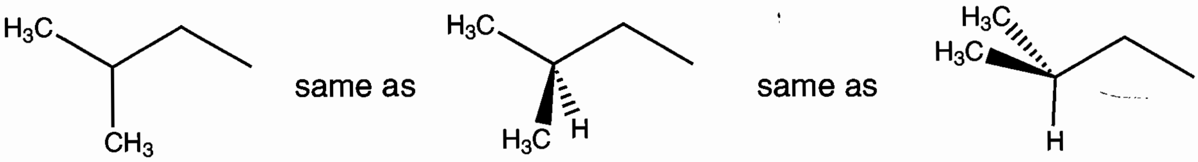
(a) There will be three signals for pentane. The methyl carbons on the ends of the molecule are identical. The methylenes on carbons 2 and 4 are identical (both have a methyl on one side and a propyl on the other). Carbon 3 is unique. It has an ethyl on both sides, so it is different from carbons 2 and 4.



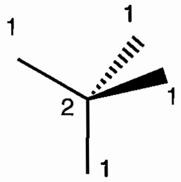
(b) There will be four signals for 2-methylbutane (isopentane). The two methyl groups on carbon 2 are equivalent.



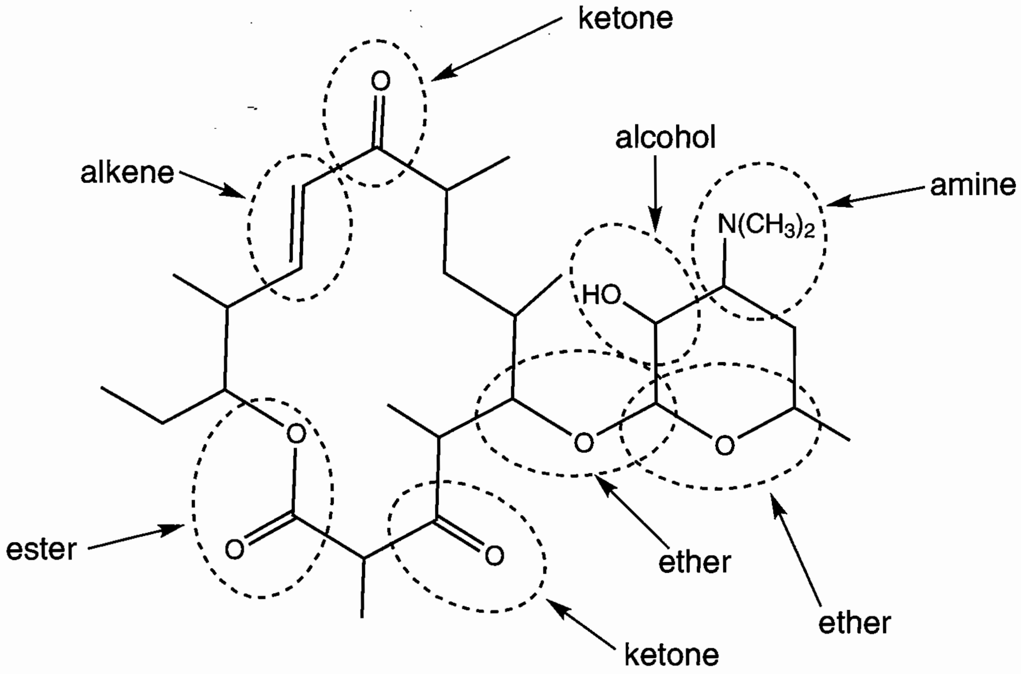
The three-dimensional drawing on the right might help you picture the identical nature of the two methyl groups on carbon 2 of 2-methylbutane.



(c) There are only two different carbons in 2,2-dimethylpropane (neopentane). Each of the methyl groups is equivalent.

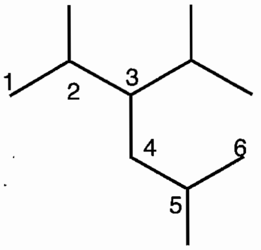


Problem 2.59



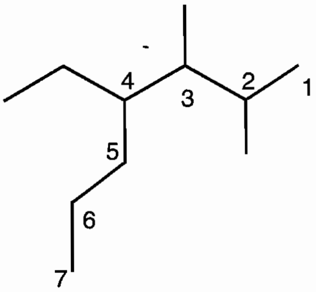
Problem 2.60

(a)



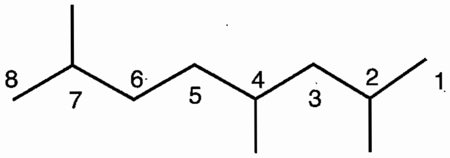
3-Isopropyl-2,5-dimethylhexane
not 3-Isobutyl-2,4-dimethylpentane
not 4-Isopropyl-2,5-dimethylhexane

(b)



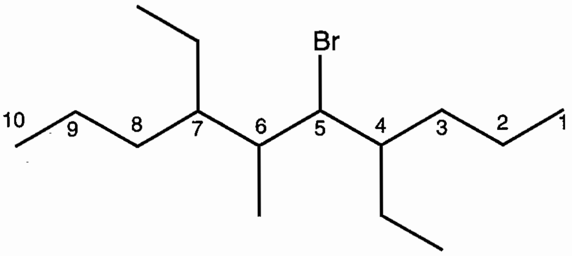
4-Ethyl-2,3-dimethylheptane
not 2,3-Dimethyl-4-propylhexane
not 4-Ethyl-5,6-dimethylheptane

(c)



2,4,7-Trimethyloctane
not 2,5,7-Trimethyloctane

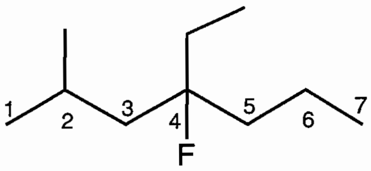
(d)



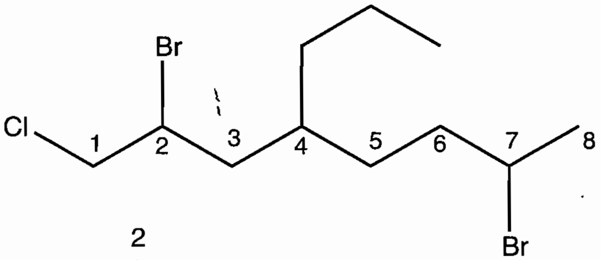
5-Bromo-4,7-diethyl-6-methyldecane
not 6-bromo-4,7-diethyl-5-methyldecane

Problem 2.61

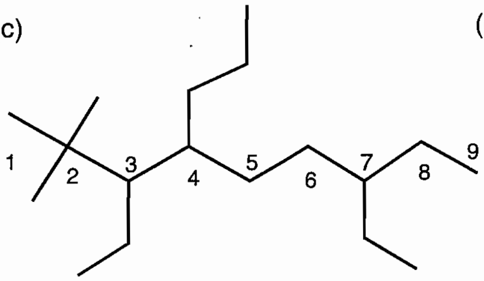
(a)



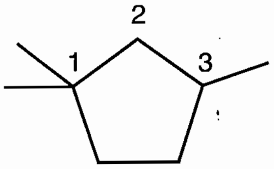
(b)



(c)

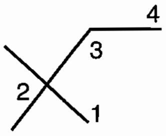


(d)



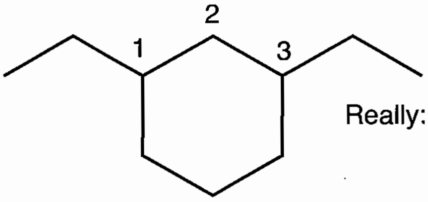
Problem 2.62

(a)



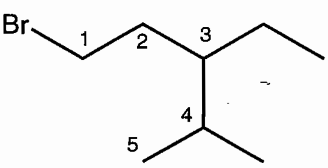
Really: 2,2-Dimethylbutane
The wrong name fails to find the longest "straight chain"

(b)



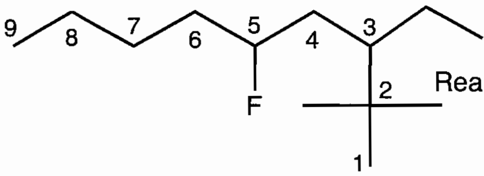
Really: 1,3-Diethylcyclohexane

(c)



1-Bromo-3-ethyl-4-methylpentane
The wrong name doesn't include the most substituents

(d)

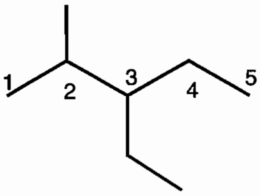


Really: 3-Ethyl-5-fluoro-2,2,8-trimethylnonane

Problem 2.63 There are two equal possibilities for the "longest straight chain." However, there is another rule to resolve this problem. (There are always other rules!) If chains of equal length compete for selection as the main chain in a saturated branched alkane, then the choice goes to the chain that has the greatest number of side chains. See, for example, Problem 2.41(c).

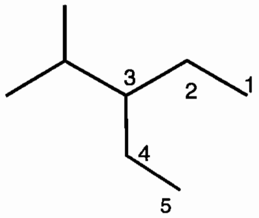
(continued)

Problem 2.63 *(continued)*



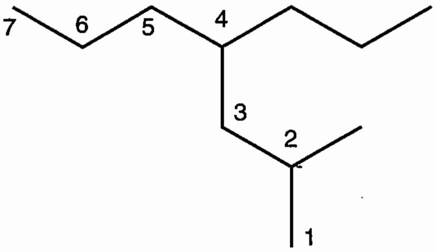
3-Ethyl-2-methylpentane

or



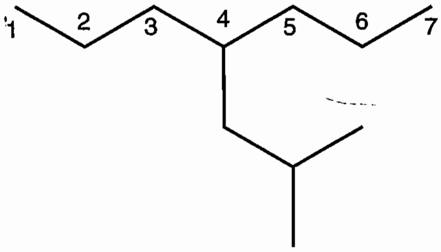
3-Isopropylpentane

Problem 2.64 This problem gives you a chance to apply the new rule of Problem 2.63. The correct name has two substituents.



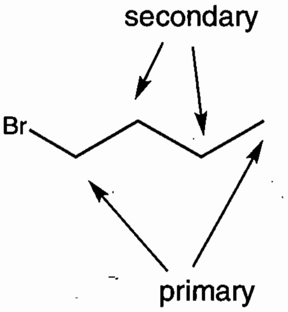
2-Methyl-4-propylheptane

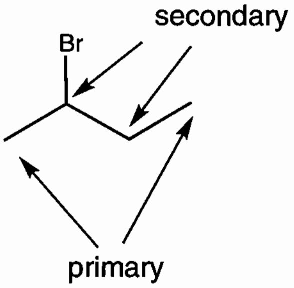
not



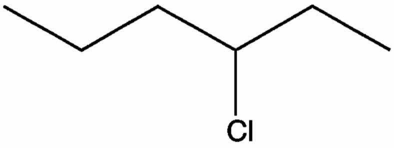
4-Isobutylheptane

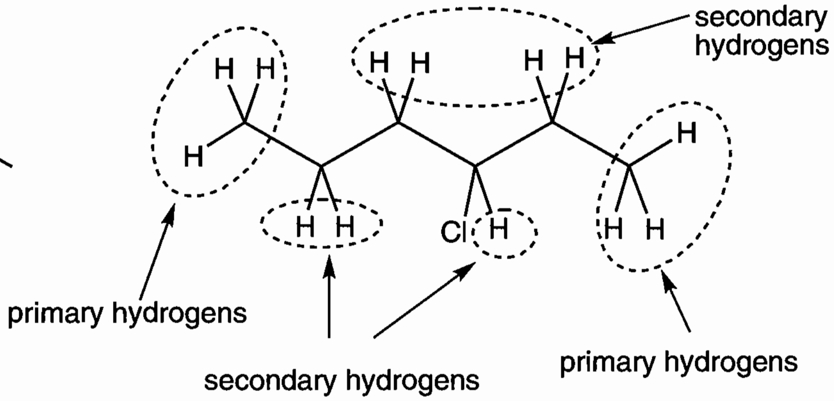
Problem 2.65 Both 1-bromobutane and 2-bromobutane have two primary carbons and two secondary carbons.





Problem 2.66 First draw 3-chlorohexane. Now draw in all of the hydrogens. There are only primary and secondary hydrogens in 3-chlorohexane.





Problem 2.67

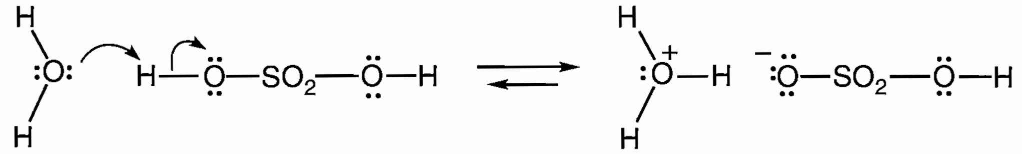
(a) This molecule is a secondary alkyl iodide. The iodo group is attached to a carbon that is bonded to two carbons.

(b) This molecule is a secondary alkyl chloride. The chloro group is attached to a carbon that is bonded to two other carbons.

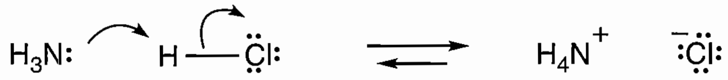
(c) This molecule is a tertiary alkyl fluoride. The fluoro group is attached to a carbon that is bonded to three other carbons.

(d) Aha! This molecule is not a primary, secondary, or tertiary bromide. We only speak of primary, secondary, and tertiary carbons when they are *sp*^{3} hybridized. The aromatic ring carbons are *sp*^{2} hybridized. This is an aryl bromide. The aryl name refers to an aromatic ring.

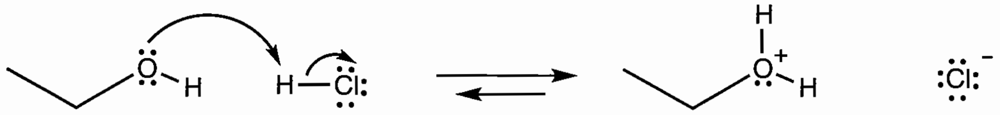
Problem 2.68



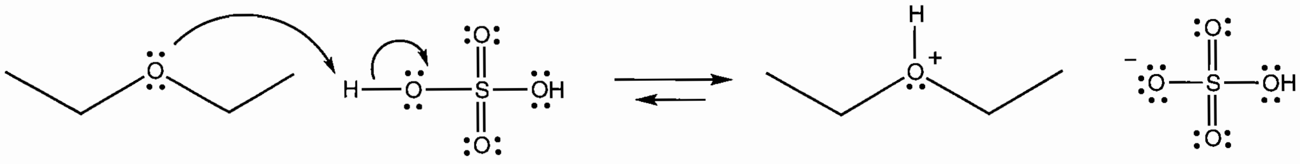
Problem 2.69



Problem 2.70



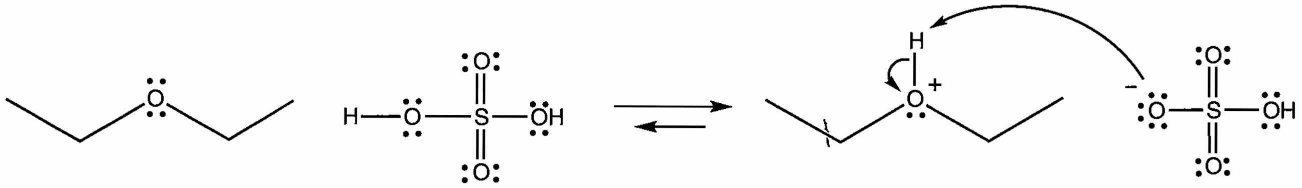
Problem 2.71 Notice that the conjugate base of H_2SO_4 (sulfuric acid) has the ability to spread the negative charge equally to three oxygens by resonance.



(continued)

Problem 2.71 *(continued)*

The reverse reaction is shown in this second drawing.



Problem 2.72. The animation represents the minimum energy for the species along the reaction pathway. If no rotation occurred, the product would be eclipsed. The staggered product is more stable, so in order to minimize energy, the rotation must happen as the reaction proceeds.

Problem 2.73 In the first step of the reaction, HBr reacts with the alkene. The alkene is using the loosely held π electrons to react with the acidic proton of HBr. So the alkene is the nucleophile (Lewis base) and the hydrogen of the HBr is the electrophile (Lewis acid). In the second step, a bromide ion reacts with the empty 2*p* orbital of the carbocation. So, the carbocation is the electrophile and the bromide ion is the nucleophile.

Problem 2.74 The nucleophile is the oxygen of the methoxide ion. The HOMO track shows that the electrons in the highest occupied orbital are found mostly on the oxygen. The electrophile is the carbon bonded to the bromine. The LUMO track shows that the electrons from the oxygen can mix with σ*, the empty orbital at the backside of the C—Br bond.

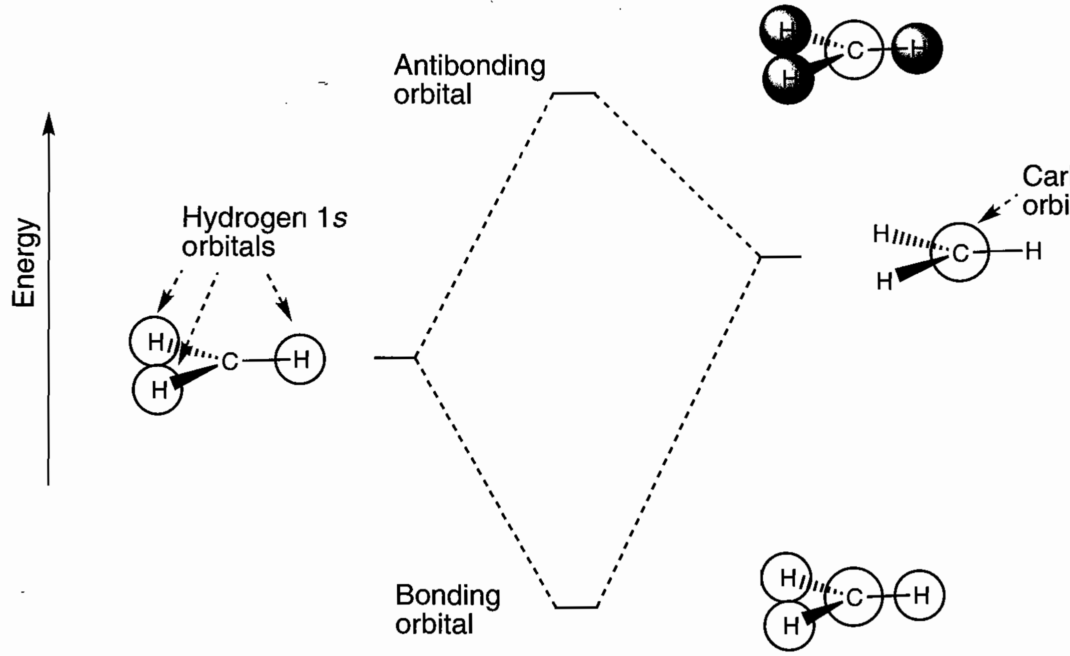
3

Alkenes and Alkynes

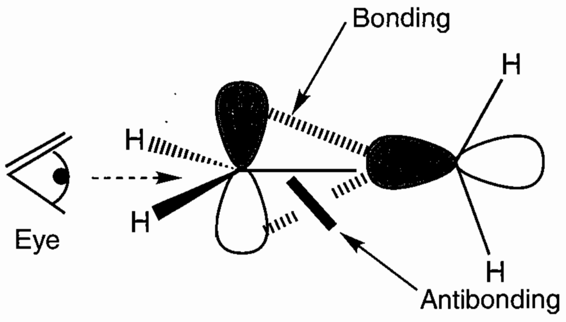
This chapter is devoted almost entirely to structure, and the following problems reflect that emphasis. Here we explore the structural consequences of sp^2 and sp hybridization in alkenes and alkynes. There is practice in finding isomers in both cyclic and acyclic molecules. Stereochemistry becomes especially important in the alkenes and ring compounds, and there are several opportunities in the following problems for you to work on stereochemical aspects of these kinds of molecules.

Questions of energy and stability also arise. The π bonds contributing to the double and triple bonds encountered here are weaker than the σ bonds emphasized in the earlier chapters. There will be a number of chances to make assessments of relative energies in the problems that follow.

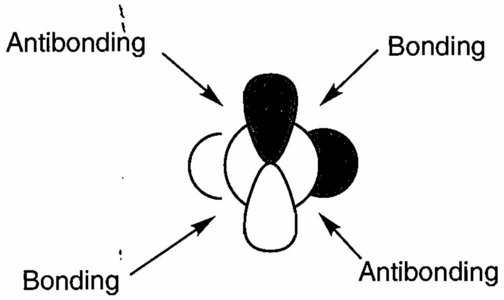
Problem 3.2 The lowest energy orbital results from mixing the four orbitals (the carbon 2*s* orbital plus the three hydrogen 1*s* orbitals) in phase. This orbital is bonding. The highest energy orbital comes from mixing the four orbitals so that there is only out-of-phase interaction (the carbon 2*s* orbital minus the three hydrogen 1*s* orbitals). This orbital is antibonding.



Problem 3.3 In the 90° form, the two *p* orbitals are of course also at 90°. In this arrangement, there is no overlap between the two orbitals because the bonding and antibonding interactions exactly cancel.

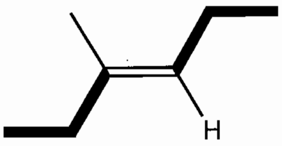


90° Form of ethylene

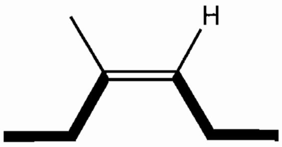


Newman projection showing only the *p* orbital interactions

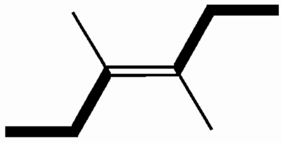
Problem 3.4 Only two of these molecules can exist in cis/trans (*Z*/*E*) forms. Here they are:



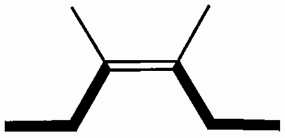
(*E*) Form



(*Z*) Form

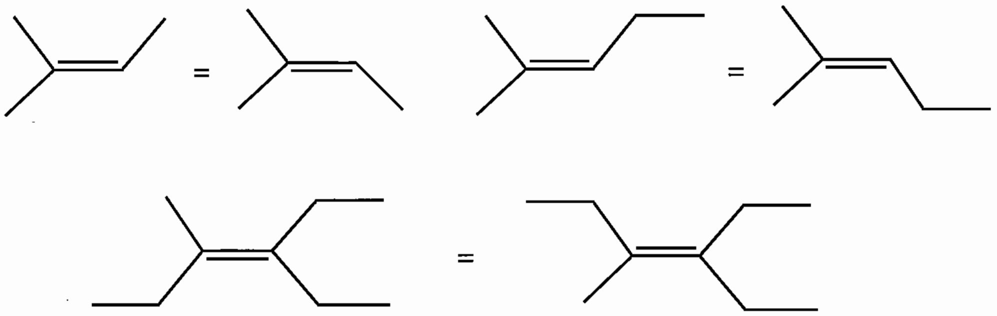


(*E*) Form



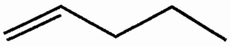
(*Z*) Form

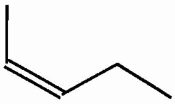
The others have only one possible form. These alkenes are flat, and the “different” isomers shown in the drawing are really identical, as one can simply be turned over to make the other. If this isn’t clear, and if the drawing doesn’t seem obvious to you, by all means make models of the “two” forms and show that they are identical by superimposing one on the other.

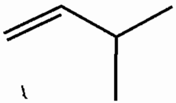


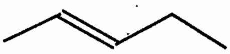
Problems 3.5 and 3.6

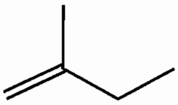
Pentenes

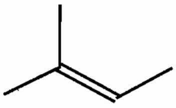

1-Pentene


(*Z*)-2-Pentene

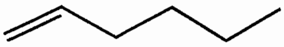

3-Methyl-1-butene

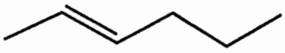

(*E*)-2-Pentene

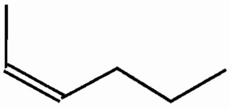

2-Methyl-1-butene

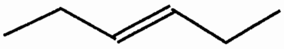

2-Methyl-2-butene

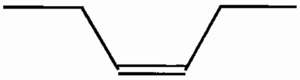
Hexenes

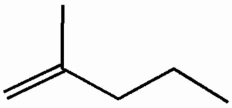

1-Hexene

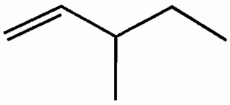

(*E*)-2-Hexene

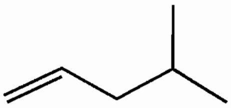

(*Z*)-2-Hexene

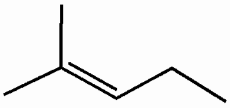

(*E*)-3-Hexene

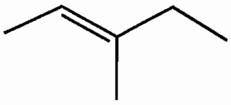

(*Z*)-3-Hexene

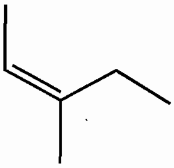

2-Methyl-1-pentene

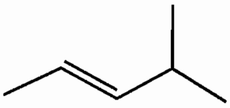

3-Methyl-1-pentene

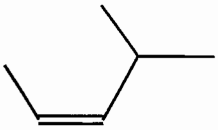

4-Methyl-1-pentene

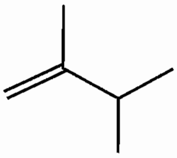

2-Methyl-2-pentene

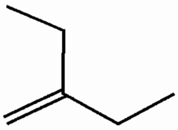

(*E*)-3-Methyl-2-pentene

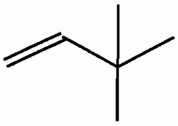

(*Z*)-3-Methyl-2-pentene

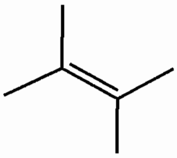

(*E*)-4-Methyl-2-pentene


(*Z*)-4-Methyl-2-pentene


2,3-Dimethyl-1-butene


2-Ethyl-1-butene


3,3-Dimethyl-1-butene


2,3-Dimethyl-2-butene

Problem 3.7

(a) $H_2C{=}CH_2$

Here the two carbons are identical. There can be only one signal

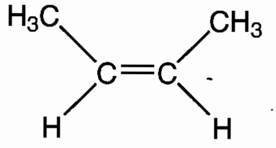
(b) $Cl{-}CH_2{-}CH{=}CH_2$

All three carbons are different. One is an *sp*^{3}-hybridized carbon attached to a chlorine, one is an *sp*^{2}-hybridized carbon attached to one hydrogen, and one is an *sp*^{2}-hybridized carbon attached to two hydrogens

(c) $H_2C{=}CH{-}CH_2CH_3$

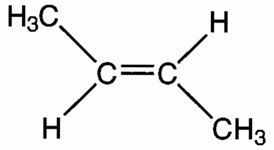
All four carbons are different, and there will be four signals

(d)



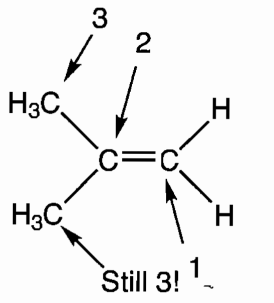
The two methyl groups are equivalent, as are the two methine groups, and there will be two signals

(e)



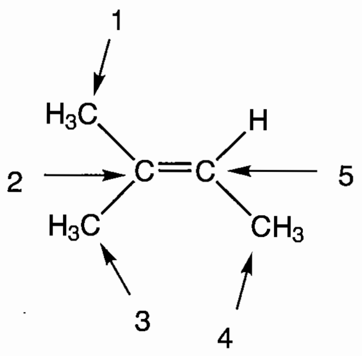
Again, the two methyl groups are equivalent, as are the two methine groups, and there will be two signals

(f)

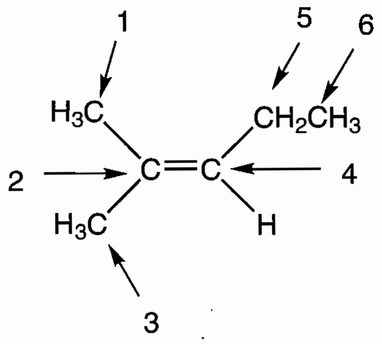


This time there is one methylene, one quaternary carbon, and two equivalent methyl carbons, and there will be three signals

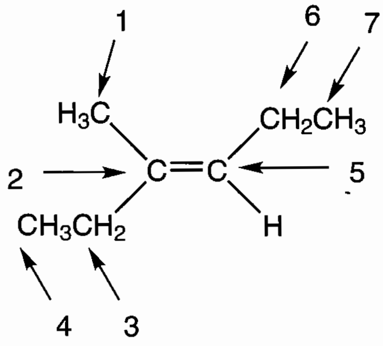
Problem 3.8



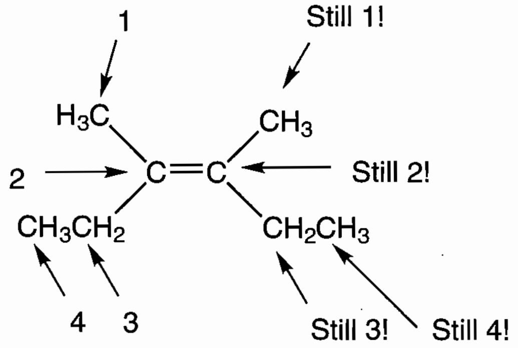
All five carbons are different, and there will be five signals. Be sure you see why the two methyls on the left (1 and 3) are different. One is cis to an H, the other is cis to another CH_3



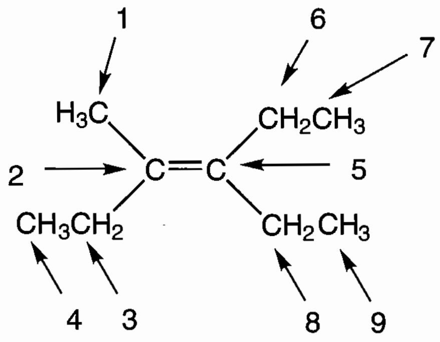
All six carbons are different. There will be six signals



All seven carbons are different. There will be seven signals

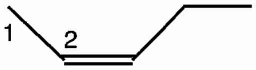


Now there is much more symmetry, and there are only four different carbons, and there will be four signals

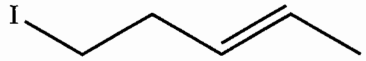


All nine carbons are different. There will be nine signals

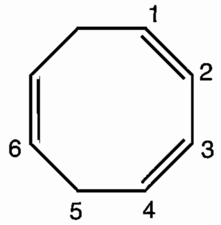
Problem 3.9



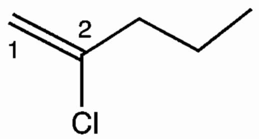
cis-2-Pentene



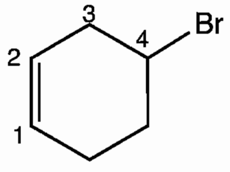
(*E*)-5-Iodo-2-pentene
(*trans*-5-iodo-2-pentene)



1,3,6-Cyclooctatriene



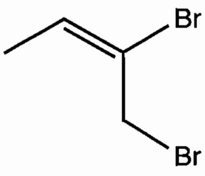
2-Chloro-1-pentene

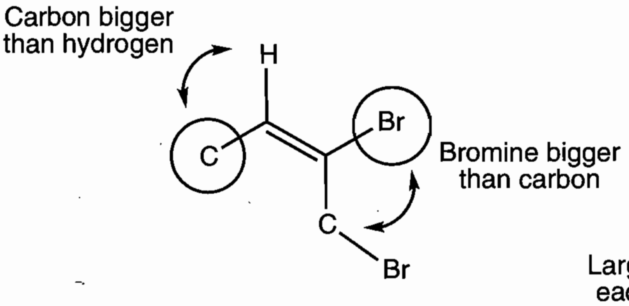


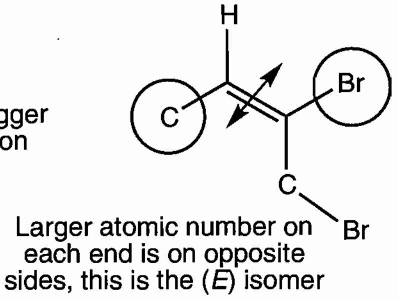
4-Bromocyclohexene

Problem 3.11 There are two carbons in each alkene. We can refer to these two carbons as one end or the other of the alkene. Look at one end and circle the substituent with the largest atomic number attached to that carbon. Look at the other end and circle the substituent with the largest atomic number. If the circled groups are on the same side of the alkene, then the molecule is a (*Z*) isomer. If the circled groups are on opposite sides, then the alkene is the (*E*) isomer.

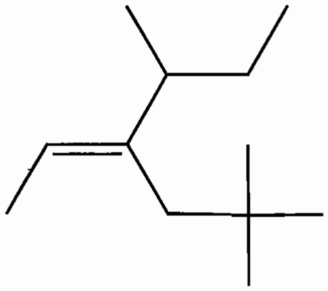
(a) On the left end, the C is larger than the H. On the right end, the Br is larger than the C. This isomer is (*E*)-1,2-dibromo-2-butene.

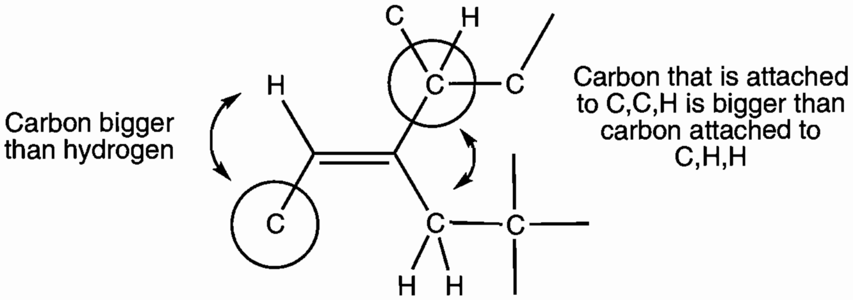




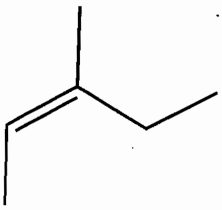


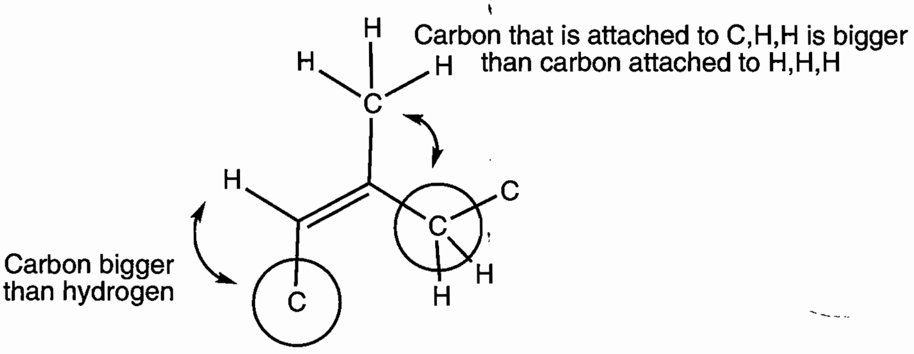
(b) On the left end, the C is larger than the H. On the right end, both attachments are carbon. So we have to go to the next attachments looking for a difference. One carbon has (C, C, H) for attachments. The other carbon has (C, H, H). The circled attachments are on opposite sides. Notice that there are two options for longest chain on this molecule. We choose numbering so that we maximize the number of substituents (see Problems 2.63 and 2.64). Which way we number does not have any bearing on the (*E*/*Z*) analysis. This molecule is (*E*)-3-(*sec*-butyl)-5,5-dimethyl-2-hexene.



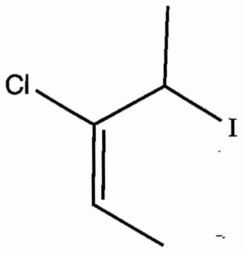


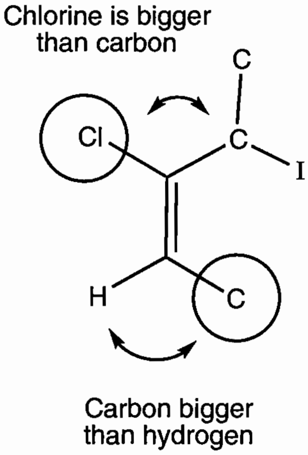
(c) On the left end, the C is larger than the H. On the right end, both attachments are carbon. We compare the next attachments to determine which group is larger. The carbon attached to (C, H, H) is larger than the carbon attached to (H, H, H). It doesn't matter what else is attached further out on the chain. It is the first difference that is compared. The circled attachments are on the same side. This molecule is (*Z*)-3-methyl-2-pentene.





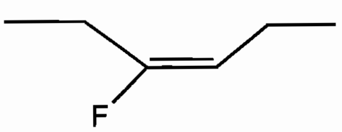
(d) On the bottom end, the C is larger than the H. On the top end, the Cl is larger than the C. It doesn't matter what else is attached further out on the chain. It is the first difference that is compared. The circled attachments are on the opposite sides. This molecule is (*E*)-3-chloro-4-iodo-2-pentene.



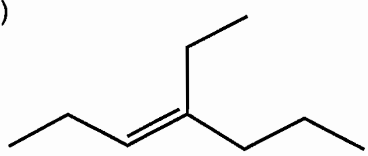


Problem 3.12 In (a), the higher priority groups are fluorine and ethyl, so the (*E*) isomer has those groups on opposite sides of the double bond. In (b), the higher priority groups are propyl and ethyl, and the (*E*) isomer must have them on opposite sides of the double bond. In (c), the higher priority groups are I and Cl. The (*Z*) isomer will have them on the same side of the double bond.

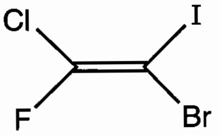
(a)



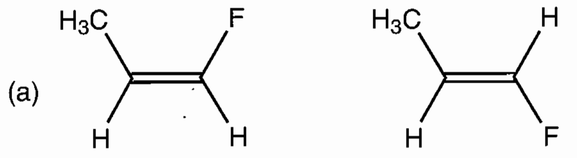
(b)



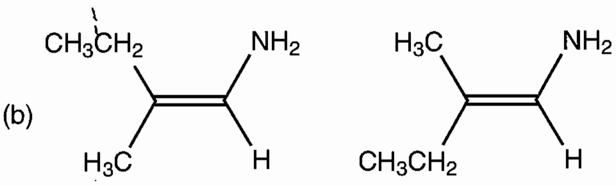
(c)



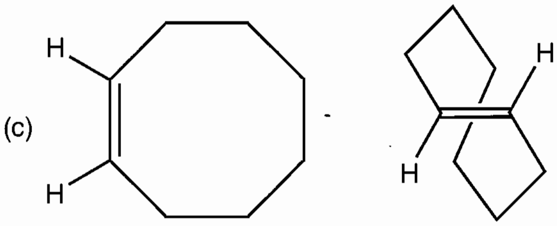
Problem 3.13 In (a), the higher priority groups are CH_3 and F. The (*Z*) isomer has them on the same side; the (*E*) isomer has them on opposite sides. In (b), the higher priority groups are ethyl (CH_3CH_2) and amino (NH_2). In (c), the higher priority groups are the methylene (CH_2) groups starting the ring. In (d), the higher priority groups are deuterium (D) and the ring carbon bearing the methyl (CH_3) group.



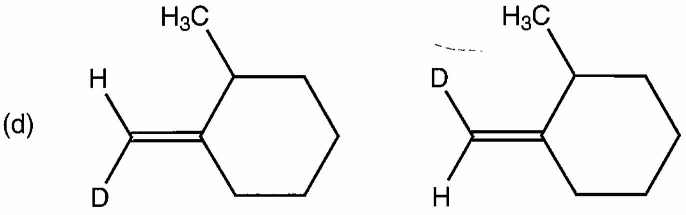
(*Z*) (*E*)



(*Z*) (*E*)

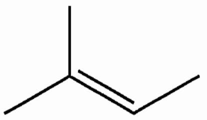


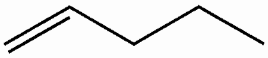
(*Z*) (*E*)

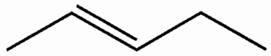


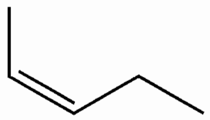
(*E*) (*Z*)

Problem 3.14

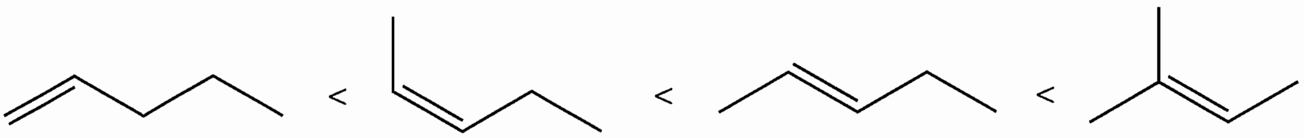

2-Methyl-2-butene


1-Pentene


(*E*)-2-Pentene

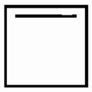

(*Z*)-2-Pentene

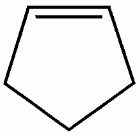
Based on the number of substituents on the double bond and based on the (*E*) isomer being more stable than the (*Z*) isomer, the following order is obtained:

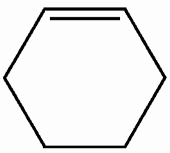


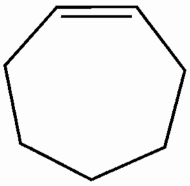
Problem 3.15


Cyclopropene

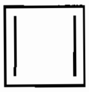

Cyclobutene


Cyclopentene

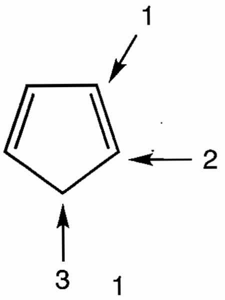

Cyclohexene


Cycloheptene

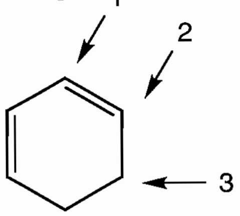
Problem 3.16



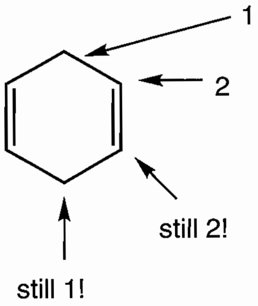
All four methine carbons are equivalent. There will be only one signal



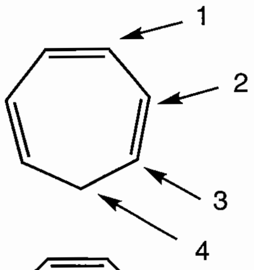
The two methine carbons are different, and there is a single methylene. There will be three signals



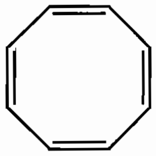
Three signals—two methines and one methylene. Note the symmetry



Note again the symmetry, which is probably more obvious in this molecule than the one above. There are only two kinds of carbon—and thus, two signals

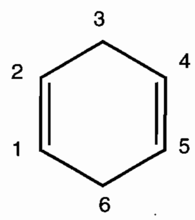


Four signals from three different methines and the one methylene

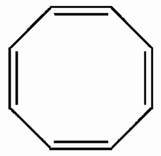


Lots of symmetry here—all eight methines are the same—one signal

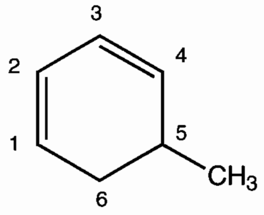
Problem 3.17



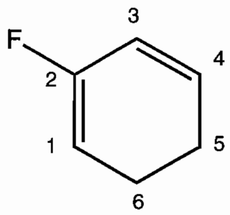
1,4-Cyclohexadiene



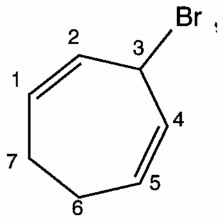
1,3,5,7-Cyclooctatetraene



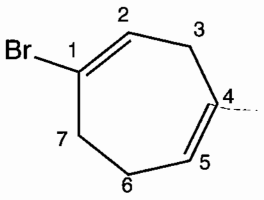
5-Methyl-1,3-cyclohexadiene



2-Fluoro-1,3-cyclohexadiene



3-Bromo-1,4-cycloheptadiene



1-Bromo-1,4-cycloheptadiene

Problem 3.19

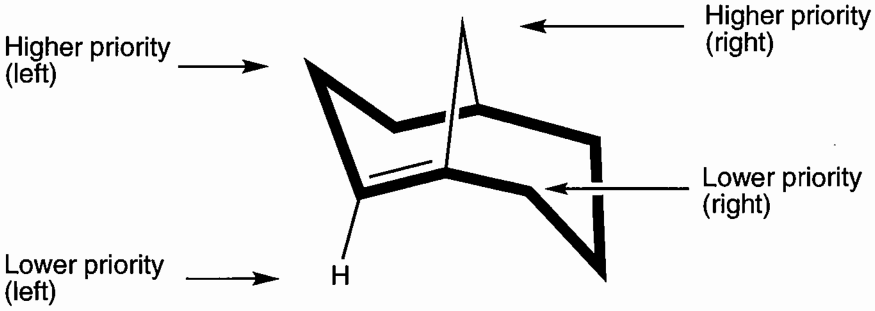
$\Delta G = -RT \ln K$. In this case,

$\Delta G = 11.4$ kcal/mol
$R = 1.986$ cal/deg·mol
$T = 298$ K

$RT = 592$ cal/mol $= 0.592$ kcal/mol

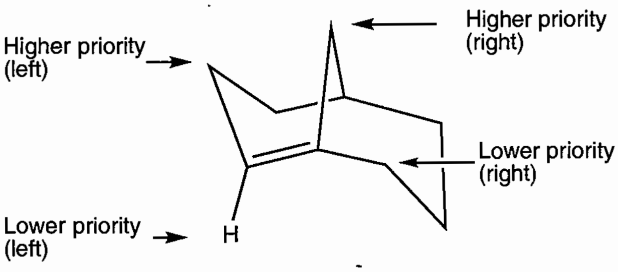
$11.4 = -(0.592)\ln K$
$\ln K = -19.26$
$K = 4 \times 10^{-9}$

Problem 3.20 The form shown in Figure 3.48 is (*Z*). On the left-hand carbon of the double bond, the higher priority group is CH_2 and the lower priority group is H. On the right-hand side of the double bond, the higher priority group is CH_2—CHC_2 and the lower priority group is CH_2—CH_2C. As the higher priority groups are on the same side of the double bond, the compound is (*Z*).

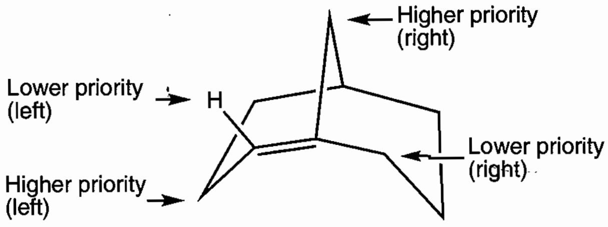


(*Z*)-Bicyclo[3.3.1]non-1-ene

Problem 3.21 The form in Figure 3.48 is (*Z*), as the higher and lower priority groups are on the same side of the double bond. On the left-hand carbon of the double bond, the higher priority group is CH_2 and the lower priority group is H. On the right-hand carbon of the double bond, the higher priority group is $CH_2—CHC_2$ and the lower priority group is $CH_2—CH_2C$. In this form, the two higher priority groups are on the same side of the double bond. Thus the correct label is (*Z*). The other form is the (*E*) structure, with the two higher priority groups on opposite sides.

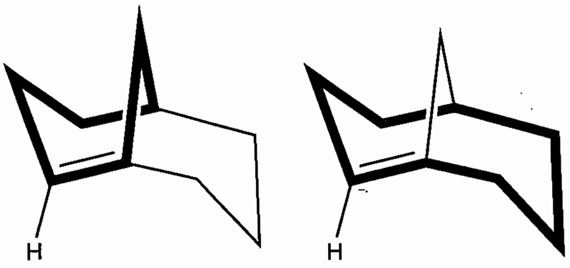


(*Z*)-Bicyclo[3.3.1]non-1-ene

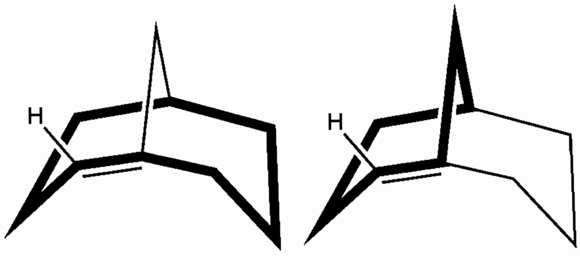


(*E*)-Bicyclo[3.3.1]non-1-ene

Note that this molecule contains a double bond in two different-sized rings. The double bond of the (*Z*) form is cis in the six-membered ring and trans in the eight-membered ring. In the (*E*) form, the double bond is cis in the eight-membered ring and trans in the six-membered ring. The smaller the ring, the less stable is a trans double bond (why?), so the (*E*) form is less stable than the (*Z*) form.

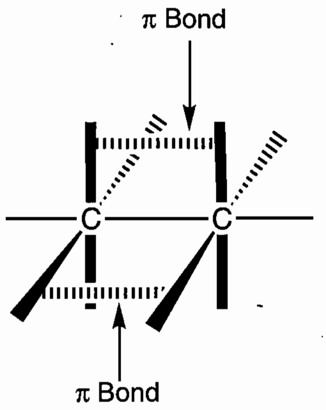


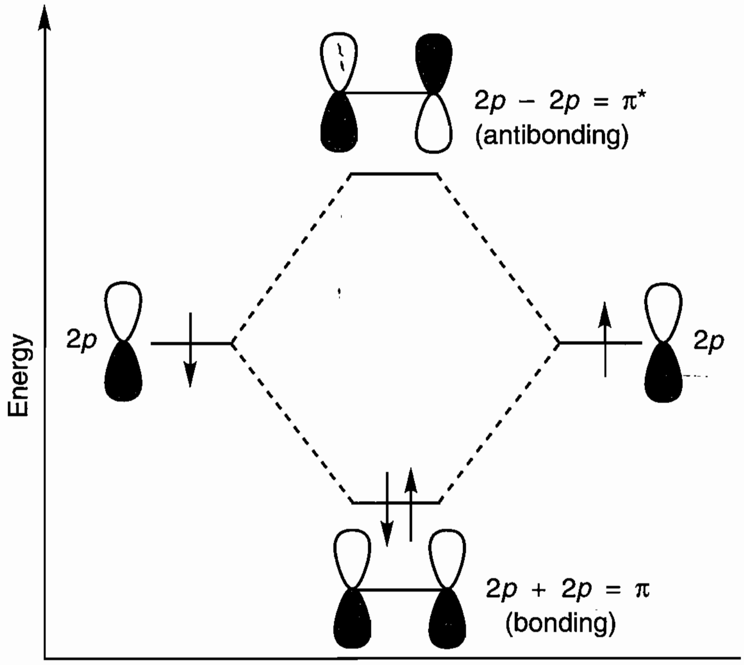
(*Z*) Form: double bond cis in six-membered ring (bold), trans in eight-membered ring (bold)



(*E*) Form: double bond cis in eight-membered ring (bold), trans in six-membered ring (bold)

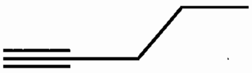
Problem 3.22 The picture is exactly the same as for alkenes (Fig. 3.12, p. 108), except that there are two π bonds at 90° to each other. The diagram shows only one orbital interaction diagram and indicates both π bonds schematically.

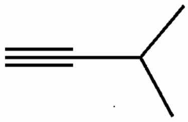




Problems 3.23 and 3.24

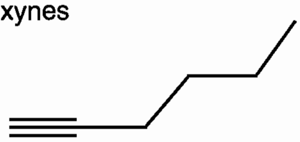
Pentynes

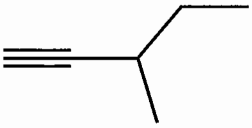

1-Pentyne

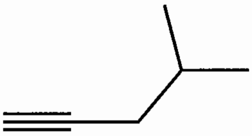

3-Methyl-1-butyne

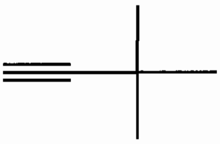

2-Pentyne

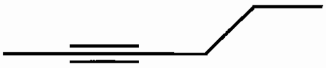
Hexynes


1-Hexyne

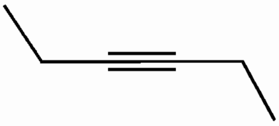

3-Methyl-1-pentyne


4-Methyl-1-pentyne

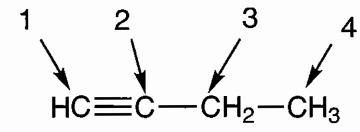

3,3-Dimethyl-1-butyne


2-Hexyne

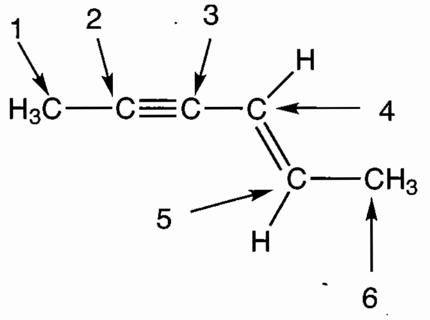

4-Methyl-2-pentyne


3-Hexyne

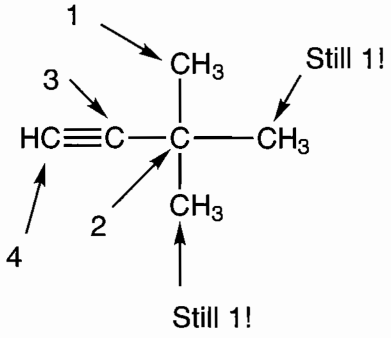
Problem 3.25



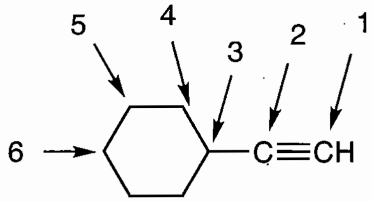
All four carbons are different—there will be four signals



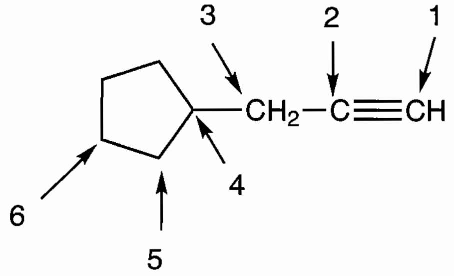
All six carbons are different—there will be six signals



The three methyl groups are equivalent, and there are three other different carbons—four signals



Watch the symmetry—there are only six different carbons here



Again, there are only six different carbons

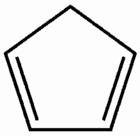
Problem 3.26

(a) C_5H_6

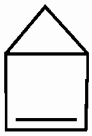
$$\frac{\overbrace{(2 \times 5) + 2}^{\text{\# of hydrogens for } C_5} - \overset{\text{\# of hydrogens in this molecule}}{6}}{2} = 3$$

There must be a total of three π bonds and/or rings. Some possibilities are

Three π bonds



One ring, two π bonds

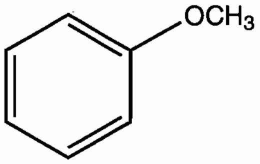


Two rings, one π bond

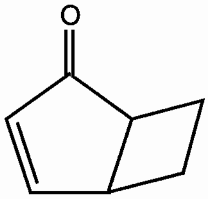
(b) C_7H_8O

$$\frac{\overbrace{(2 \times 7) + 2}^{\text{\# of hydrogens for } C_7} - \overset{\text{\# of hydrogens in this molecule}}{8}}{2} = 4$$

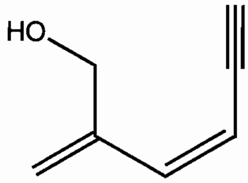
Notice that oxygen does not get included in the calculation. A molecule of C_7H_8O must have 4 degrees of unsaturation. This means there must be a total of four π bonds and/or rings. Some possibilities are



One ring, three π bonds



Two rings, two π bonds

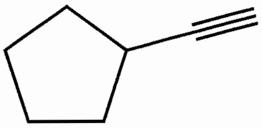


Four π bonds

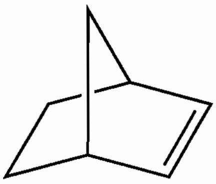
(c) C_7H_{10}

$$\frac{\overbrace{(2\times 7)+2}^{\text{\# of hydrogens for } C_7} - \overset{\text{\# of hydrogens in this molecule}}{10}}{2} = 3$$

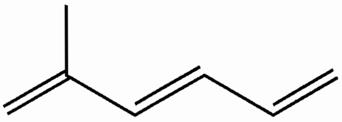
A molecule of C_7H_{10} must have 3 degrees of unsaturation. This means there must be a total of three π bonds and/or rings. Some possibilities are



One ring, two π bonds



Two rings, one π bond

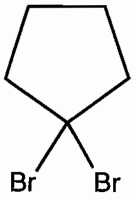


Three π bonds

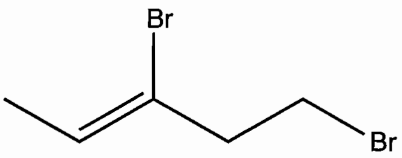
(d) $C_5H_8Br_2$

$$\frac{\overbrace{(2\times 5)+2}^{\text{\# of hydrogens for } C_5} - \overset{\text{\# of hydrogens and halogens in this molecule}}{10}}{2} = 1$$

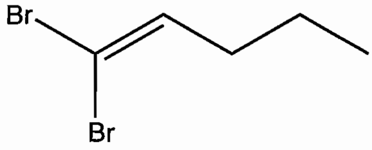
A molecule of C_5H_8Br must have 1 degree of unsaturation. This means there must be a π bond or a ring. Some possibilities are



One ring

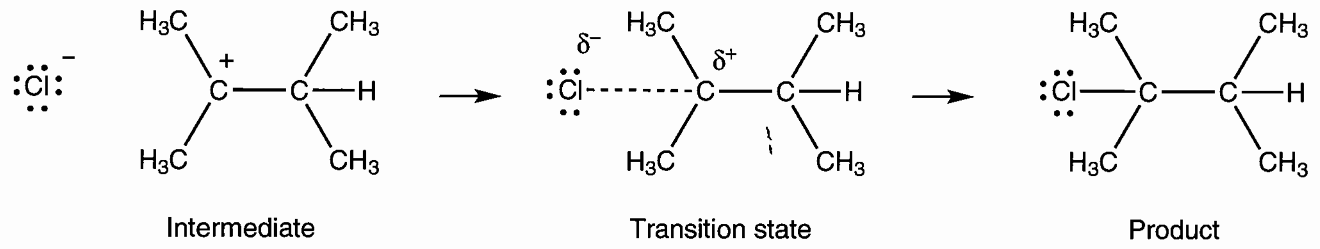


One π bond

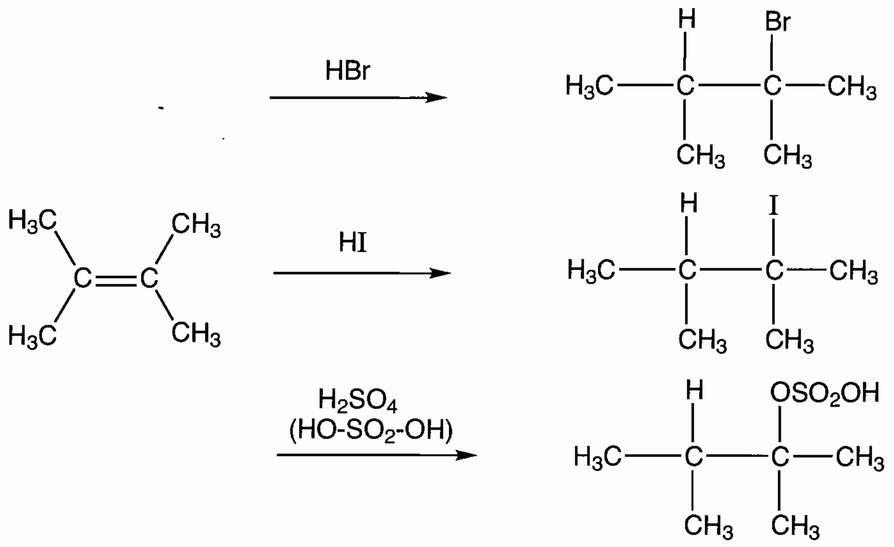


One π bond

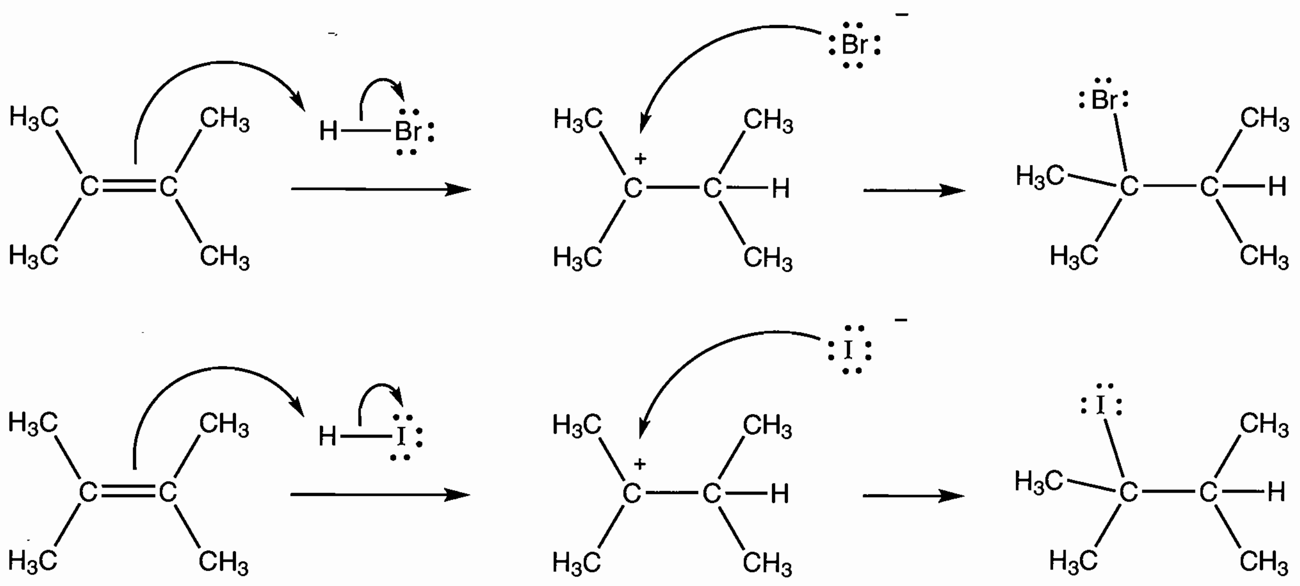
Problem 3.29

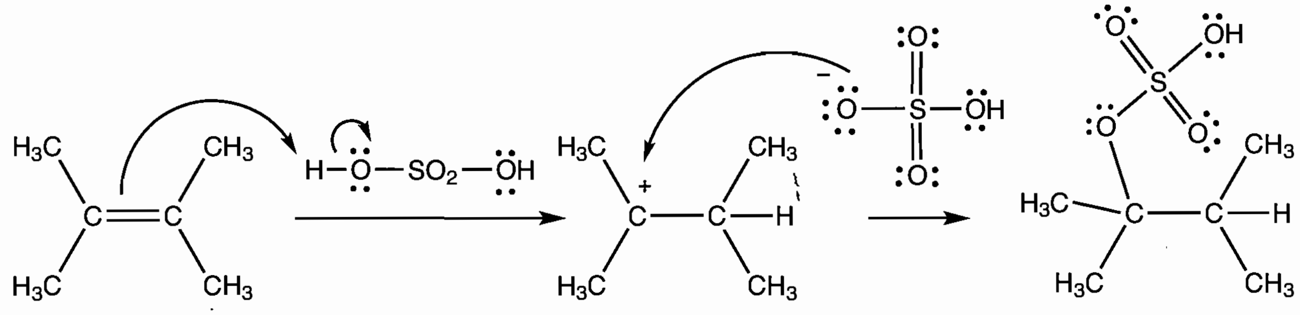


Problem 3.30 These reactions are "standard" additions of H—X across the double bond of 2,3-dimethyl-2-butene. Only H_2SO_4 might cause problems—you have to see it as HO—SO_2—OH, just another "H—X."

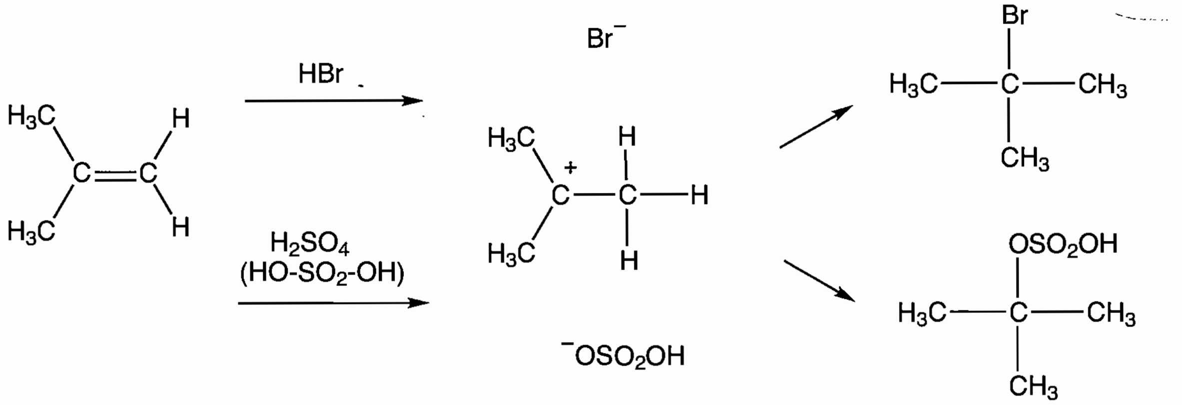


Problem 3.31

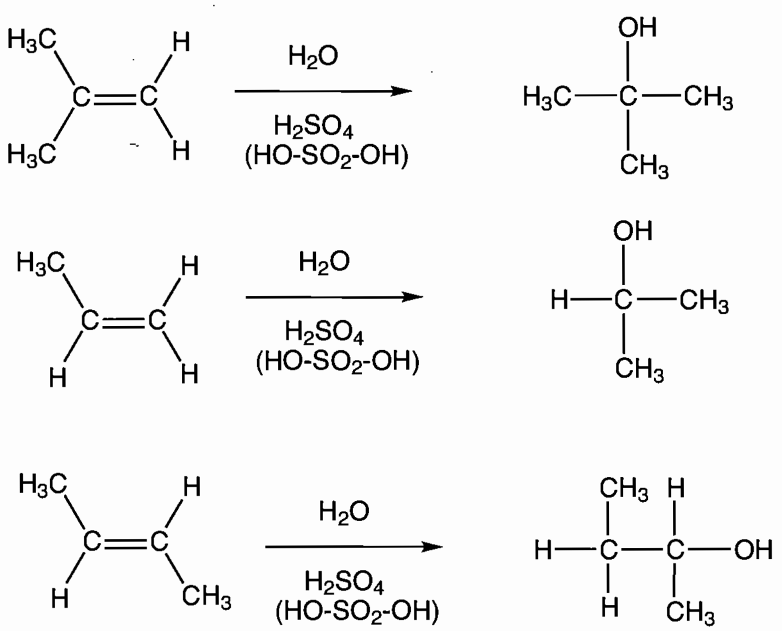




Problem 3.32 Here are two more additions of "H—X." This time, however, you have to deal with the direction of addition, the regiochemistry. In each case, the alkene will be protonated to give the *tertiary* carbocation, to which X⁻ will add. Here are the products:



Problem 3.34 Each of these alcohols can be made through an acid-catalyzed addition of water to an alkene:



Additional Problem Answers

Problem 3.35 First, find the weight of carbon present in the carbon dioxide. This must also be the weight of carbon present in the sample compound (MW = molecular weight).

$$\text{Wt (C)} = \frac{\text{MW (C)}}{\text{MW (CO}_2\text{)}} \times \text{Wt (CO}_2\text{)} = \frac{12.011 \text{ g/mol}}{44.009 \text{ g/mol}} \times 16.90 \text{ mg} = 4.61 \text{ mg}$$

Similarly, the weight of hydrogen can be calculated from the weight of water:

$$\text{Wt (H)} = \frac{2 \times \text{MW (H)}}{\text{MW (H}_2\text{O)}} \times \text{Wt (H}_2\text{O)} = \frac{2 \times 1.008 \text{ g/mol}}{18.015 \text{ g/mol}} \times 3.46 \text{ mg} = 0.39 \text{ mg}$$

Note that the sum of the weights of carbon and hydrogen equals the weight of the sample. The sample must have contained only carbon and hydrogen.

The weight percents of carbon and hydrogen can now easily be calculated:

$$\%\text{C} = \frac{4.61 \text{ mg}}{5.00 \text{ mg}} \times 100 = 92.2\% \qquad \%\text{H} = \frac{0.39 \text{ mg}}{5.00 \text{ mg}} \times 100 = 7.8\%$$

Problem 3.36 The "missing" weight percent is oxygen, in this case, 23.50%. Now, assume a 100 g sample of the compound in question and compute the number of moles of each element present in a sample of this size. If the compound contains 70.58% carbon, 100 g of sample will contain 70.58 g, or 5.88 mol:

$$\text{C} = \frac{70.58 \text{ g}}{12.011 \text{ g/mol}} = 5.88 \text{ mol}$$

Similarly, we can determine the number of moles of H and O:

$$\text{H} = \frac{5.92 \text{ g}}{1.008 \text{ g/mol}} = 5.87 \text{ mol} \qquad \text{O} = \frac{23.50 \text{ g}}{15.999 \text{ g/mol}} = 1.47 \text{ mol}$$

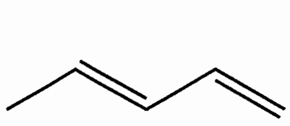
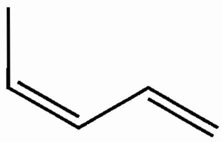
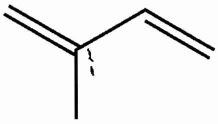
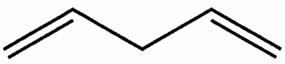
Therefore, a formula that expresses the relative molar proportions of carbon, hydrogen, and oxygen is $C_{5.88}H_{5.87}O_{1.47}$.

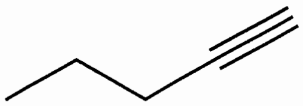
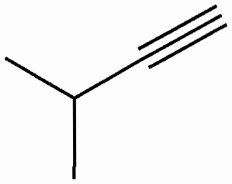
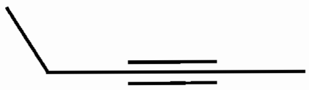
Now you need to convert this formula into one in which the elements are present in whole number ratios. Divide through by the element present in the smallest amount, in this case, oxygen:

$$\text{C} = \frac{5.88}{1.47} = 4.00 \qquad \text{H} = \frac{5.87}{1.47} = 3.99 \qquad \text{O} = \frac{1.47}{1.47} = 1.00$$

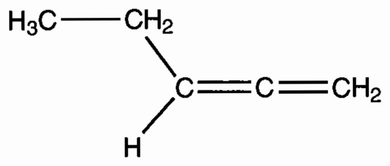
This calculation yields an empirical formula of C_4H_4O. As C_4H_4O has a molecular weight of 68 g/mol, it can't be the molecular formula in this case because you know that the molecular weight is about 135 g/mol. However, simply multiplying by 2 gives the correct molecular formula of $C_8H_8O_2$, MW = 136 g/mol.

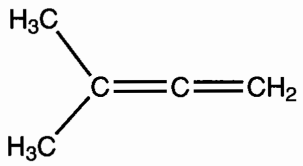
Problem 3.37 A molecule with the formula of C_5H_8 will have 2 degrees of unsaturation. Here are the possible acyclic isomers that you should be able to predict:

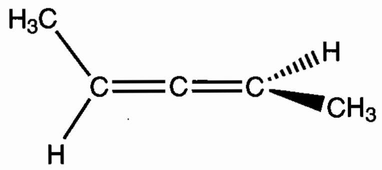





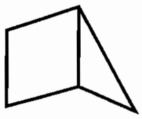
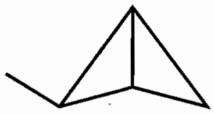
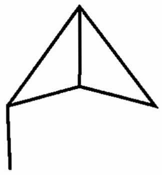
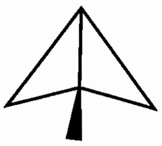
Here are a few other acyclic isomers that are a little more esoteric:

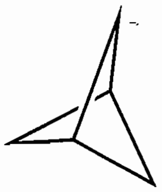
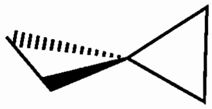






If a C_5H_8 molecule has no π bonds, it must have two rings. Here are the possible bicyclic isomers:

Problem 3.38

(a) This is an aromatic ring attached to a bromine. There are three π bonds and one ring. There are 4 degrees of unsaturation in this molecule.

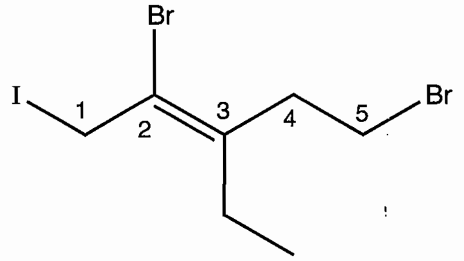
(b) There are two rings and one π bond. There are 3 degrees of unsaturation in this molecule.

(c) There is one double bond and one triple bond in this molecule. There are 3 degrees of unsaturation in this molecule.

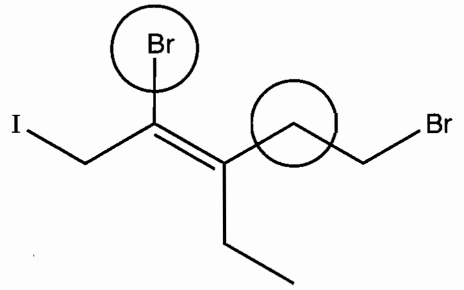
(d) There are two double bonds and no rings in this molecule. Thus there are 2 degrees of unsaturation in this molecule.

Problem 3.39

(a) This molecule is an alkene, which is the priority group. Find the longest carbon chain that contains both carbons of the alkene. There are two possible longest chains. Both are five carbons long. Pick the longest carbon chain that has the maximum groups attached. Number the chain so that the priority group gets the lowest possible number. Therefore, this molecule is a 2-pentene.

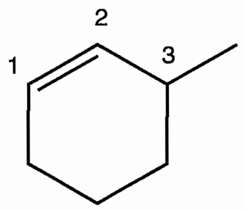


Find the substituents and indicate the location of attachment. We have 1-iodo and 2,5-dibromo and 3-ethyl. Now alphabetize the substituents in the prefix. That means we have 2,5-dibromo-3-ethyl-1-iodo-2-pentene. We aren't finished. There is the issue of (*E*) or (*Z*) isomer. On carbon number 2 the larger atomic numbered substituent is the Br. On carbon number 3 the substituents are both carbons. Each of the carbons is attached to (C, H, H). So we must look to the next attachment. Comparing the next carbons, carbon number 5 has (Br, H, H) and the second carbon of the ethyl group has (H, H, H). The circled groups are on the same side. This molecule is (*Z*)-2,5-dibromo-3-ethyl-1-iodo-2-pentene.

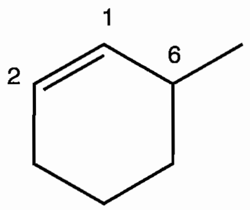


(b) The priority group in this molecule is the alkene. The larger chain is the six-membered ring. This molecule is a cyclohexene. Because the alkene is the only priority group, the cyclohexene is known to have the double bond between carbons number 1 and number 2. We don't call this 1-cyclohexene. There is no other choice.

There are two options for numbering the ring: clockwise and counterclockwise. Because the alkene carbons must be numbered consecutively, the clockwise numbering puts the substituent on carbon number 3 and the counterclockwise numbering puts the substituent on carbon number 6.



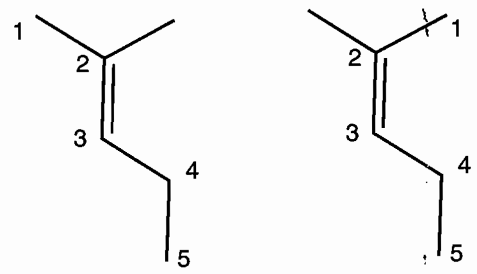
Clockwise numbering



Counterclockwise numbering

We see there is only one substituent, so there is no need to worry about the alphabetical order in the prefix. It is a 3-methyl group. We know that only the (*Z*) isomer is stable for cycloalkenes with a ring size smaller than eight carbons. So we don't need to indicate that this is the (*Z*) isomer. It is assumed to be the (*Z*) isomer. This molecule is 3-methylcyclohexene.

(c) The priority group in this molecule is an alkene. We find the longest chain with both carbons of the alkene and number the chain so that the lowest possible number is used for the priority group. We have another 2-pentene. It doesn't matter which methyl group on carbon number 2 we use in the numbering.



There is only one substituent, the methyl group on carbon number 2. This molecule is a 2-methyl-2-pentene. We do the (*E*) or (*Z*) analysis and we find that the two groups on carbon number 2 are the same atomic number and there is no difference in further attachment. Both carbons have attachment of (H, H, H). That means there is no (*E*) or (*Z*) for this molecule. This molecule is 2-methyl-2-pentene.

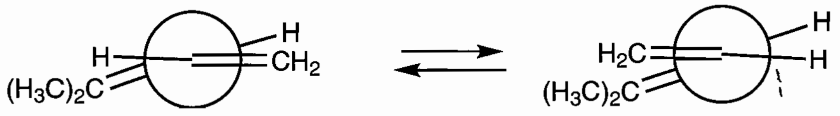
(d) The priority group in this molecule is a diene. We find the longest chain with all four carbons of the diene and number the chain so that the lowest possible numbers are used. This molecule is a 1,3-pentadiene, not a 2,4-pentadiene.

We find the substituents for this molecule. We will have 3-chloro and 2,4-dimethyl in the prefix. The attachments on carbon number 1 are both hydrogens. So there is no (*E*) or (*Z*) for the first alkene. The attachments on carbon number 4 are both methyl groups. So the second alkene is also neither (*E*) nor (*Z*). This molecule is 3-chloro-2,4-dimethyl-1,3-pentadiene.

Problem 3.40 These molecules are conformational isomers. They differ only by the rotation around a C—C single bond. You might need to build the molecule using your model set to convince yourself that they will interconvert at room temperature. The Newman projections show that the isomer (a) would be more stable. Isomer (b) is higher in energy because of steric interactions. The bulky groups are eclipsing each other, *and* the hydrogens on one of the methyls, labeled C(5) in the drawing, are competing for space with one of the C(1) vinyl hydrogens. Your model set will show this more clearly.

(continued)

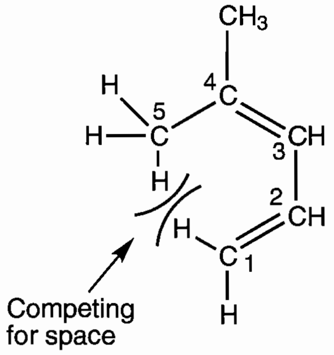
Problem 3.40 *(continued)*



(a)

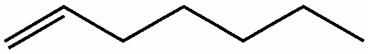
(b)

Newman projections looking down the C(2)—C(3) bond

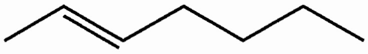


(b)

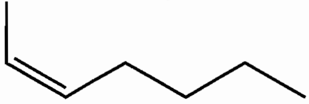
Problem 3.41



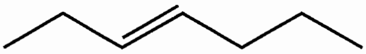
1-Heptene



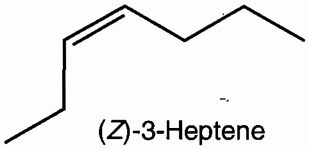
(*E*)-2-Heptene



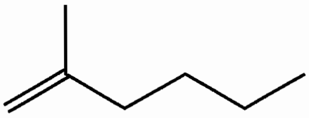
(*Z*)-2-Heptene



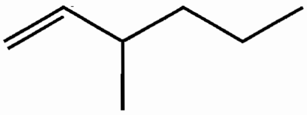
(*E*)-3-Heptene



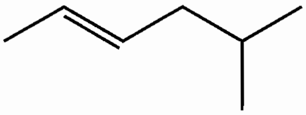
(*Z*)-3-Heptene



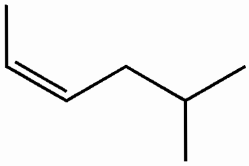
2-Methyl-1-hexene



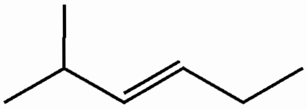
3-Methyl-1-hexene



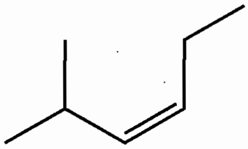
(*E*)-5-Methyl-2-hexene



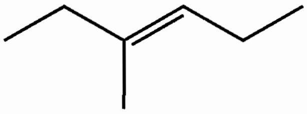
(*Z*)-5-Methyl-2-hexene



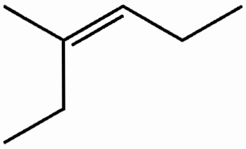
(*E*)-2-Methyl-3-hexene



(*Z*)-2-Methyl-3-hexene



(*E*)-3-Methyl-3-hexene



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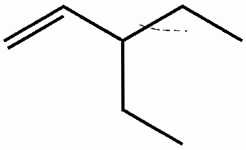
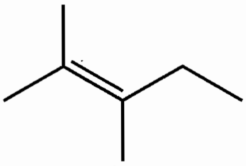
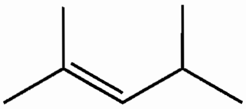


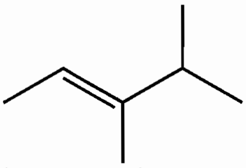
3-Ethyl-1-pentene



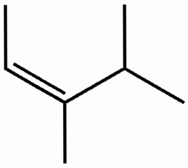
2,3-Dimethyl-2-pentene



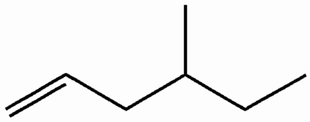
2,4-Dimethyl-2-pentene



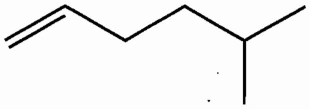
(*E*)-3,4-Dimethyl-2-pentene



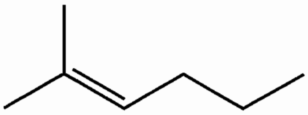
(*Z*)-3,4-Dimethyl-2-pentene



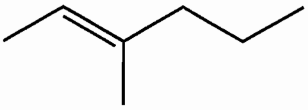
4-Methyl-1-hexene



5-Methyl-1-hexene



2-Methyl-2-hexene



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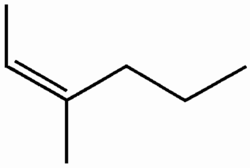

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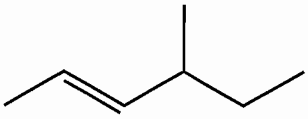

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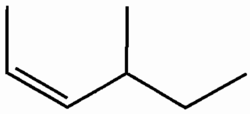
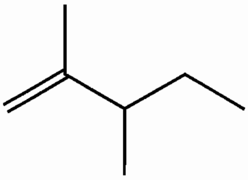
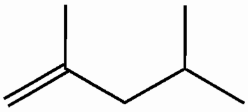


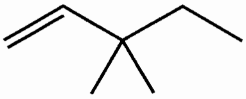
(*Z*)-4-Methyl-2-hexene



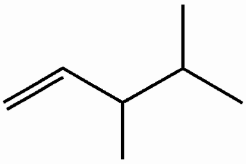
2,3-Dimethyl-1-pentene



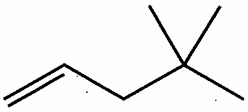
2,4-Dimethyl-1-pentene



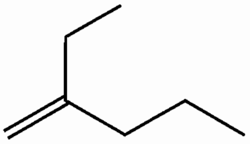
3,3-Dimethyl-1-pentene



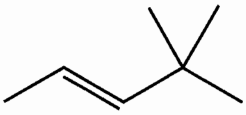
3,4-Dimethyl-1-pentene



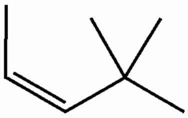
4,4-Dimethyl-1-pentene



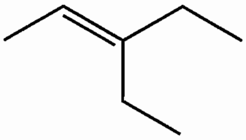
2-Ethyl-1-pentene



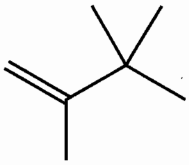
(*E*)-4,4-Dimethyl-2-pentene



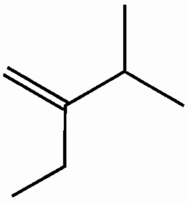
(*Z*)-4,4-Dimethyl-2-pentene



3-Ethyl-2-pentene

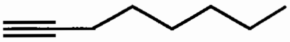


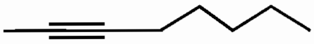
2,4,4-Trimethyl-1-butene



2-Ethyl-3-methyl-1-butene

Problem 3.42


1-Octyne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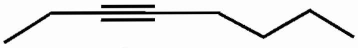
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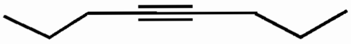
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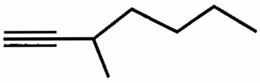
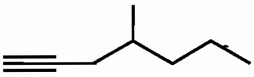

3-Methyl-1-heptyne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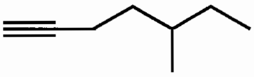
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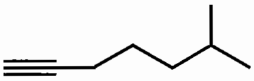
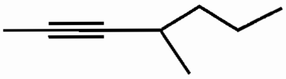
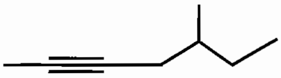
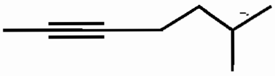

6-Methyl-1-heptyne


4-Methyl-2-heptyne


5-Methyl-2-heptyne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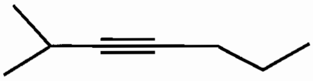
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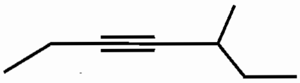
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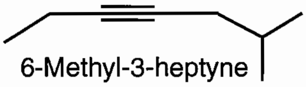
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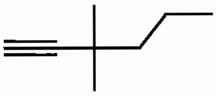
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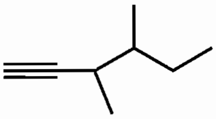
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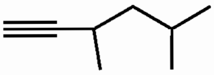
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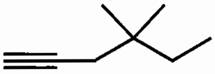
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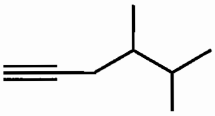
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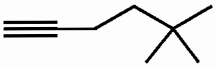
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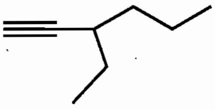
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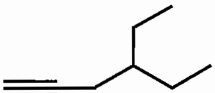
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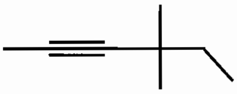
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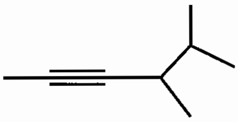
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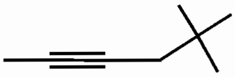
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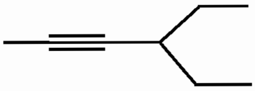
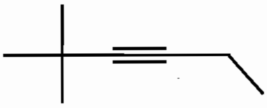

4-Ethyl-2-hexyne


2,5-Dimethyl-3-hexyne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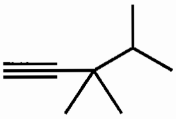
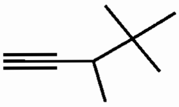
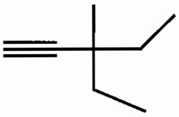
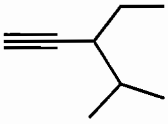
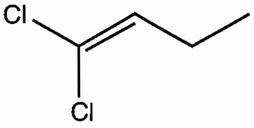

3,3,4-Trimethyl-1-pentyne

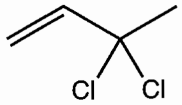

3,4,4-Trimethyl-1-pentyne

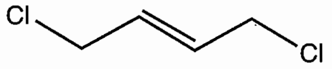

3-Ethyl-3-methyl-1-pentyne

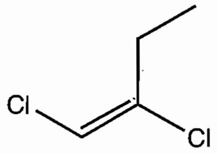

3-Ethyl-4-methyl-1-pentyne

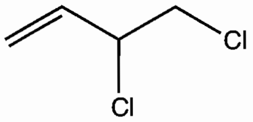
Problem 3.43

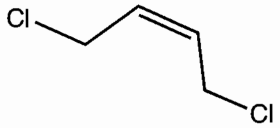

1,1-Dichloro-1-butene

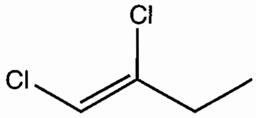

3,3-Dichloro-1-butene

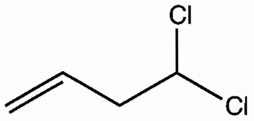

(*E*)-1,4-Dichloro-2-butene

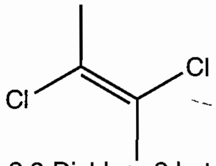

(*E*)-1,2-Dichloro-1-butene

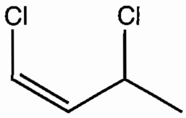

3,4-Dichloro-1-butene

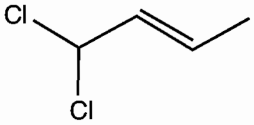

(*Z*)-1,4-Dichloro-2-butene


(*Z*)-1,2-Dichloro-1-butene


4,4-Dichloro-1-butene


(*E*)-2,3-Dichloro-2-butene


(*Z*)-1,3-Dichloro-1-butene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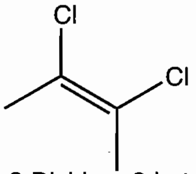
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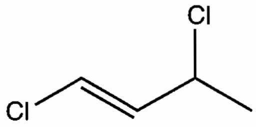
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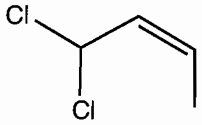
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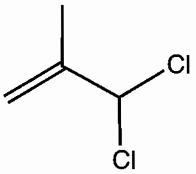
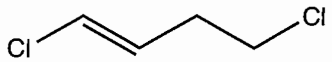
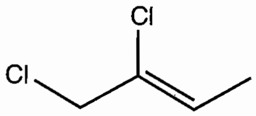
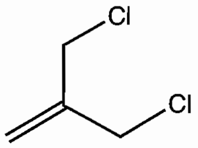
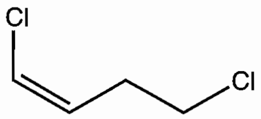

3,3-Dichloro-2-methyl-1-propene


(*E*)-1,4-Dichloro-1-butene


(*Z*)-1,2-Dichloro-2-butene


3-Chloro-2-(chloromethyl)-1-propene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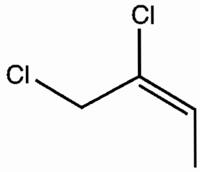
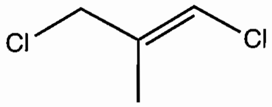
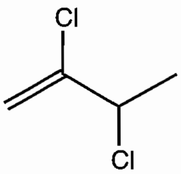
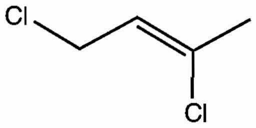
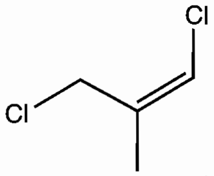
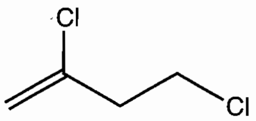

(*E*)-1,2-Dichloro-2-butene

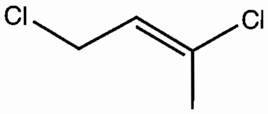

(*E*)-1,3-Dichloro-2-methyl-1-propene

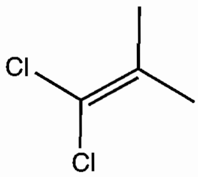

2,3-Dichloro-1-butene


(*Z*)-1,3-Dichloro-2-butene


(*Z*)-1,3-Dichloro-2-methyl-1-propene


2,4-Dichloro-1-butene

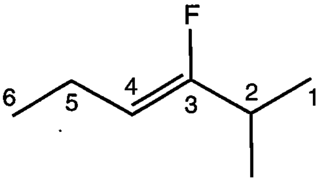

(*E*)-1,3-Dichloro-2-butene


1,1-Dichloro-2-methyl-1-propene

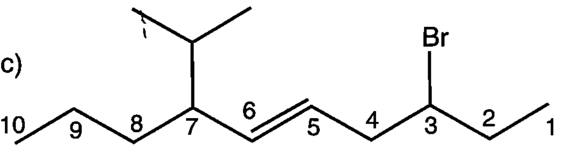
Problem 3.44 (a) (*E*)-5-iodo-2,7-dimethyl-3-nonene (the di- is ignored, so iodo comes before dimethyl), (b) (*Z*)-2-chloro-3-ethyl-3-hexene, (c) 4-bromo-5-isopropyl-2-octyne, (d) (*Z*)-4,4-dimethyl-2-hepten-5-yne (-ene gets priority over -yne).

Problem 3.45

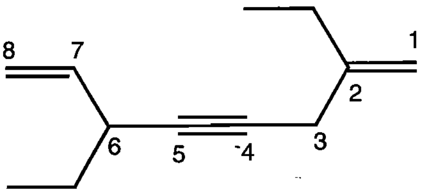
(a)



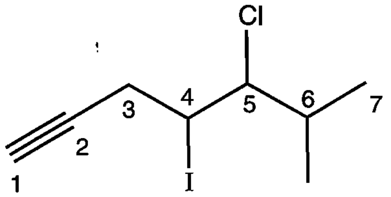
(c)



(b)

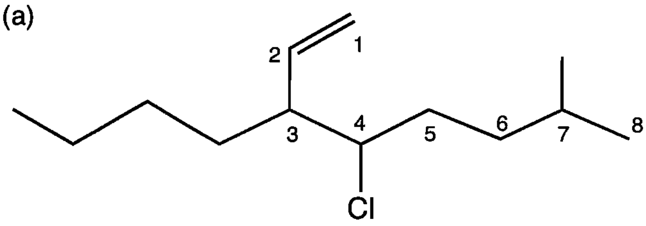


(d)



Problem 3.46

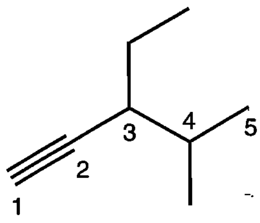
(a)



3-Butyl-4-chloro-7-methyl-1-octene

The name is based on the longest chain containing the double bond, even though it is not the longest chain in the molecule

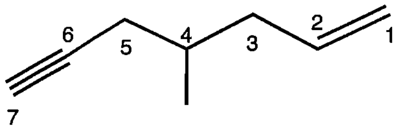
(b)



3-Ethyl-4-methyl-1-pentyne

When chains of equal length compete for selection as the longest chain, the choice goes to the chain that has the greatest number of substituents

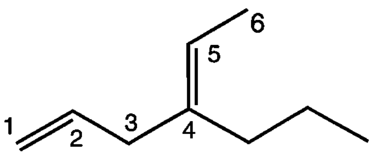
(c)



4-Methyl-1-hepten-6-yne

When the numbering scheme produces two names in which the lower number could go to either the -ene or the -yne, the -ene has priority

(d)

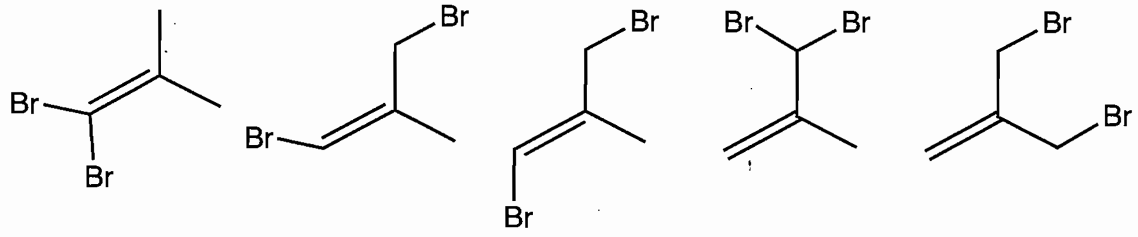


(*E*)-4-Propyl-1,4-hexadiene

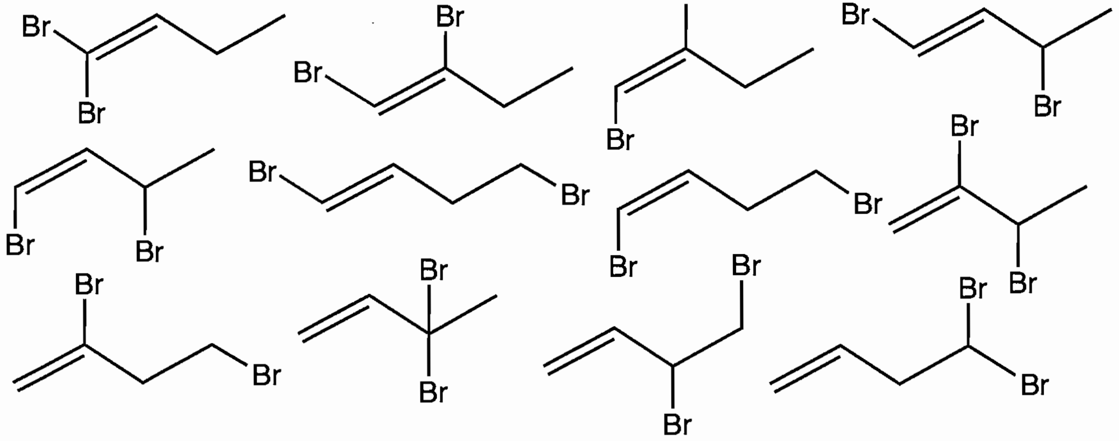
The diene chain is the priority group; when numbering the diene, "1,4" is preferred over "2,5" because of the lower numbers; note that the allyl group on C(4) has a larger overall atomic than the propyl group on C(4), giving the (*E*) designation

Problem 3.47 The first thing to do is to determine the number of degrees of unsaturation in $C_4H_6Br_2$. Because we have a molecule with four carbons, the related *saturated* alkane is C_4H_{10}. The bromines in the compound $C_4H_6Br_2$ are univalent and can be treated as hydrogens for the purpose of counting. So, $10 - 8 = 2/2 = 1$ degree of unsaturation. The compounds in question must contain only one ring or one π bond. Let's take this question step by step. There are three noncyclic chains to consider: propene, 1-butene, and 2-butene. Two bromines can be arranged in the following ways:

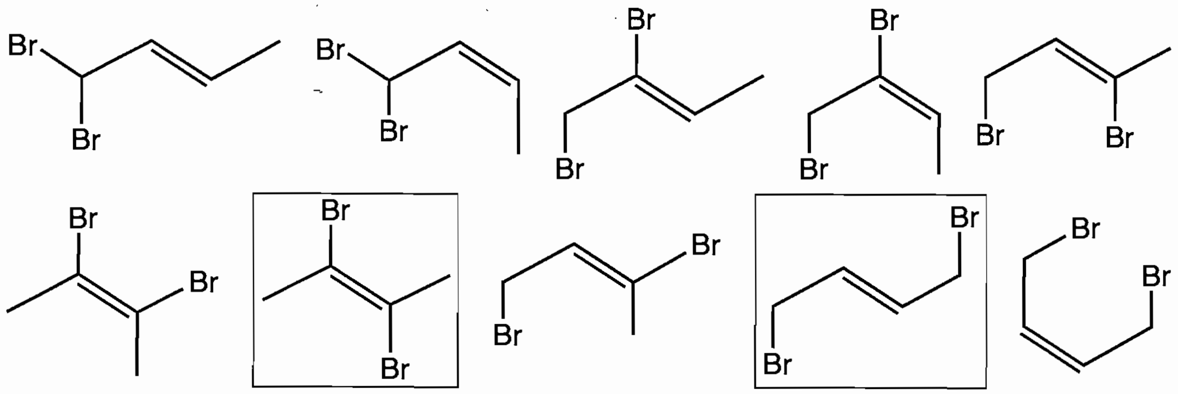
Propene-based molecules



1-Butene–based molecules



2-Butene–based molecules

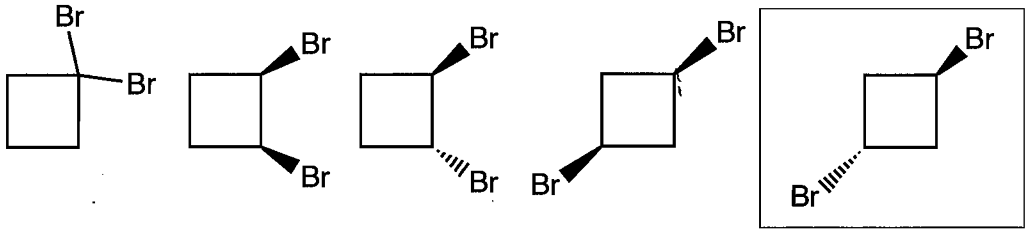


Only the molecules in the boxes have zero dipole moments.

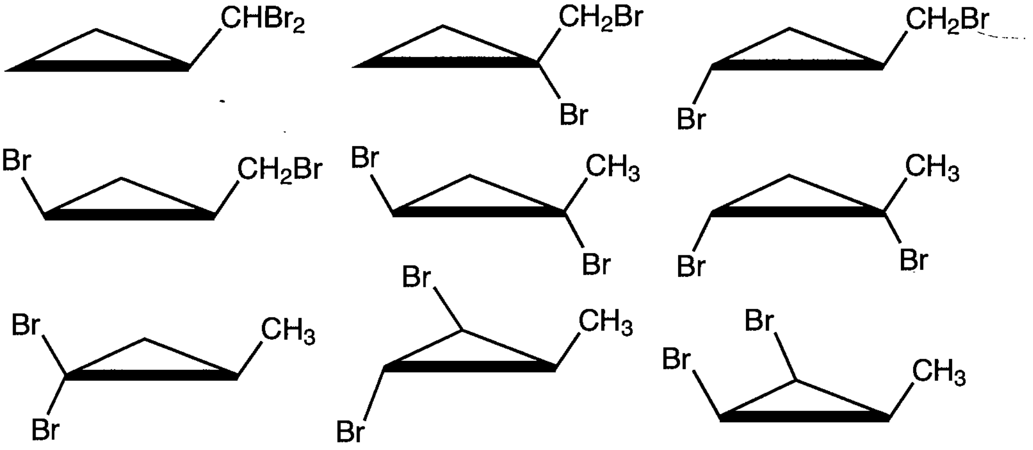
(continued)

Problem 3.47 *(continued)*

There are five possible molecules containing a four-membered ring, but only the indicated isomer has a zero dipole moment.

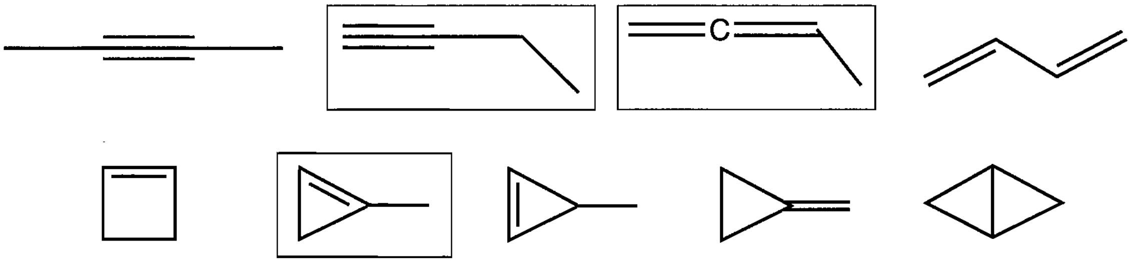


There are nine molecules containing a three-membered ring, but none has a zero dipole moment.



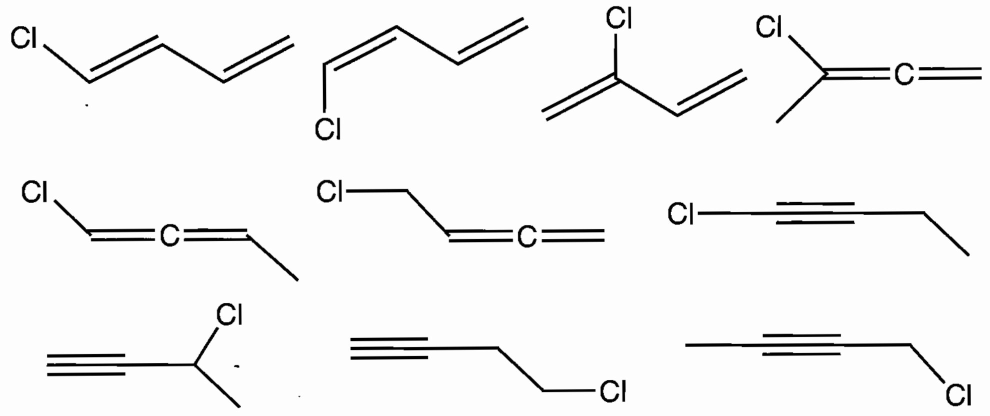
So we find 14 cyclic isomers. It has been claimed (*J. Chem. Educ.* 1992, *69*, 452—an article on finding isomers that is well worth a look) that there are 15. Who's wrong? Well, we were. There is a 15th isomer, and it is an easy one to find. It is the 1,2-dibromo-3-methylcyclopropane with both bromines trans to the methyl group. How we missed it, we don't know. See how hard this "easy" stuff is?

Problem 3.48 The saturated hydrocarbon is C_4H_{10}. The formula is (10 – 6) = 4/2 = 2. There are 2 degrees of unsaturation in this molecule, and so the possible combinations are two rings, one ring and one π bond, and two π bonds. The possible molecules are given below, with the ones with four different carbon atoms in boxes.

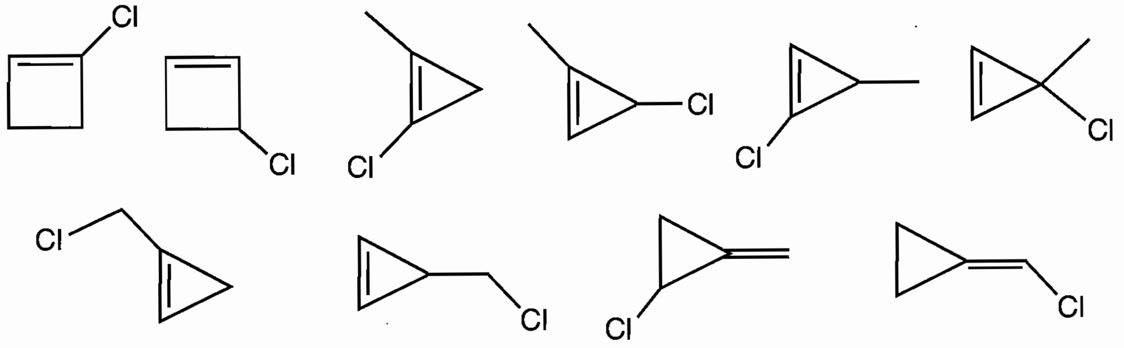


Problem 3.49 First, determine the degrees of unsaturation. The chlorine is univalent and can be treated as a hydrogen, so the related saturated alkane is C_4H_{10}, where (10 – 6) = 4/2 = 2 degrees of unsaturation. You must look for compounds containing two π bonds, one π bond and one ring, or two rings.

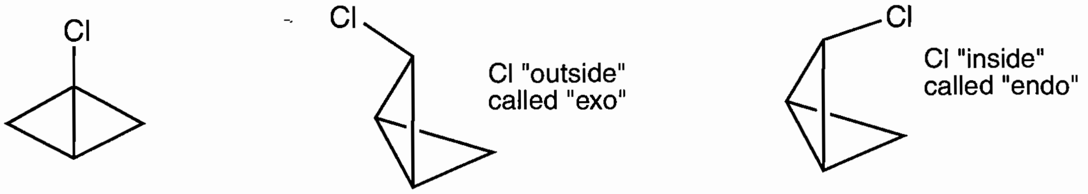
There are 10 isomers containing two π bonds:



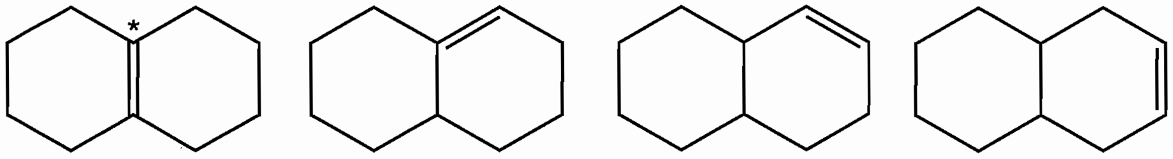
There are also 10 compounds with one ring and one π bond:



Finally, there are three structures containing two rings and no π bonds:

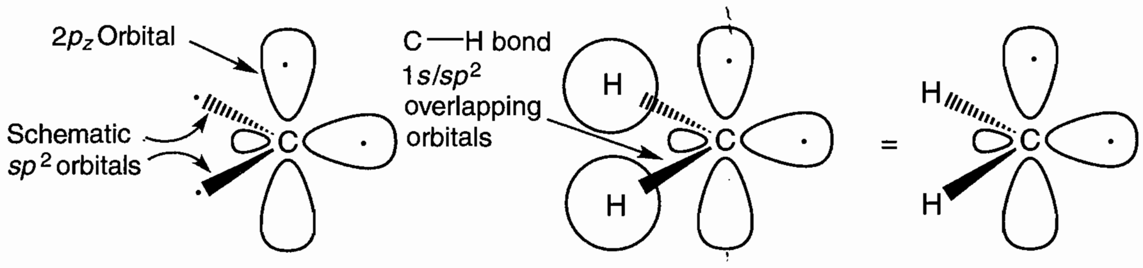


Problem 3.50 The saturated alkane would have 22 hydrogens ($C_{10}H_{22}$). The formula shows that there are 3 degrees of unsaturation in this compound (22 – 16) = 6/2 = 3. If there must be only two rings, and if the rings must be six membered, there must be one π bond. The possibilities are

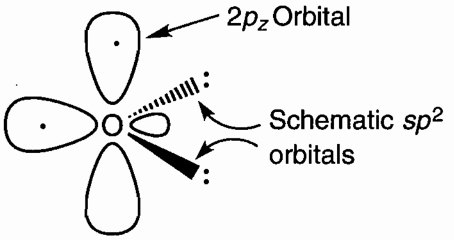


The asterisk shows the one with only three kinds of carbon: the double-bonded carbon and the two different methylenes.

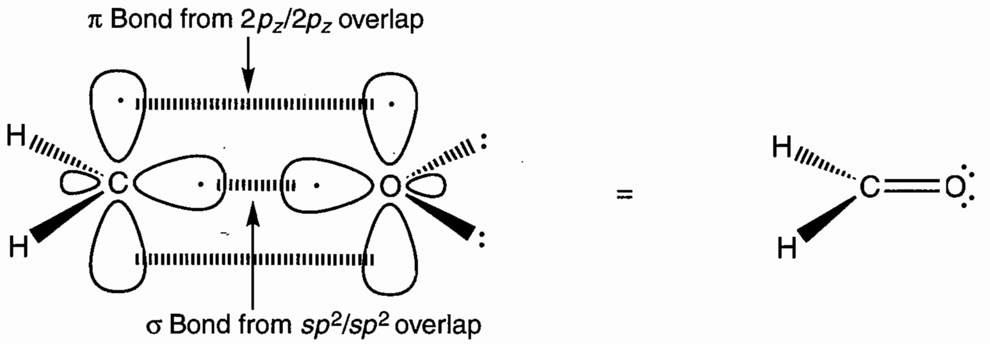
Problem 3.51 An sp^2-hybridized carbon atom is shown. In the figure, two sp^2 hybrids are shown schematically, one coming toward you (solid wedge), the other retreating (dashed wedge). In the first figure, the four valence electrons of carbon are shown as dots, one in each of the three sp^2 hybrids, and one in the unhybridized $2p_z$ orbital. The C—H bonds are shown as overlapping 1*s* and sp^2 orbitals and then as schematic "line" bonds.



An oxygen atom has six valence electrons, and so two of the sp^2 hybrids must be doubly occupied.

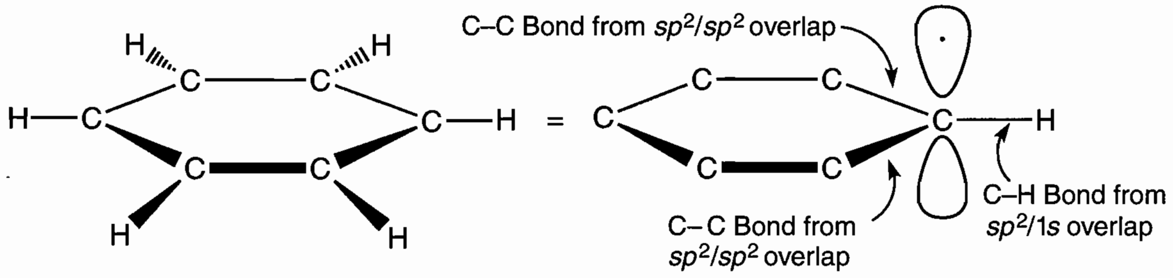


In our scheme, we will form one σ bond through sp^2/sp^2 overlap and a π bond through $2p_z/2p_z$ overlap. Don't forget that these overlapping orbitals produce both a bonding combination (σ and π) and an antibonding combination (σ* and π*). The result is a double bond, σ and π, shown as a pair of identical lines between C and O.

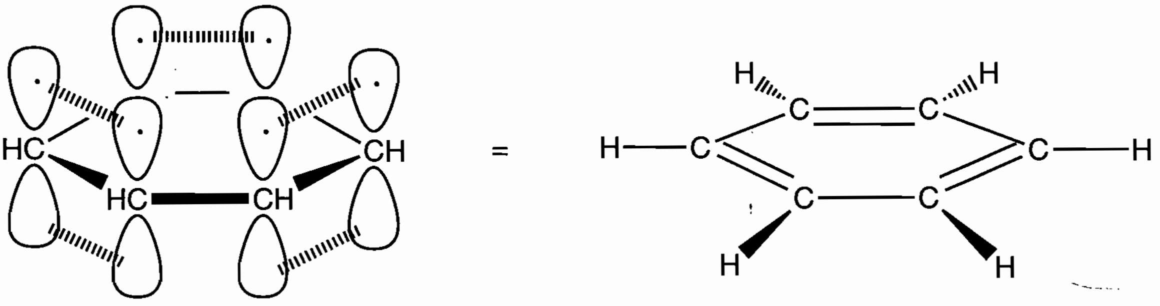


Problem 3.52

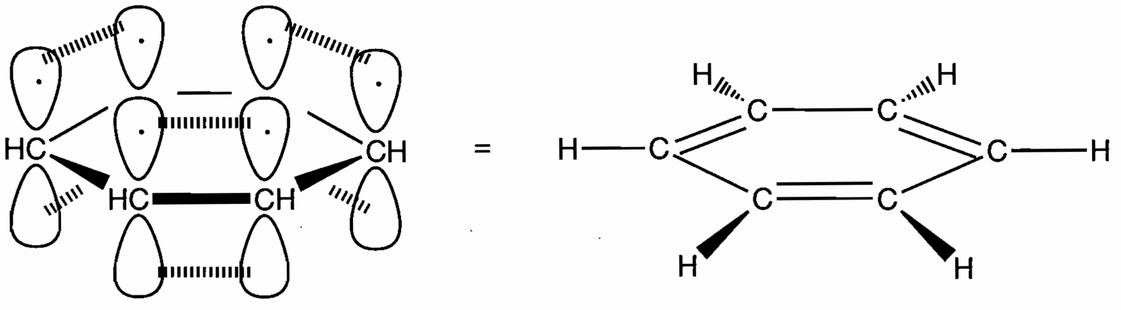
(a) We can use the sp^2 hybrid orbitals to bond to the hydrogen and the two neighboring carbons. The figure first shows the planar six-membered ring with the carbons and hydrogens and then focuses on one sp^2-hybridized carbon and the bonds to it.



Each carbon in the ring is identical, so let's now look at the six singly occupied $2p_z$ orbitals. In the left-hand figure, the lower lobes of the $2p_z$ orbitals on the back two carbons are not shown, and the C—H bonds are not drawn in. In the right-hand figure, we draw in three π bonds made from the usual $2p_z/2p_z$ overlap.



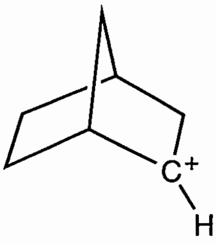
(b) Clearly, if there is only one C—C bond distance in this molecule, there cannot be simple, alternating single and double bonds, which must be different lengths. However, we made an arbitrary decision in the previous figure to let certain $2p_z$ orbitals overlap and ignore others. Why not do it another way? Our second drawing of this molecule is a resonance structure of the drawing in (a).



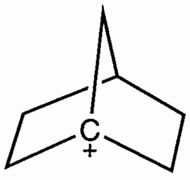
In fact, all the $2p_z$ orbitals are the same and must overlap equally with their right-hand and left-hand neighboring $2p_z$ orbitals. At this point, we can't do too much better than this—just note that there is excellent overlap among these $2p_z$ orbitals above and below the plane of the ring. This molecule is an aromatic ring, which we will discuss in detail in Chapter 14.

Problem 3.53 The two carbocations in question are

(a)



(b)

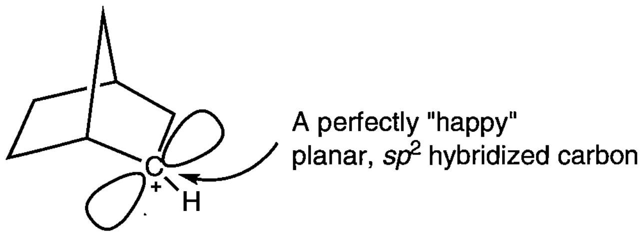


(continued)

Problem 3.53 *(continued)*

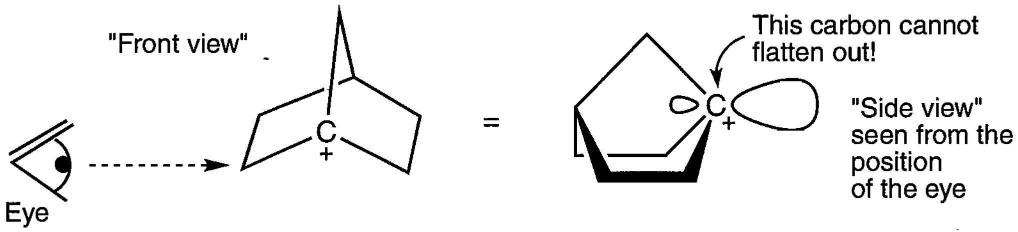
There is no problem accommodating a planar carbocation in (a):

(a)

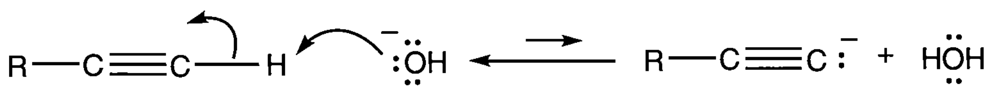


However, the drawing of (b) is harder to see (a model should make everything crystal clear). There is no way to flatten out this molecule at this "bridgehead" position. As carbocations are most stable when planar, this introduces a necessary instability into this cation and makes it difficult to form.

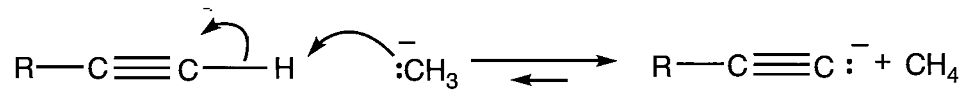
(b)



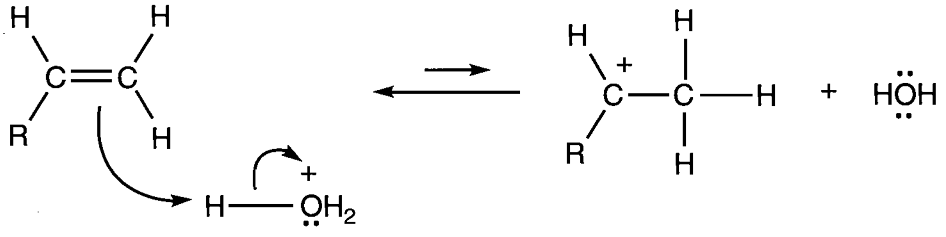
Problem 3.54



The pK_a for the terminal hydrogen of an alkyne is about 25, whereas the pK_a of water is 15.7. Water is a far stronger acid, and therefore the equilibrium lies to the left.

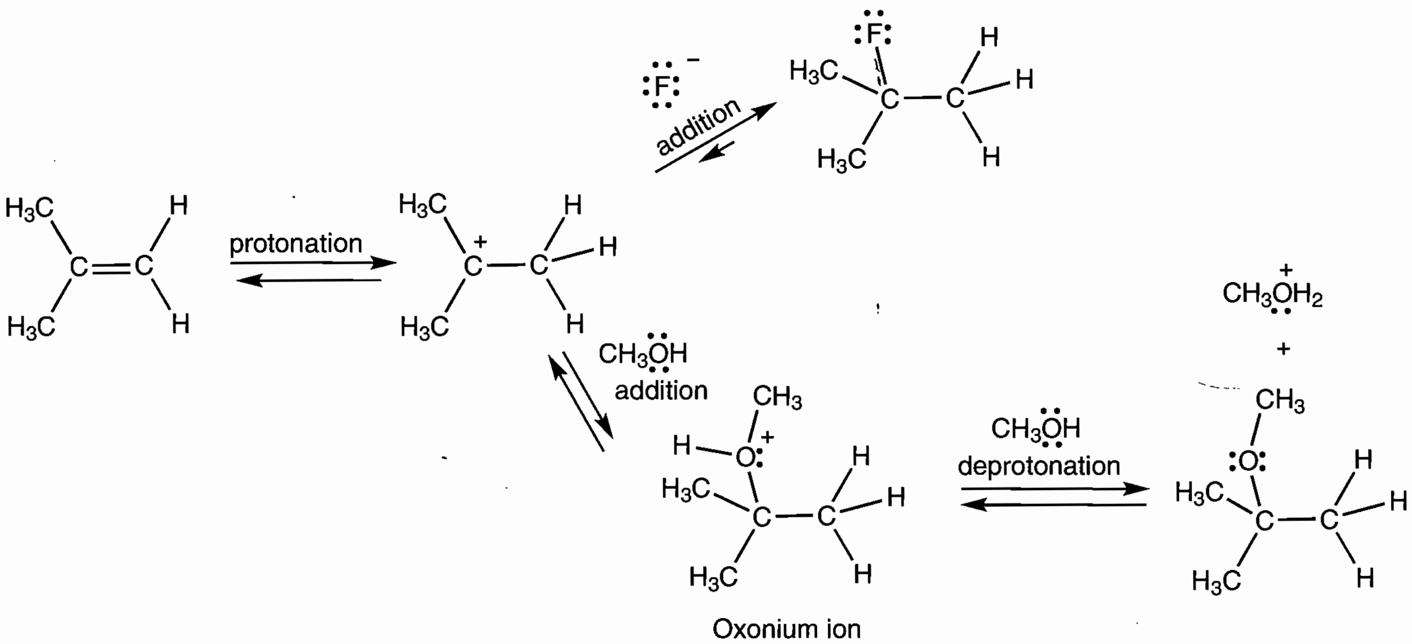


The pK_a for the terminal hydrogen of an alkyne is about 25, whereas the pK_a of methane is at least 60. Methane is a far, far weaker acid, and therefore the equilibrium lies to the right.

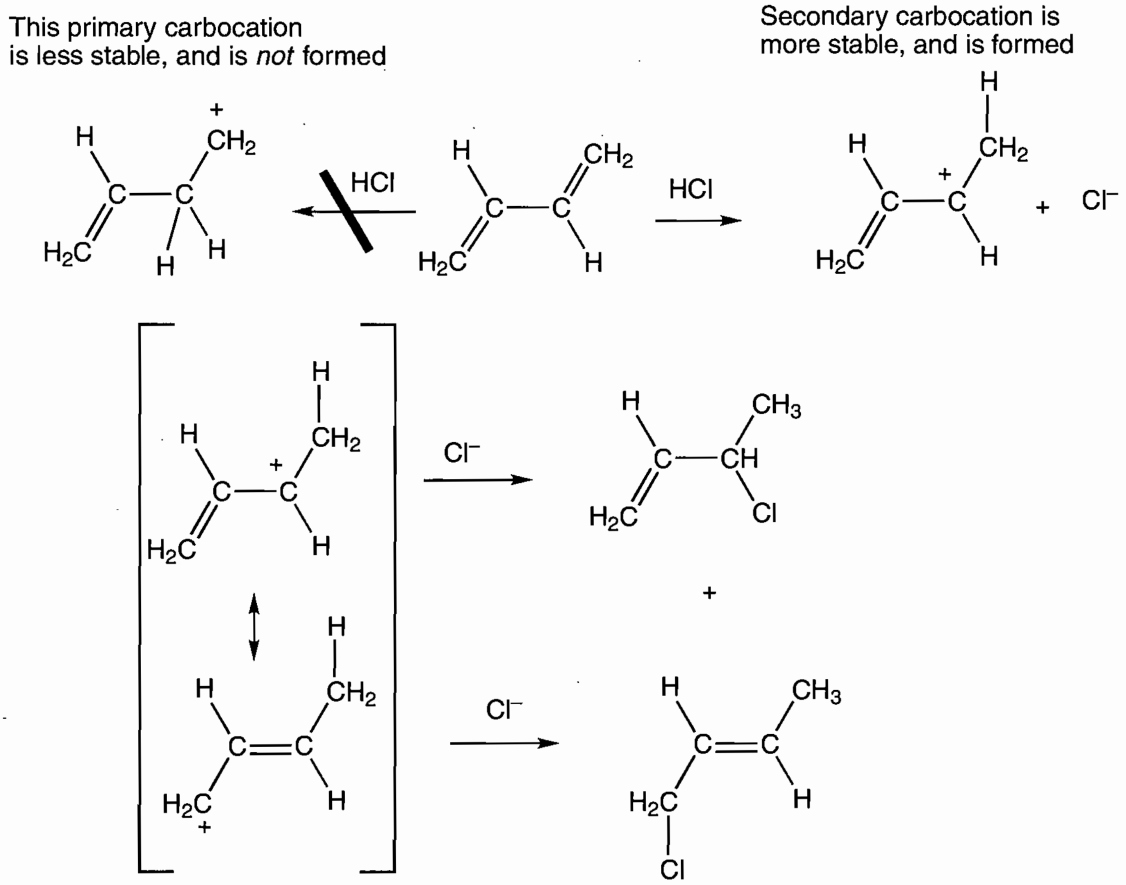


The pK_a for the hydronium ion is about –2. We will see in Chapter 7 that the pK_a of a hydrogen on a carbon adjacent to a carbocation is about –11.

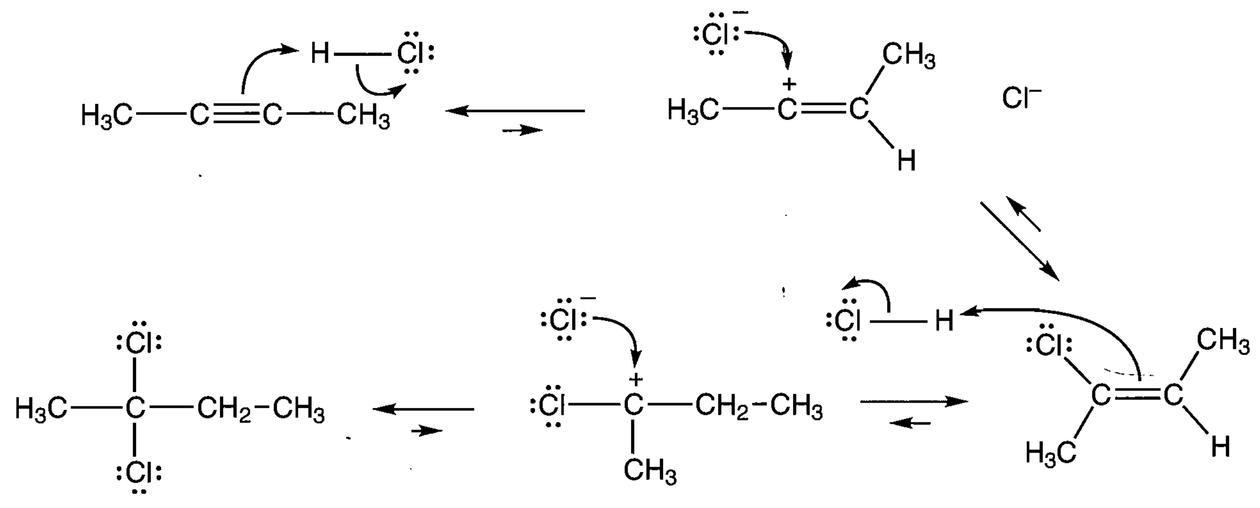
Problem 3.55 Here are two HX additions. Just be careful to get the direction of addition—the regiochemistry—right. Protonation must always occur so as to give the more stable (more substituted) carbocation.



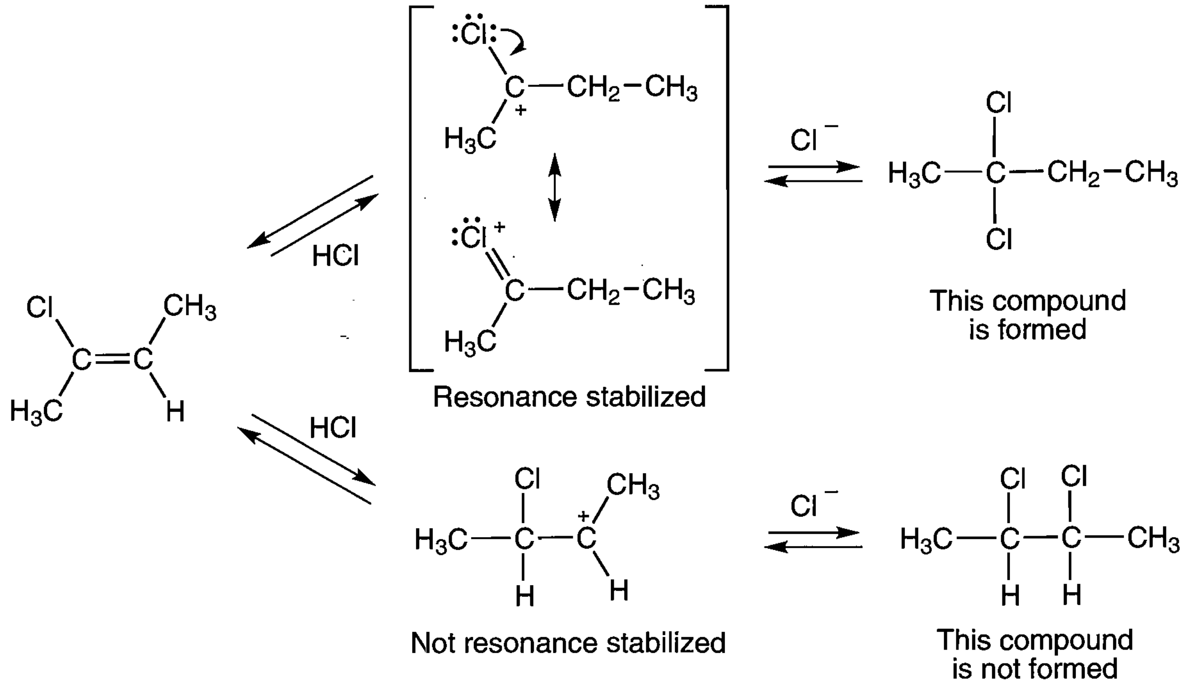
Problem 3.56 Protonation will occur so as to give the resonance-stabilized secondary carbocation, not the hideously unstable primary carbocation. The positive charge in the carbocation is shared by two carbons. The nucleophile (chloride ion here) can add at both of those positive carbons to give the two products.



Problem 3.57 As the starting material is an alkyne, with two π bonds, the initial addition reaction leads to an alkene. Both (*Z*)-2-chloro-2-butene and (*E*)-2-chloro-2-butene would be formed. Only the (*Z*) isomer is shown. A second addition is now possible to give 2,2-dichlorobutane.

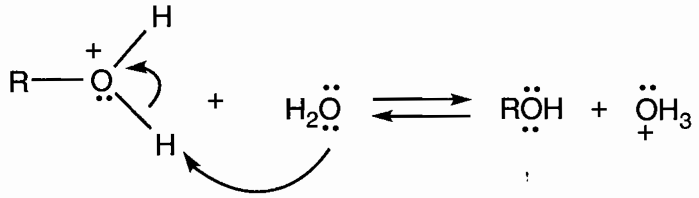


Problem 3.58 Two carbocations are possible when the initial product is protonated. One is far more stable than the other because it is stabilized by resonance. Its formation will be favored, and therefore the final product will come from addition of chloride to it, as shown.

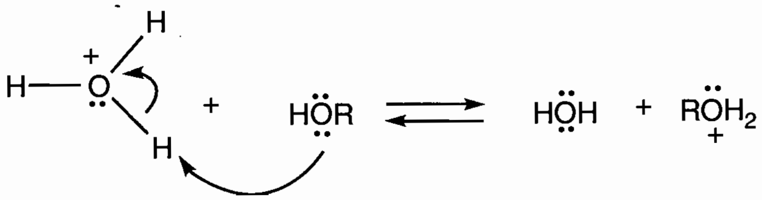


Problem 3.59 The hydrogen perpendicular to the π system is not involved. We call these nonmixing orbitals orthogonal. They don't "see" each other or "talk to" each other. The electrons can't move between the two. The electrons in the bonds to the hydrogens that are perpendicular to the π system are not able to mix with the π system because they are orthogonal to it.

Problem 3.60 The electron pushing for the reaction left to right is

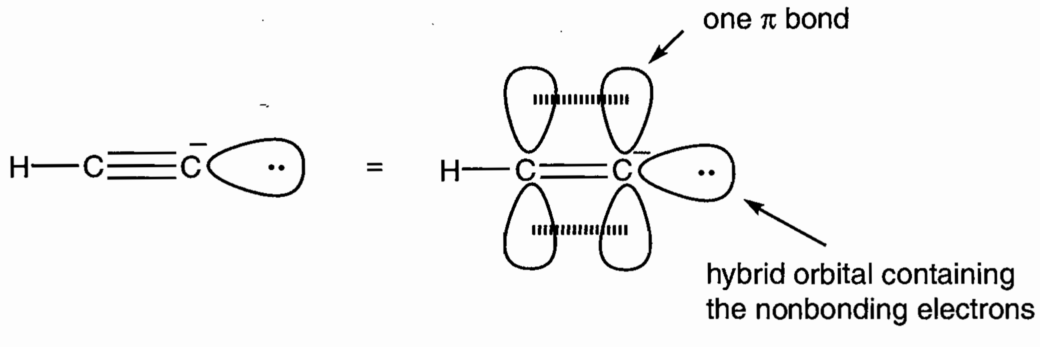


The electron pushing for the reaction from right to left is



The two directions are very similar. The equilibrium constant is nearly 1. The neutral alcohol could be obtained by neutralizing the solution.

Problem 3.61 No, the π orbitals do not mix with the orbital containing the nonbonding electrons of the acetylide anion. The electrons of the carbanion are in an orbital that is orthogonal to the alkyne's π orbitals.



4

Stereochemistry

In this chapter, we deal with the details of molecular structure. There can be no hiding the fact that stereochemistry is difficult for many people, but it will yield to careful work and practice. Moreover, at this point we must reemphasize the idea that you cannot simply read this material and hope to get it. That approach is hopeless—repeat, *hopeless*. In this chapter, we see the consequences of the three-dimensional nature of molecules, and from now on you will have to be able to visualize molecules in three dimensions. Do not trust the two dimensions available to this book, or the blackboard, or a piece of paper.

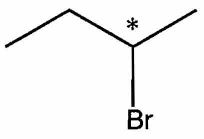
The notion that organic chemistry is to be "read with a pencil" has been emphasized many times, and nowhere is that admonition more appropriate than here. Indeed, you should work through these problems with your models at the ready; there will be many points when they will be helpful or even essential.

Why is stereochemistry so important? Soon we are going to look at reactions in detail and try to work out how and why they proceed in the ways they do. As you will see, stereochemistry plays a huge role in this analysis. Working out the mechanistic details requires an ability to keep the stereochemical nuances of structure in mind. In turn, when we come to organic synthesis, the construction of molecules from simpler starting materials, we will always have to keep stereochemistry in mind. It is not enough to devise a synthesis that builds a molecule with its constituent parts more or less in the right place. They must be exactly right, perfectly positioned. Stereochemical control is vital, and to achieve that, you must understand the subject itself well.

Practice, practice, practice! The following problems, none of them especially difficult, give you a chance to start. Later, more complicated stereochemical analyses will accompany our discussions of many of the mechanisms of organic reactions.

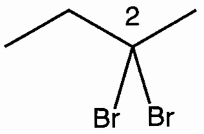
Problem 4.1

(a) Carbon number 2 has four different groups (–H, $-CH_3$, –Br, and $-CH_2CH_3$). There is no plane of symmetry in the molecule. 2-Bromobutane is chiral.



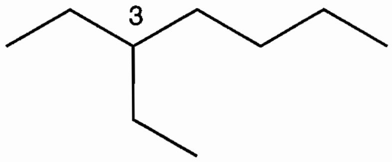
2-Bromobutane

(b) There are no stereogenic atoms. Carbon number 2 has two bromines. 2,2-Dibromobutane is achiral.



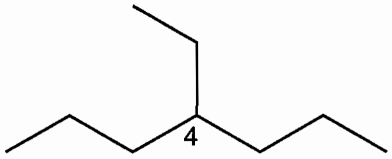
2,2-Dibromobutane

(c) There are no stereogenic atoms. Carbon number 3 has two ethyl groups attached. 3-Ethylheptane is achiral.



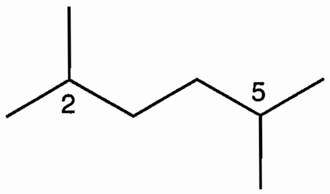
3-Ethylheptane

(d) There are no stereogenic atoms. Carbon number 4 has two propyl groups attached. 4-Ethylheptane is achiral.



4-Ethylheptane

(e) There are no stereogenic atoms. Carbon number 2 has two methyl groups. Carbon number 5 also has two methyl groups. 2,5-Dimethylhexane is achiral.

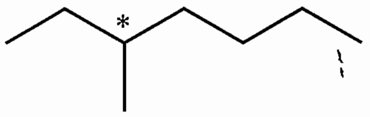


2,5-Dimethylhexane

(continued)

Problem 4.1 *(continued)*

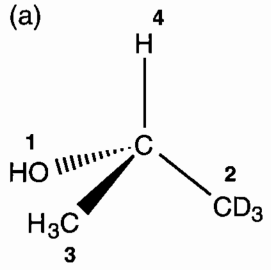
(f) Carbon number 3 has four different groups attached (–H, $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_2CH_3$), and there is no plane of symmetry in the molecule. 3-Methylheptane is chiral.



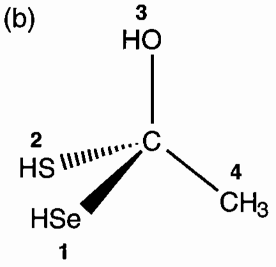
3-Methylheptane

Problem 4.2

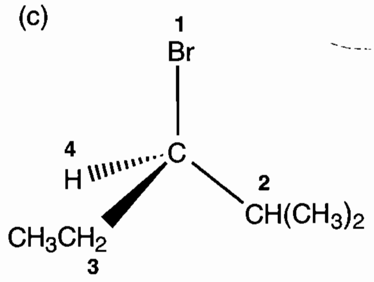
(a)



(b)



(c)

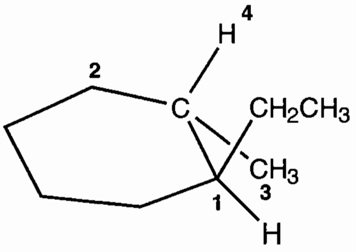


(a) H is **4** and O is **1** on the basis of atomic number. The tie between CH_3 and CD_3 is broken by the greater atomic weight of D over H.

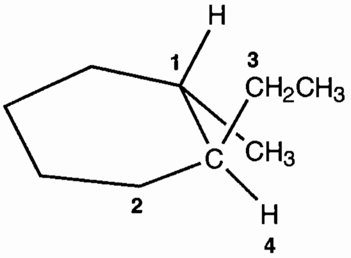
(b) Priorities can be assigned strictly by atomic number.

(c) Atomic number makes H priority **4** and Br priority **1**. The tie between the two carbons is broken by working out along the chain. The ethyl carbon is attached to C, H, H (**3**) and the isopropyl carbon to C, C, H (**2**).

(d) There are two stereogenic carbons in this molecule. For the rear carbon, H is priority **4**, but the other three substituents are carbon. The methyl carbon (attached to H, H, H) is priority **3**, the ring CH_2 group priority **2** (attached to C, H, H), and the other ring carbon **1** (attached to C, C, H). A similar tie-breaking procedure serves to assign priorities to the front carbon.

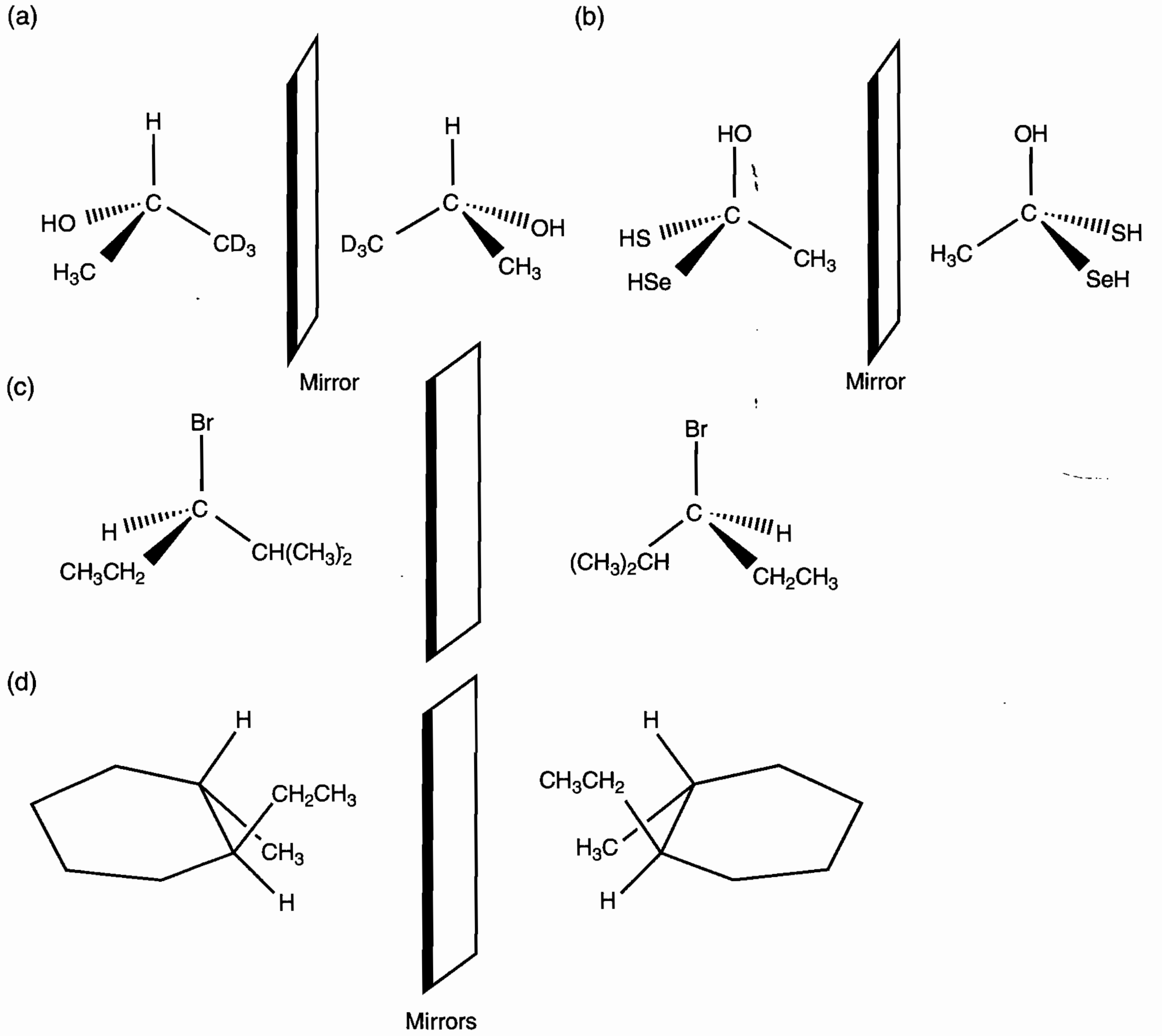


Analysis for C(2) in
1-ethyl-2-methylcycloh exane

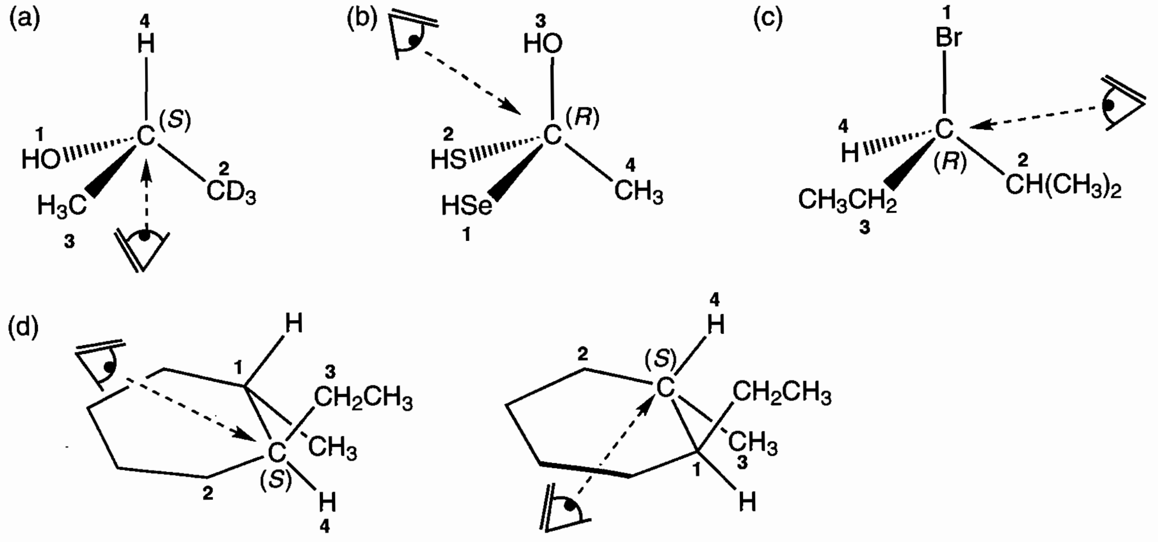


Analysis for C(1) in
1-ethyl-2-methylcycloh exane

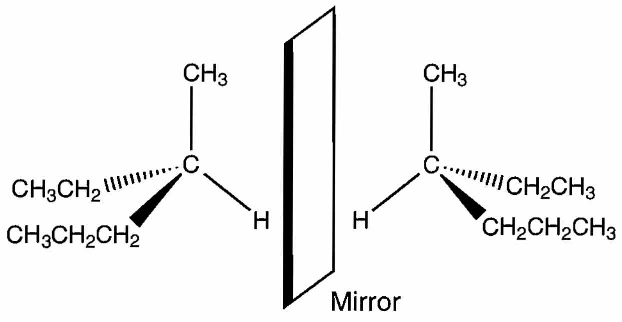
Problem 4.3 This problem may seem easy, even mindless. But watch out! First of all, drawing mirror images requires practice, and ring compounds introduce strange difficulties for many people. It is well worth your time to practice drawing mirror images a bit. Invent some more problems for yourself.

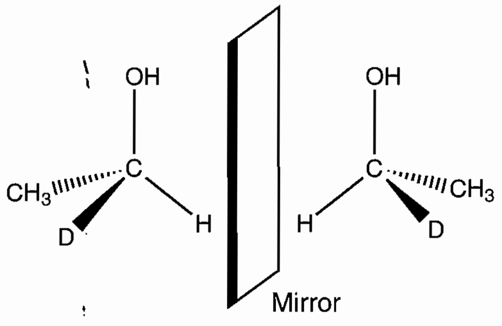


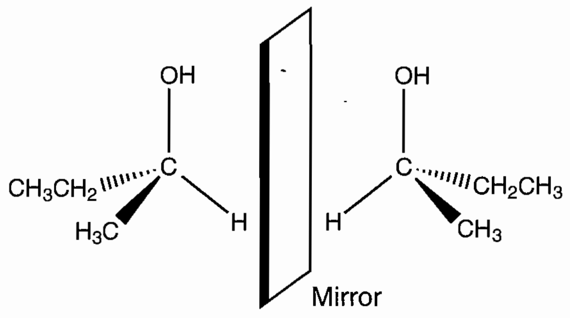
Problem 4.4 Remember, look down the C—priority **4** bond (arrow) and connect the groups **1**→**2**→**3**. The priorities were assigned in the usual way, through the Cahn–Ingold–Prelog protocol.

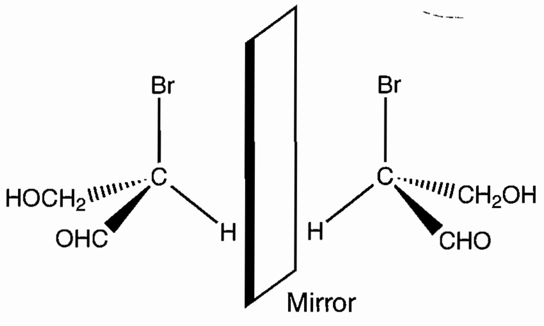


Problem 4.5 Here is more practice in drawing mirror images.









Problem 4.6 First we need to solve for the specific rotation of (*S*)-2-bromobutane. We are told that the observed rotation is + 2.31° for a solution of 10.0 g in 100 mL hexane. That means

$$[\alpha] = \frac{2.31^\circ}{10\text{ g}/100\text{ mL}} = 23.1^\circ$$

So the specific rotation of (*S*)-2-bromobutane is +23.1°. By the way, that means the specific rotation for (*R*)-2-bromobutane is –23.1°.

To determine the measured rotation for a mixture of (*S*) and (*R*) enantiomers, we first need to determine the enantiomeric excess. How much of the (*S*) enantiomer is not canceled out by the (*R*) enantiomer? There are 7.5 g of (*S*) enantiomer and 2.5 g of (*R*) enantiomer. That leaves 5.0 g of (*S*) enantiomer not canceled out by the (*R*). That amount is the enantiomeric excess in this example. Now we can use the same formula to determine the observed rotation for such a solution.

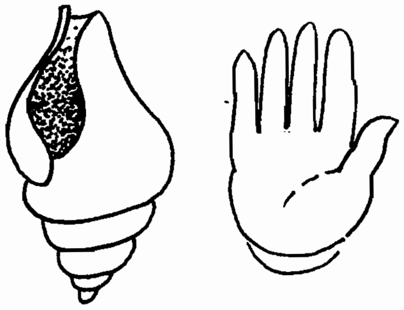
That means

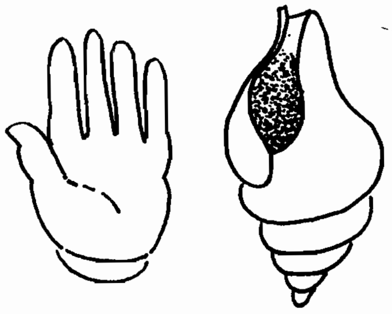
$$23.1^\circ = \frac{\alpha}{5\text{ g}/100\text{ mL}}$$

Solving for α, we find that the measured rotation for this solution is +1.16°.

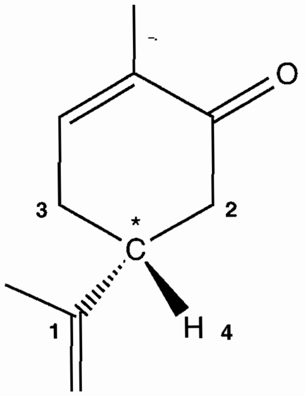
Problem 4.8 Here is an opportunity to look for a plane of symmetry in everyday objects. A chiral object cannot have a plane of symmetry. Here are some likely answers: scissors, knives that are serrated on one side, a refrigerator that has a freezer on top or on bottom, a microwave oven, books (although a book with blank pages might be achiral), a face clock, a calendar, artwork (although there might be some art out there that has a plane of symmetry), gloves that fit one hand but not the other, shoes that fit one foot but not the other, button-up or zipper clothing (shirts, pants, sweaters, coats), a toilet that has a handle on one side, a piano (if the keys are visible), people living in the house (although I suppose it is possible, I have never met an achiral person).

Problem 4.9 Here is the interaction of an inverted shell and a pair of hands. The interactions with the enantiomeric pair of hands are still different. Turning the shell makes no difference whatsoever.

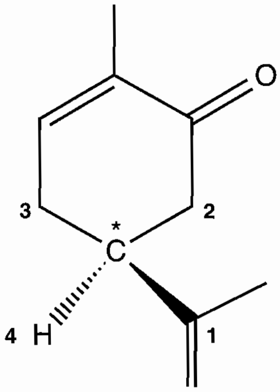




Problem 4.11 This problem is a nuts and bolts question, but, as we have said many times, cyclic systems are sometimes inexplicably difficult. So here is a chance to practice dealing with rings and priority assignment. The priorities are assigned as shown. H is (**4**), and the doubly bonded carbon is (**1**). The C—C—O gets a higher priority (**2**) than the C—C—C (**3**) because of the higher atomic number of oxygen than carbon.

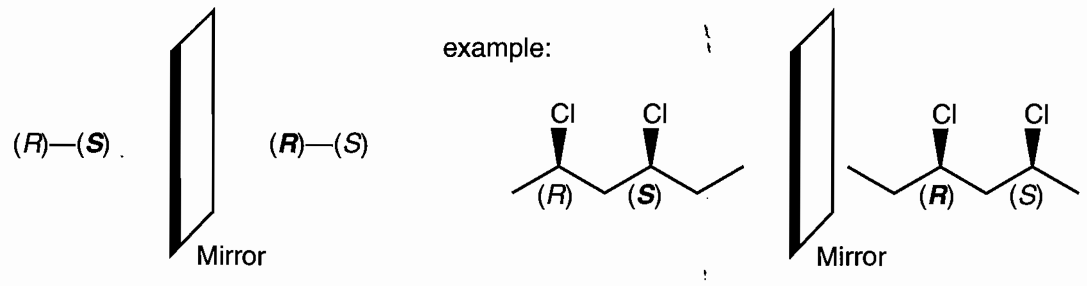


(*R*)-(–)-Carvone

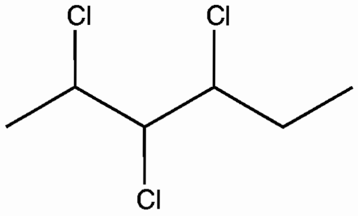


(*S*)-(+)-Carvone

Problem 4.12 Ha! The mirror image of "(*R*)—(***S***)" is "(***R***)—(*S*)." Most people say, too quickly, "(*S*)—(*R*)." The boldface "(***S***)" is reflected as "(***R***)."

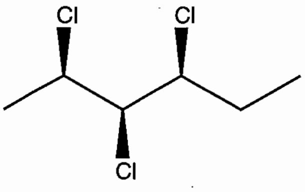


Problem 4.14 You might have drawn a very complex molecule. Or perhaps you drew something like 2,3,4-trichlorohexane.

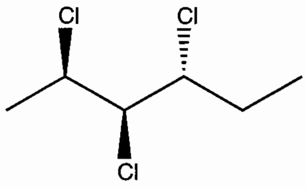


A molecule with three stereogenic carbons can have at most eight stereoisomers. Each stereogenic carbon can be either (*R*) or (*S*). So we have the following possible structures: *RRR*, *RRS*, *RSR*, *SRR*, *RSS*, *SRS*, *SSR*, and *SSS*. The enantiomers are the ones that are exactly opposite. That means that *RRR* and SSS are enantiomers. So are *RRS* and *SSR*; *RSR* and *SRS*; and *SRR* and *RSS*. Any other comparisons are diastereomers. That means *RRR* is a diastereomer of *RRS*, *RSR*, *SRR*, *RSS*, *SRS*, and *SSR*. The *RRS* is a diastereomer of *RRR*, *RRS*, *RSR*, *SRR*, *RSS*, *SRS*, and *SSS*. To make a diastereomer of any molecule with two or more stereogenic carbons, you need to change at least one but not all of the stereocenters.

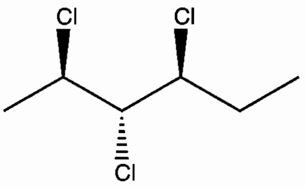
If we look at our 2,3,4-trichlorohexane, we can easily draw two diastereomers.



(2*R*,3*S*,4*S*)-2,3,4-Trichlorohexane

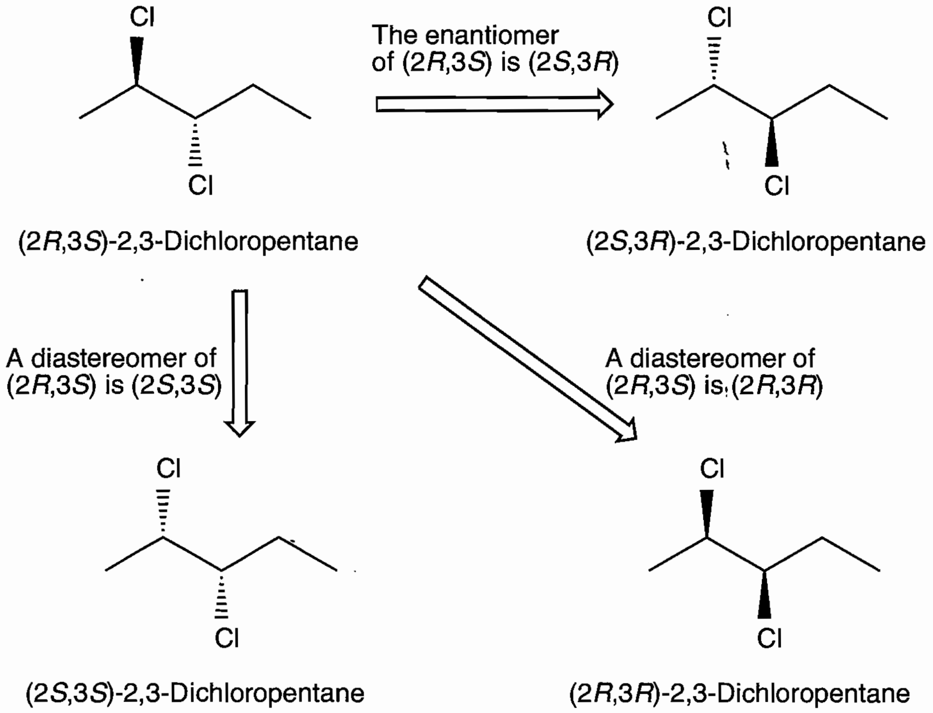


(2*R*,3*S*,4*R*)-2,3,4-Trichlorohexane

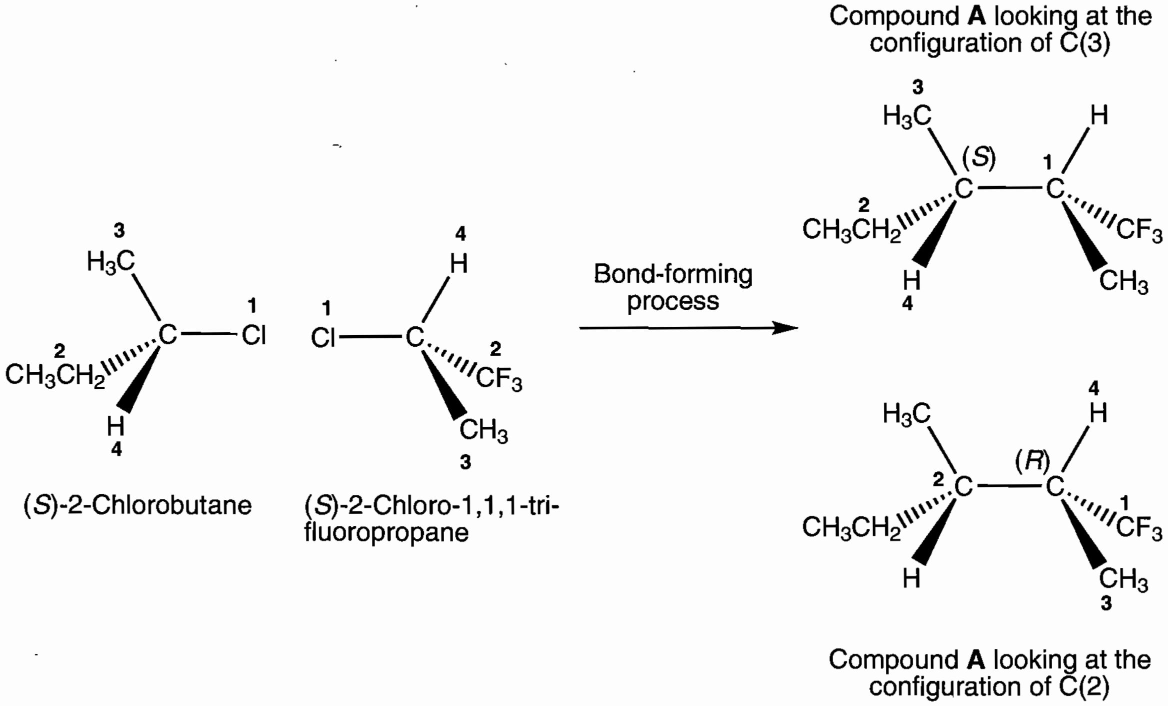


(2*R*,3*R*,4*S*)-2,3,4-Trichlorohexane

Problem 4.15

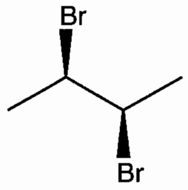


Problem 4.16 There is no problem here. The designations "(*S*)" and "(*R*)" come from the *individual priority* assignments for the two stereogenic carbons in **A**. In the hypothetical bond-forming process we have developed, the right-hand carbon comes from (*S*)-2-chloro-1,1,1-trifluoropropane, in which it is the Cl that is priority **1**. In the new compound, **A**, this chlorine is no longer there. Now the priority **1** is the trifluoromethyl group, and a proper priority count shows that the right-hand carbon is "(*R*)."

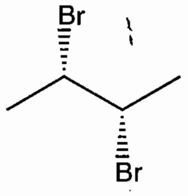


Problems 4.17 and 4.19 The stereoisomers of 2,3-dibromobutane can be determined by drawing all possible structures and checking to see if there are any duplications. There are two stereogenic carbons, so we need to draw the (*R*,*R*), (*S*,*S*), (*R*,*S*), and (*S*,*R*) structures.

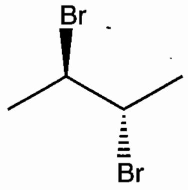
(a)



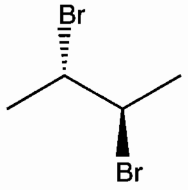
(2*R*,3*R*)-2,3-Dibromobutane
chiral



(2*S*,3*S*)-2,3-Dibromobutane
chiral

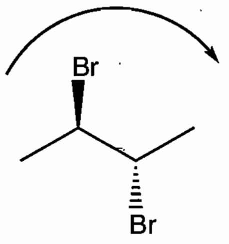


(2*R*,3*S*)-2,3-Dibromobutane
achiral

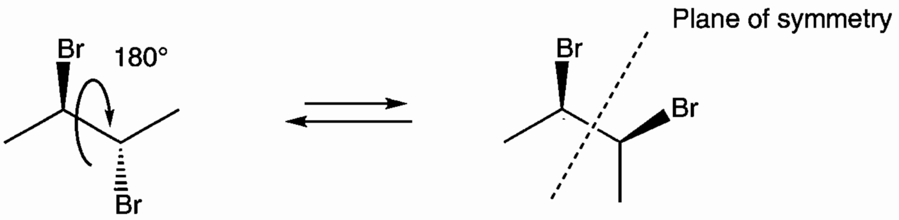


(2*S*,3*R*)-2,3-Dibromobutane
achiral

These two molecules are the same. Rotate the molecule on the left 180° in the plane of the paper as indicated below and you get the molecule on the right

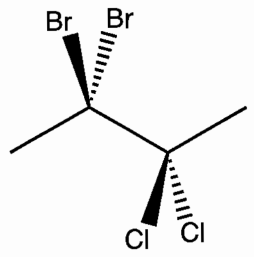


(2*R*,3*S*)-2,3-Dibromobutane is a meso molecule. It is easier to see that it is meso by rotating the C(2)—C(3) bond 180° to the eclipsed conformation. We can now see the plane of symmetry in the molecule.

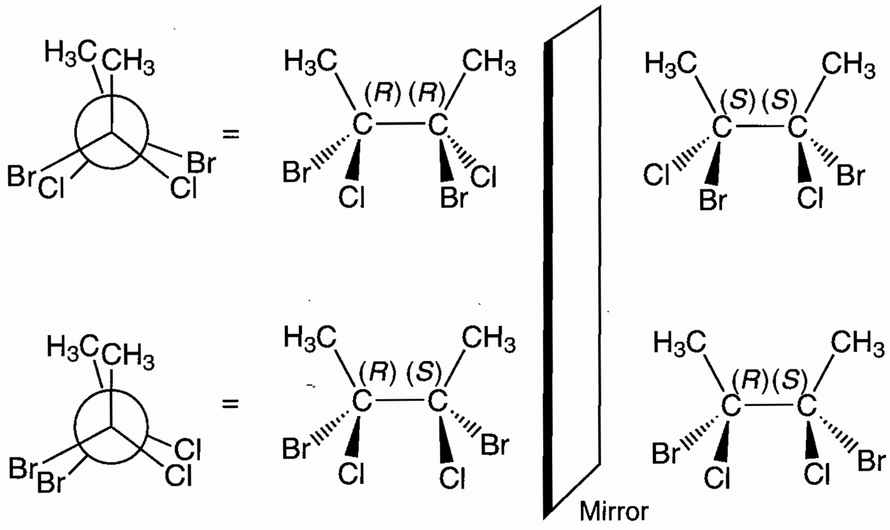


meso-2,3-Dibromobutane

(b) 2,2-Dibromo-3,3-dichlorobutane has no stereogenic carbons. There is a plane of symmetry in the molecule, which is the plane of the paper. The molecule is achiral and has no stereoisomers.



(c) 2,3-Dibromo-2,3-dichlorobutane has three stereoisomers—a pair of enantiomers and a meso compound. Priorities are assigned in the usual way.



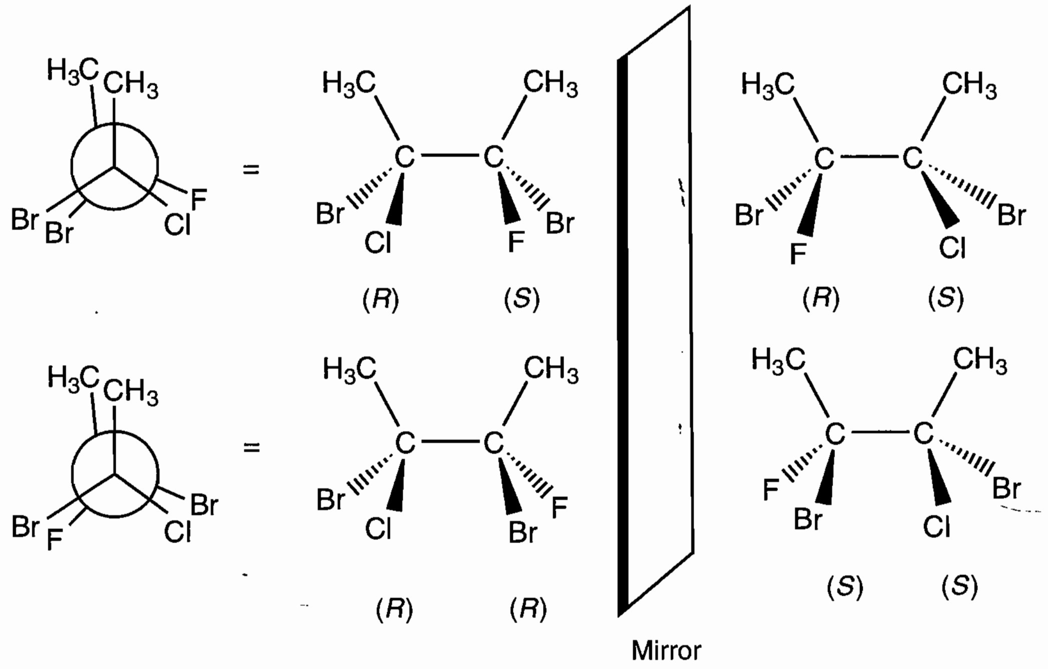
These isomers are enantiomers; the mirror image is not superimposable on the original

This molecule is a meso compound as the mirror image is superimposable on the original

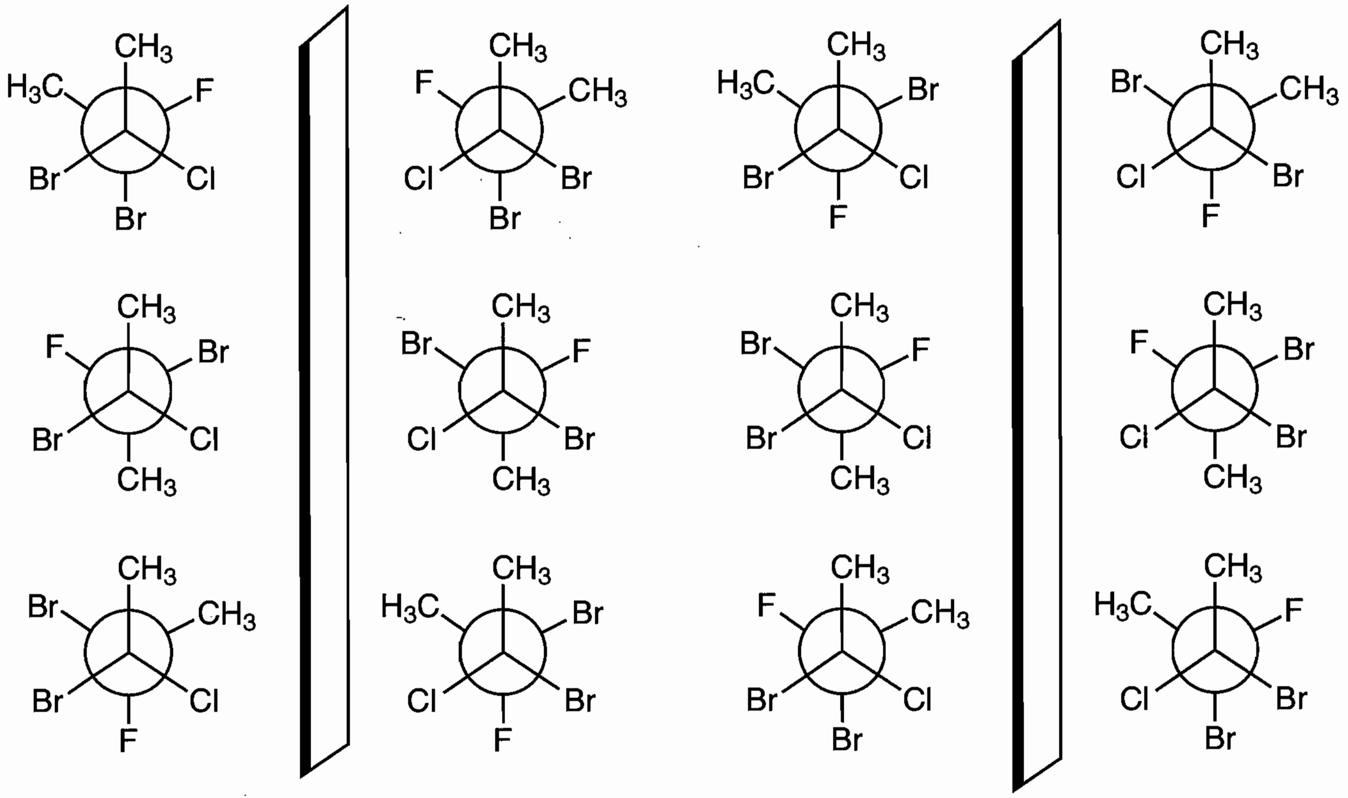
(d) This molecule contains stereogenic carbons and yields the full complement of $2^2 = 4$ stereoisomers. The molecules are shown in eclipsed forms for clarity and ease of analysis, but these are not the minimum energy arrangements, which will have staggered bonds.

(continued)

Problems 4.17 and 4.19 *(continued)*

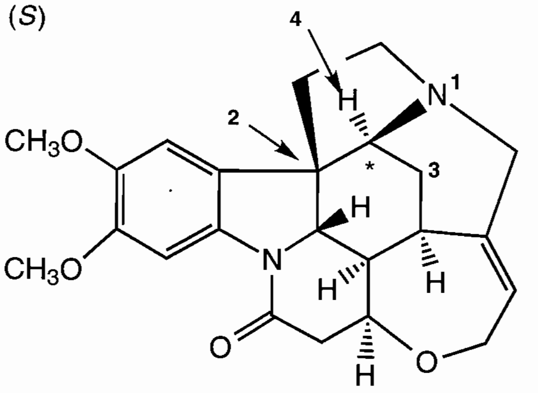


Problem 4.18 If rotational barriers were high, then each staggered form would be isolable. The number of isomers increases dramatically, as each isolable staggered form will have an enantiomer. Now there are 12 total isomers, in six pairs of enantiomers. The answer is given in Newman projections.

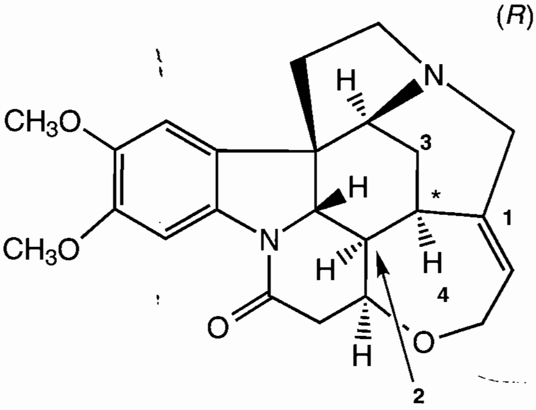


Problem 4.21 The (*R*) and (*S*) designations are assigned from the following priorities:

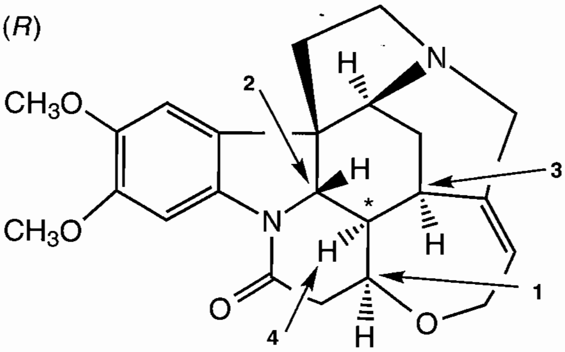
(*S*)



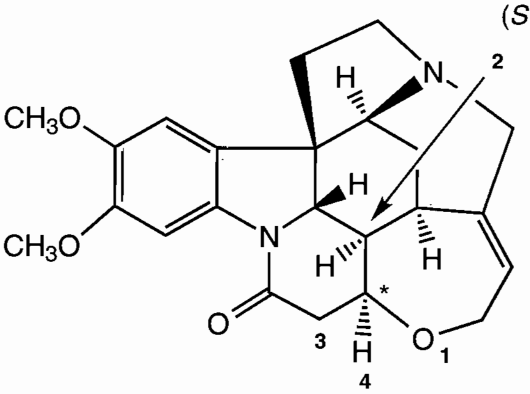
(*R*)



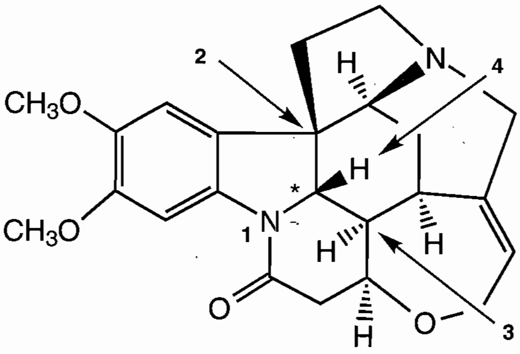
(*R*)



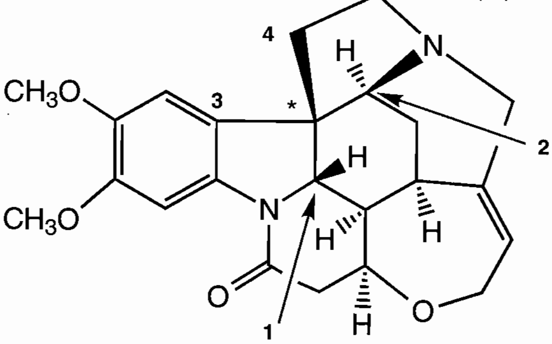
(*S*)



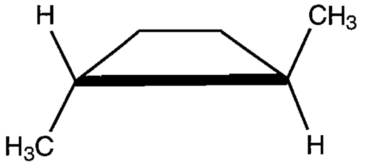
(*S*)



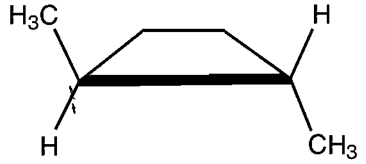
(*R*)



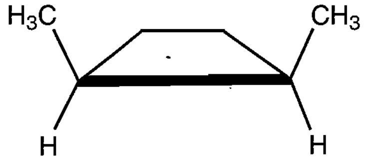
Problem 4.22



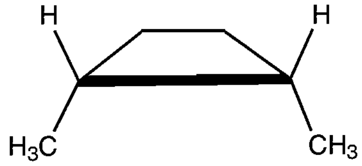
(1*R*,2*R*)-1,2-Dimethylcyclobutane
chiral



(1*S*,2*S*)-1,2-Dimethylcyclobutane
chiral



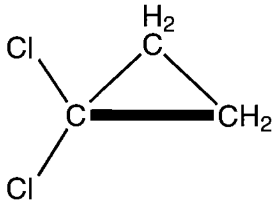
(1*S*,2*R*)-1,2-Dimethylcyclobutane
achiral



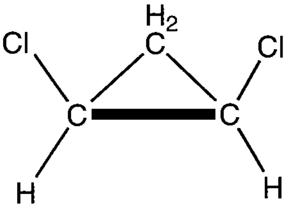
(1*R*,2*S*)-1,2-Dimethylcyclobutane
achiral

These two molecules are the same. Take the structure on the left and flip it over. It is the same as the structure on the right. This molecule can be adequately described as *cis*-1,2-dimethylcyclobutane. It is also meso.

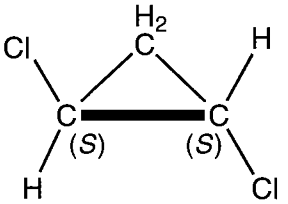
Problem 4.23



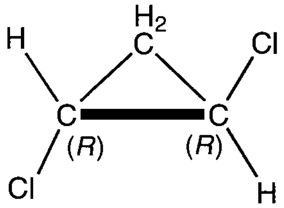
A



B



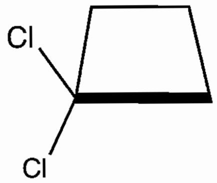
C

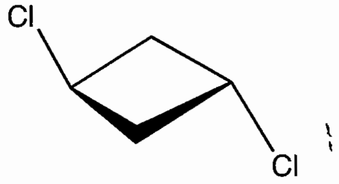


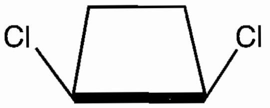
C'

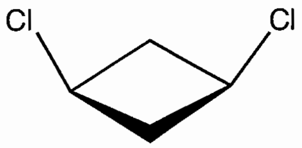
Compound **A** is a structural isomer of **B**, **C**, and **C**′. Compounds **C** and **C**′ are enantiomers; **B** and **C** and **B** and **C**′ are pairs of diastereomers.

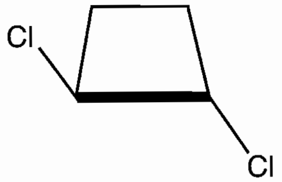
Problem 4.24

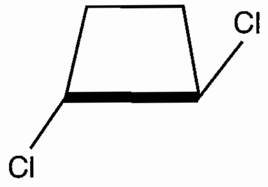

1,1-Dichlorocyclobutane


trans-1,3-Dichlorocyclobutane

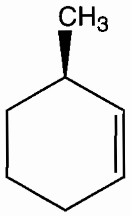

cis-1,2-Dichlorocyclobutane

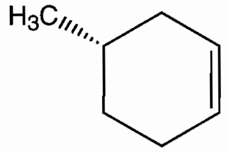

cis-1,3-Dichlorocyclobutane


trans-1(*S*),2(*S*)-Dichlorocyclobutane

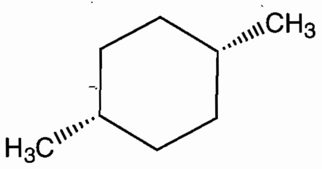

trans-1(*R*),2(*R*)-Dichlorocyclobutane

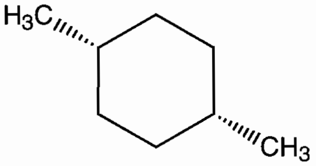
Problem 4.25


(*R*)-3-Methylcyclohexene


(*S*)-4-Methylcyclohexene

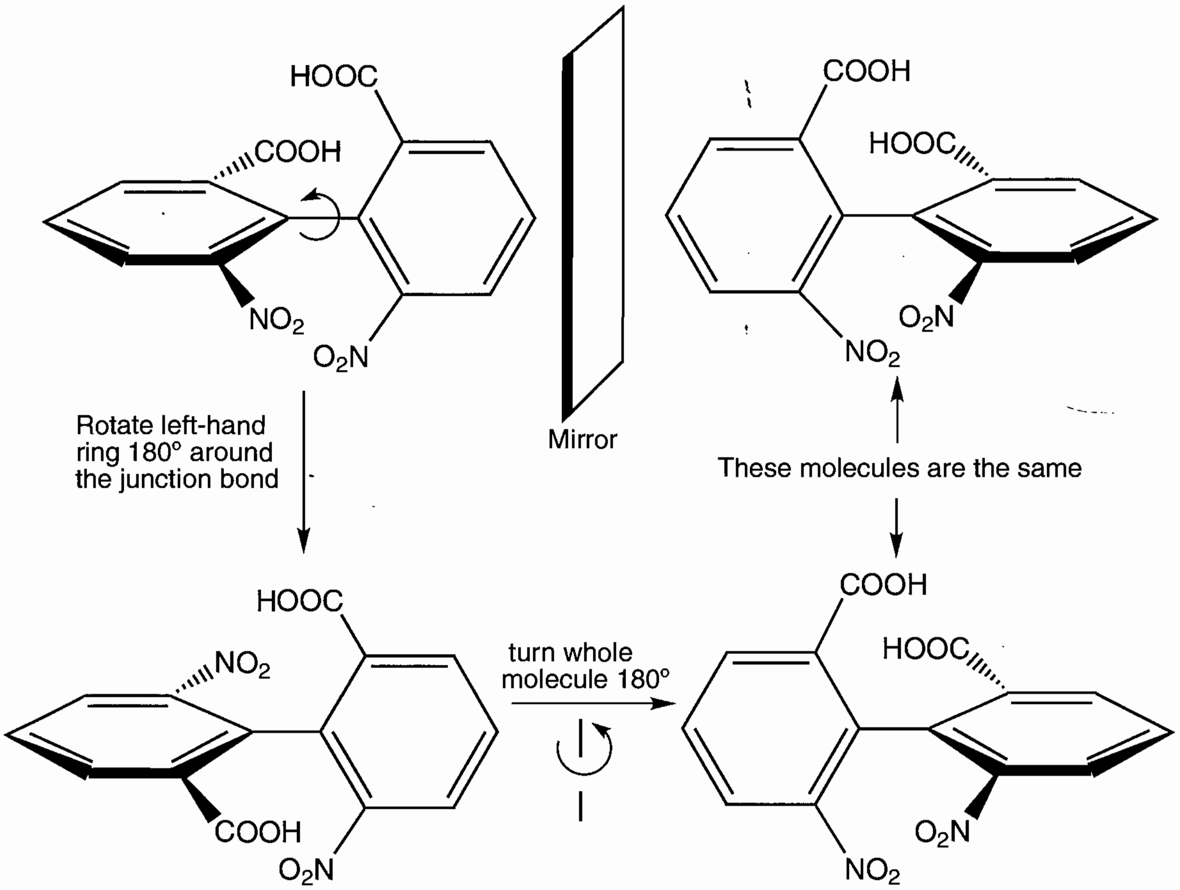
(*R*)-3-Methylcyclohexene and (*S*)-4-methylcyclohexene have the same molecular formula (C_7H_{12}). But they do not have all connections to the same atoms: one is a 3-methyl and the other is a 4-methyl. These molecules are constitutional isomers.


cis-1,4-Dimethylcyclohexene
A

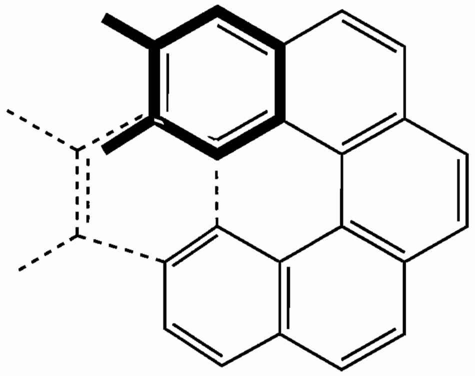

B

Question 1: **A** and **B** have the same molecular formula.
Question 2: All the connections are to the same atoms.
Question 3: Compounds **A** and **B** are superimposable. These molecules are identical. There is no stereogenic atom, so the molecule is not meso.

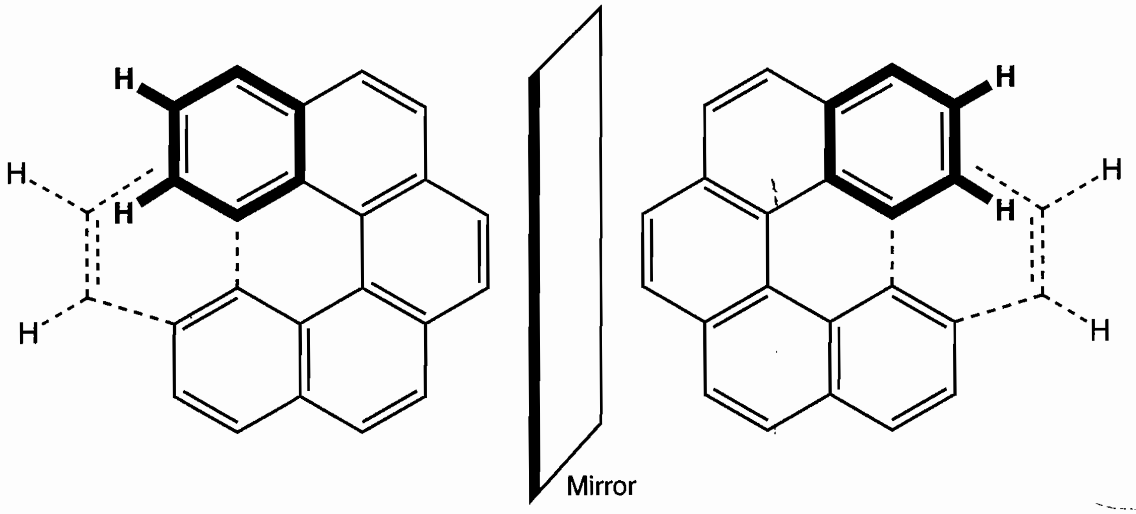
Problem 4.30



Problem 4.31 Were hexahelicene to be planar, the atoms of the "end" rings would have to occupy the same space. Accordingly, one ring (dark lines) slips over the other (dotted lines). A coil or helix is formed.

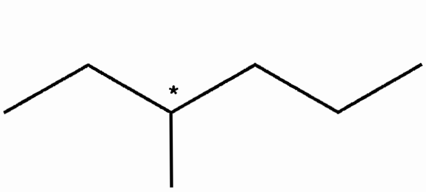


Helices are chiral and can spiral in a right-handed or left-handed way. The right-handed helix and the left-handed helix are nonsuperimposable mirror images:

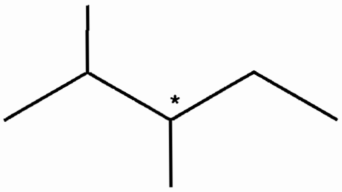


Additional Problem Answers

Problem 4.32 This one is not bad at all; there are only two.



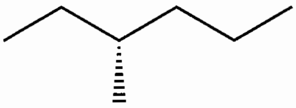
3-Methylhexane



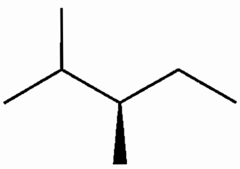
2,3-Dimethylpentane

Problem 4.33

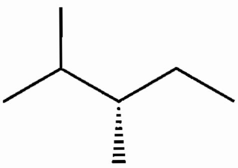
(*S*)-3-Methylhexane



(*R*)-3-Methylhexane



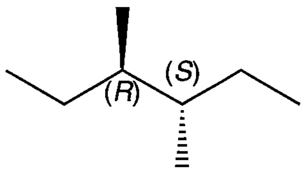
(*R*)-2,3-Dimethylpentane



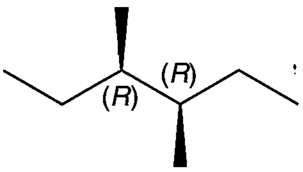
(*S*)-2,3-Dimethylpentane

Problems 4.34 To be a meso compound, there must be at least two stereogenic carbons in the octane isomer. Therefore, the molecule must be a dimethyl isomer. There are no diethyl isomers possible (try drawing them). The only trimethyl isomer with a plane of symmetry is the 2,3,4-trimethylpentane. But it cannot be meso because it has no stereogenic carbons.

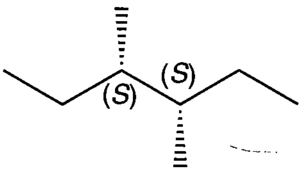
The dimethyl-containing isomer of octane that has potential for being meso is 3,4-dimethylhexane. The meso isomer is the (*R*,*S*) version. The (*R*,*R*) and the (*S*,*S*) are chiral and have no plane of symmetry. Build the model, if you need to be convinced.



meso-3,4-Dimethylhexane
achiral

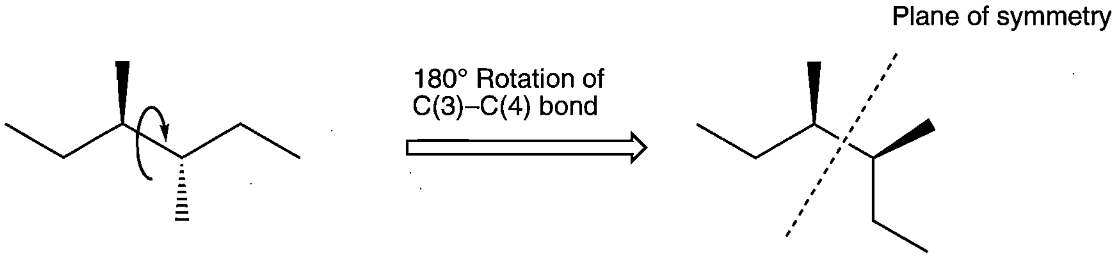


(*R*,*R*)-3,4-Dimethylhexane
chiral



(*S*,*S*)-3,4-Dimethylhexane
chiral

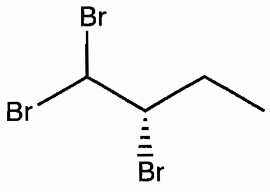
The (*R*,*S*)-dimethylhexane is meso because it is a molecule with stereogenic carbons and it has a plane of symmetry. It is achiral. To see the plane of symmetry, you need to rotate the C(3)—C(4) bond by 180°, as shown.



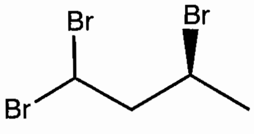
Problem 4.35 There's no big trick to this problem. You have three bromines to locate on a 4-carbon chain. Think of all the possible attachments in an orderly fashion. We could have all the bromines on the same carbon to give 1,1,1 (it's achiral). All three bromines on the other end of the butane gives 4,4,4, which is actually 1,1,1-tribromobutane again.

Now move one bromine to another carbon to give 1,1,2 (chiral), then 1,1,3 (chiral), then 1,1,4 (achiral). We could have two bromines on carbon number 2 to give 1,2,2 (achiral), and two bromines on carbon number 3 is 1,3,3, which is actually 2,2,1 using lowest numbers (achiral), and 1,4,4, which is actually 1,1,4 (achiral). The only other isomer that has two bromines on one carbon is 2,2,3 (chiral).

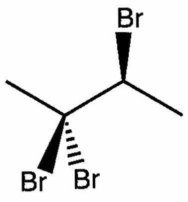
We can now consider the isomers that have bromines on three different carbons. That gives us 1,2,3 (chiral) and 1,2,4 (chiral). That gives us the five isomers that are chiral.



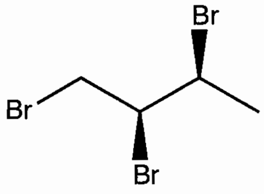
(*S*)-1,1,2-Tribromobutane



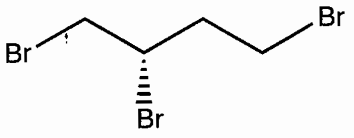
(*S*)-1,1,3-Tribromobutane



(*S*)-2,2,3-Tribromobutane

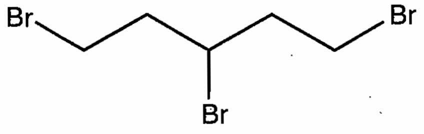


(2*S*,3*S*)-1,2,3-Tribromobutane
Note that there are two stereogenic
carbons in this isomer.

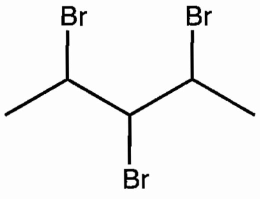


(*S*)-1,2,4-Tribromobutane

Problem 4.36 Drawing one meso molecule shouldn't be too hard. To be meso, the molecule must have stereogenic carbons and a plane of symmetry. That means one of the bromines must be on the central carbon. We can't have a plane of symmetry with two bromines on one side and one on the other. The only symmetrical options are 1,3,5-tribromopentane and 2,3,4-tribromopentane. As you can see, 1,3,5-tribromopentane has no stereogenic carbons. The 2,3,4-tribromopentane can be meso. Where is the second meso compound?

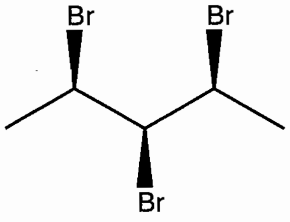


1,3,5-Tribromopentane
achiral

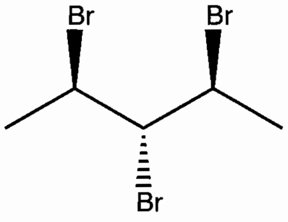


2,3,4-Tribromopentane
meso

Finding the two meso molecules is a tougher challenge. To be meso, the bromines on carbons number 2 and number 4 must be both out (or both back). But the bromine on the central carbon can be either direction. It can be coming out or going back. And that gives us the two meso isomers!



meso-2,3,4-Tribromopentane



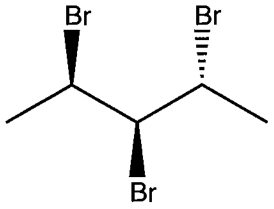
meso-2,3,4-Tribromopentane

(continued)

Problem 4.36 *(continued)*

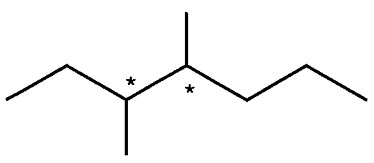
We aren't through. We are asked to determine the number of stereogenic carbons for each isomer. It's tempting to say two for each, but that isn't quite correct. This is really an advanced organic chemistry question. So feeling challenged at this point is totally allowed. The carbons number 2 and number 4 in both isomers are stereogenic carbons. That much you should know. Carbon number 3 in both isomers is also a stereogenic carbon. Look at the molecule with all three bromines coming out of the plane of the paper. The group to the left of carbon number 3 has the (*R*) configuration and the group on the right of carbon number 3 has the (*S*) configuration. They are different groups. To determine the (*R*) and (*S*) configuration of carbon number 3, we give the (*R*) stereochemistry priority over the (*S*). Therefore the molecule on the left is (2*R*,3*R*,4*S*)-2,3,4-tribromopentane. The molecule on the right is (2*R*,3*S*,4*S*)-2,3,4-tribromopentane. Both molecules have three stereogenic carbons.

You might have guessed that the following isomer is chiral (not meso) and it has only two stereogenic carbons!

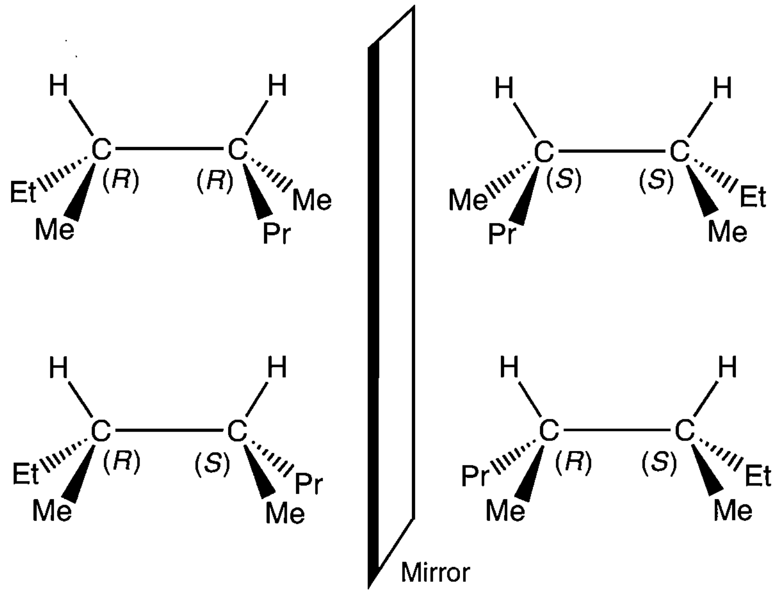


(2*R*,4*R*)-2,3,4-Tribromopentane

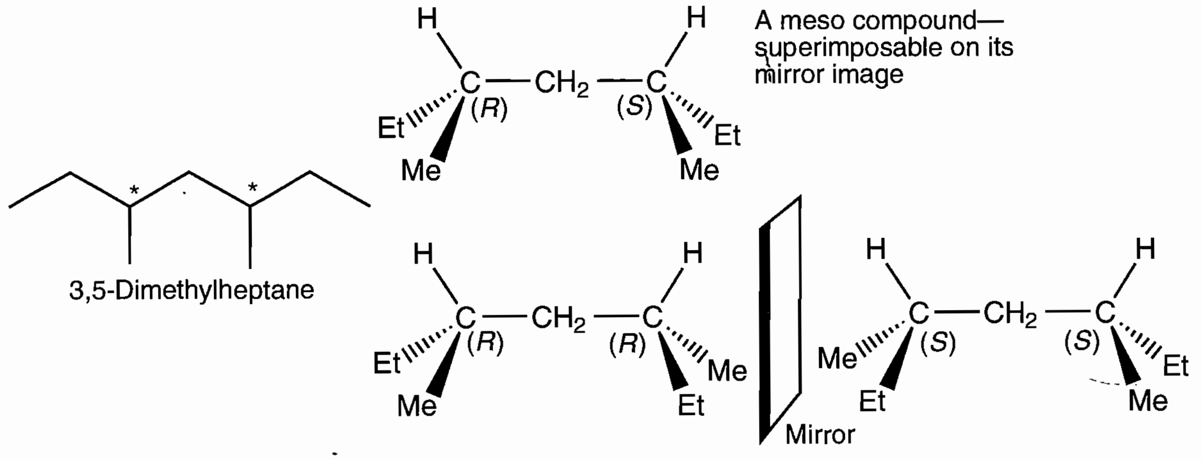
Problem 4.37 3,4-Dimethylheptane has two stereogenic carbons, so the maximum number of stereoisomers is $2^2 = 4$. These appear as two pairs of enantiomers. Me = methyl, Et = ethyl, and Pr = propyl.



3,4-Dimethylheptane



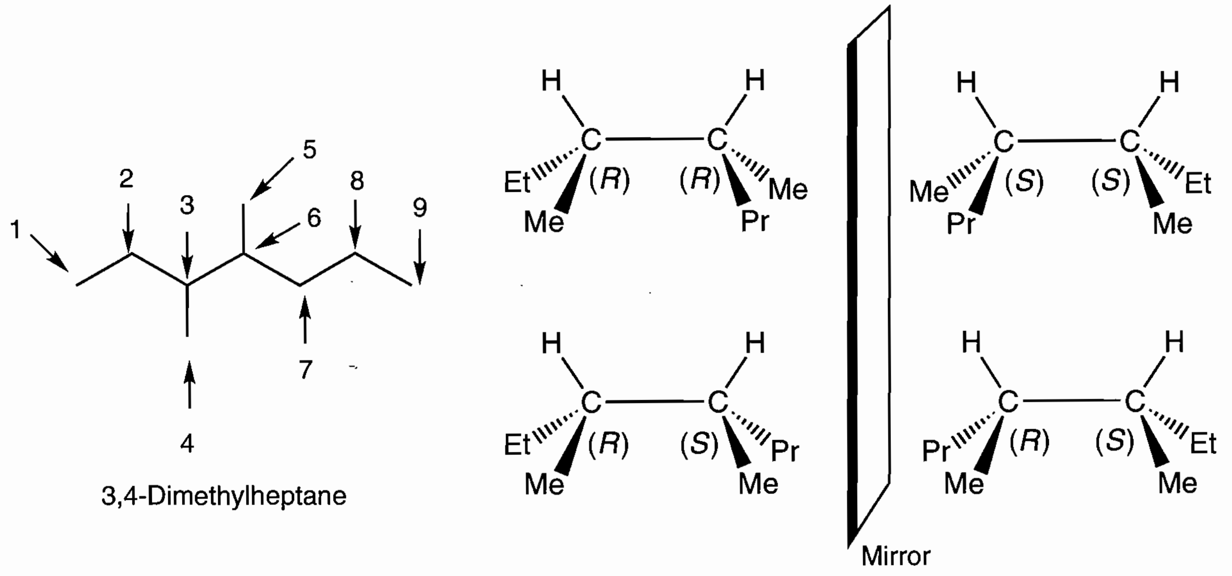
3,5-Dimethylheptane also has two stereogenic carbons, but there is a plane of symmetry in this molecule, and there are only three stereoisomers: one pair of enantiomers and a meso compound.



3,5-Dimethylheptane

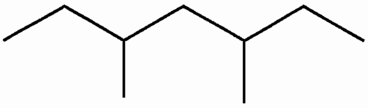
A meso compound—superimposable on its mirror image

Problem 4.38 Each of the diastereomers will have a set of nine different carbons. So, barring accidental overlapping of signals, we should see a total of 18 different signals. The enantiomers will not have separable signals in an achiral solvent such as $CDCl_3$.

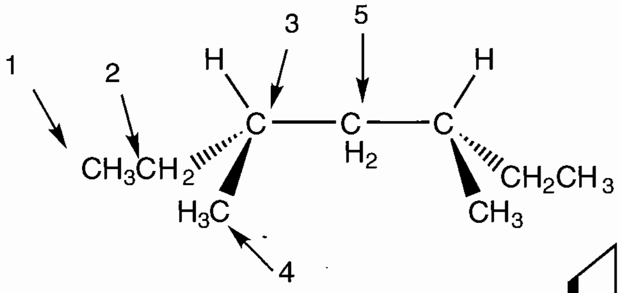


3,4-Dimethylheptane

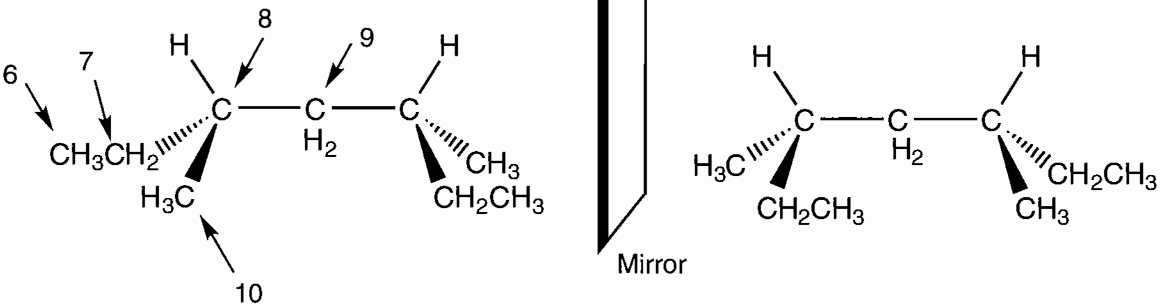
Problem 4.39 Here we also have two diastereomers, but one is a meso compound. There will be 5 signals from the meso compound and 5 more from the pair of enantiomers for a total of 10.



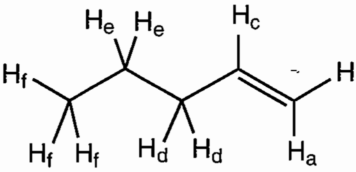
3,5-Dimethylheptane



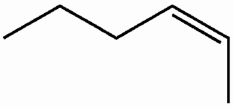
A meso compound—superimposable on its mirror image



Problem 4.40 We can draw 1-pentene and consider the six different hydrogens. Replacing each of those different hydrogens (H_a–H_f) with a methyl group (one at a time) gives six different isomers. A quick inspection tells us that 3-methyl-1-pentene is the only chiral isomer.

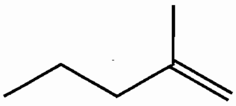


1-Pentene

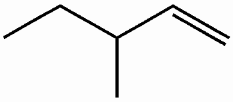


(*Z*)-2-Hexene

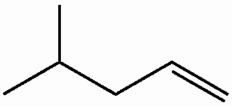
(*E*)-2-Hexene



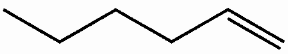
2-Methyl-1-pentene



3-Methyl-1-pentene

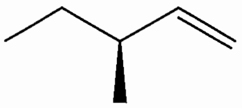


4-Methyl-1-pentene

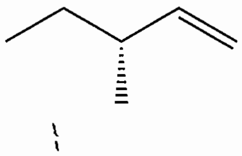


1-Hexene

The two enantiomers of 3-methyl-1-pentene are the (*S*) and (*R*) structures drawn here.



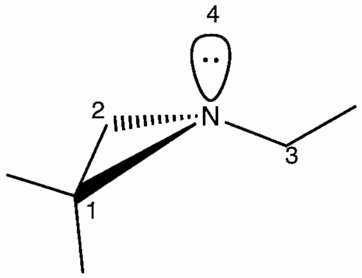
(*S*)-3-Methyl-1-pentene



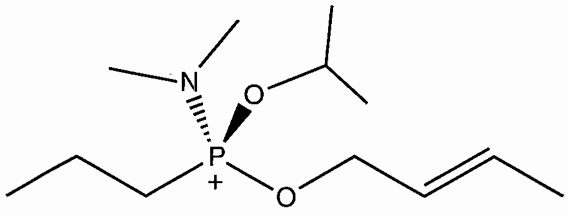
(*R*)-3-Methyl-1-pentene

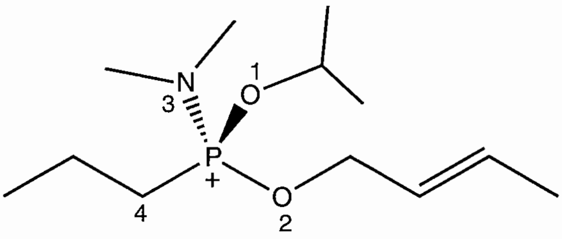
Problem 4.41

(a) The nitrogen is the only stereogenic atom in this molecule. We know that the amine nitrogen can undergo inversion at room temperature, but as drawn, the configuration is (*S*). The lone pair gets the lowest assignment because it has an atomic number of zero. The three atoms attached to the stereogenic nitrogen are all carbons. So we have to compare the next level of attachment. The ring carbon coming out at us has attachments of (C, C, C). The ring carbon going back has (C, H, H), and the carbon of the ethyl group to the right has (C, H, H). That means the carbon coming out toward us is number 1 in our (*R*/*S*) analysis. The other two carbons both have (C, H, H) attachment. So we have to go to the next level. The next carbon on the ring has (C, C, N). The next carbon on the ethyl group has (H, H, H). So we have the order as shown. Without moving anything, we can draw an arrow from 1 to 2 to 3 and see that the circle is clockwise as looking from above. But that is looking from above with number 4 (the lone pair) in front. So reverse your answer. The counterclockwise direction tells us this is the (*S*) enantiomer.



(b) The phosphorus atom is the only stereogenic atom in this molecule. The attachments are C, N, and two O's. The carbon is the lowest atomic number, so it is number 4. Nitrogen is next lowest, so it is number 3. The oxygens are the same, so we must go out to the next attachment, which is carbon for both. The carbon of the isopropyl group is attached to (C, C, H). The group to the right has its carbon attached to (C, H, H). So the isopropyl group is number 1. Without moving anything, we can draw an arrow from 1 to 2 to 3 and see that the circle is clockwise as looking from the left. But looking from the left has number 4 (the propyl group) in front. So reverse your answer. The counterclockwise direction tells us this enantiomer is (*S*).

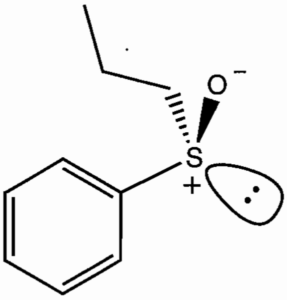


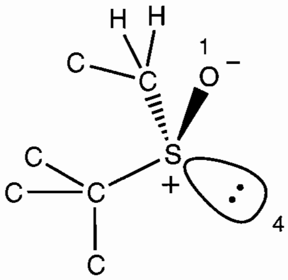


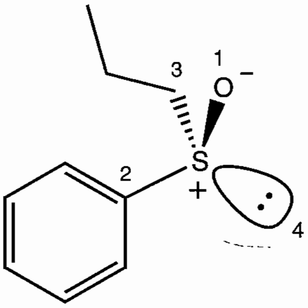
(continued)

Problem 4.41 *(continued)*

(c) The sulfur is the stereogenic atom in this molecule. It has a lone pair, an oxygen, and two carbons directly attached. The lone pair is number 4 and the oxygen is number 1. The two carbons need to be analyzed further to differentiate them. As shown in the middle structure, the aromatic ring carbon has three bonds to carbons (C, C, C). The propyl group carbon has attachments of (C, H, H). So the aromatic ring is number 2. Without moving anything, we can draw an arrow from 1 to 2 to 3 and see that the circle is clockwise as looking from the left with the number 4 group (the lone pair) in back. The clockwise direction tells us this enantiomer is (*R*).

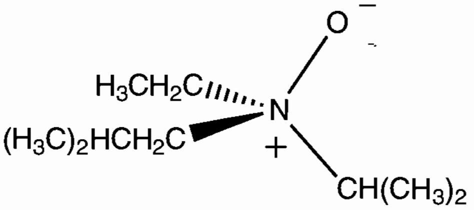


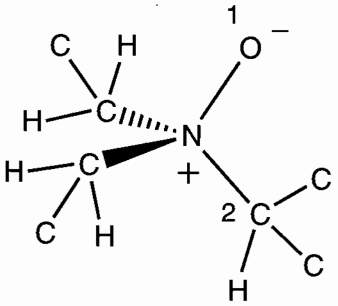


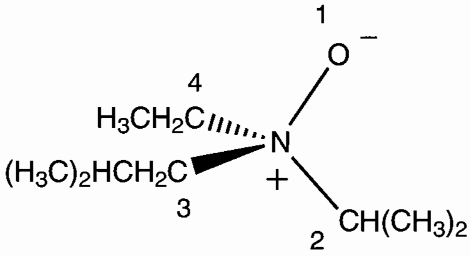


(d) The nitrogen is the stereogenic atom in this molecule. It is attached to an oxygen, an isopropyl group, an ethyl group, and an isobutyl group. The oxygen has the larger atomic number, so it is number 1. The other attachments are to carbon and must be compared by looking at their attachments as shown in the middle structure. The carbon coming out at us has (C, H, H). The carbon to the right of the isopropyl group has (C, C, H). The carbon going back has (C, H, H). So the carbon of the isopropyl group to the right is assigned number 2. Now we compare the next attachment for the two remaining groups. The carbon on the group going back (the ethyl group) is attached to (H, H, H). The carbon on the isobutyl group coming out has (C, C, H). So the isobutyl group is number 3 and the ethyl group is number 4.

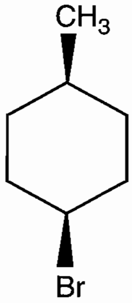
Without moving anything, we can draw an arrow from 1 to 2 to 3 and see that the circle is clockwise as looking from the front with the number 4 group (the ethyl) in back. The clockwise direction tells us this enantiomer is (*R*).

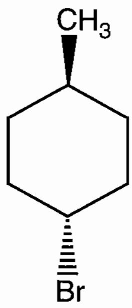




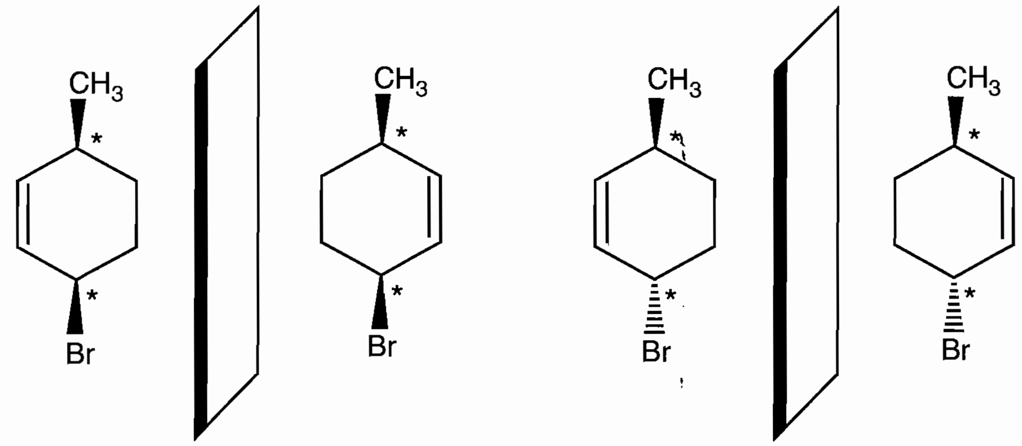


Problem 4.42 (a) No stereogenic carbons (*), two stereoisomers:

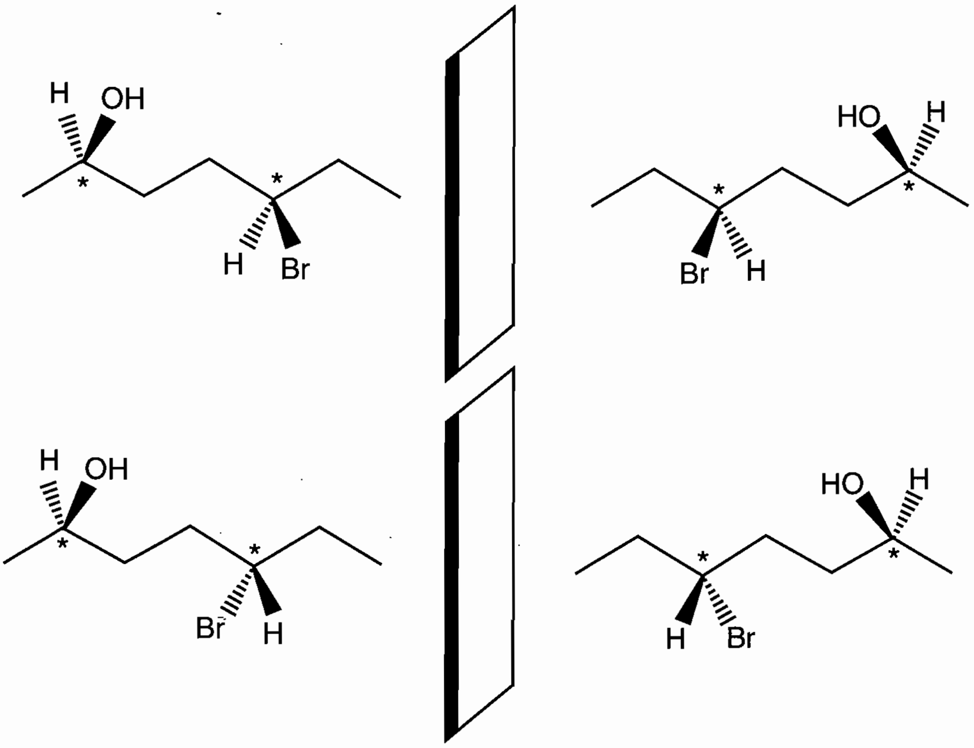




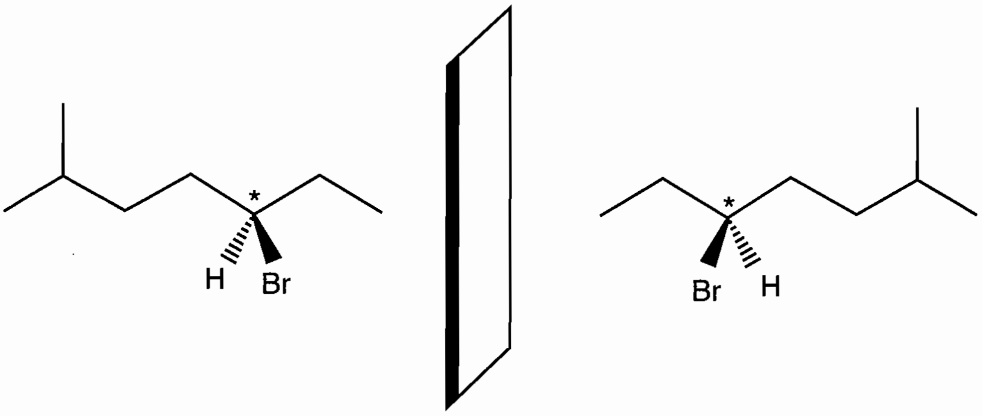
(b) Two stereogenic carbons (*), four stereoisomers:



(c) Two stereogenic carbons (*), four stereoisomers:

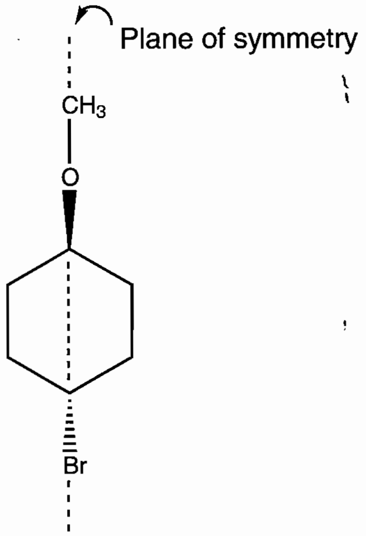


(d) One stereogenic carbon (*), two stereoisomers:

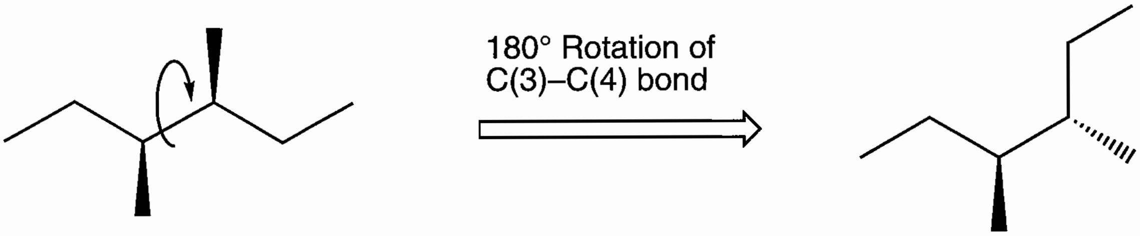


Problem 4.43

(a) Achiral. The plane of symmetry bisects the bromine, the ring, and the OCH_3 group.

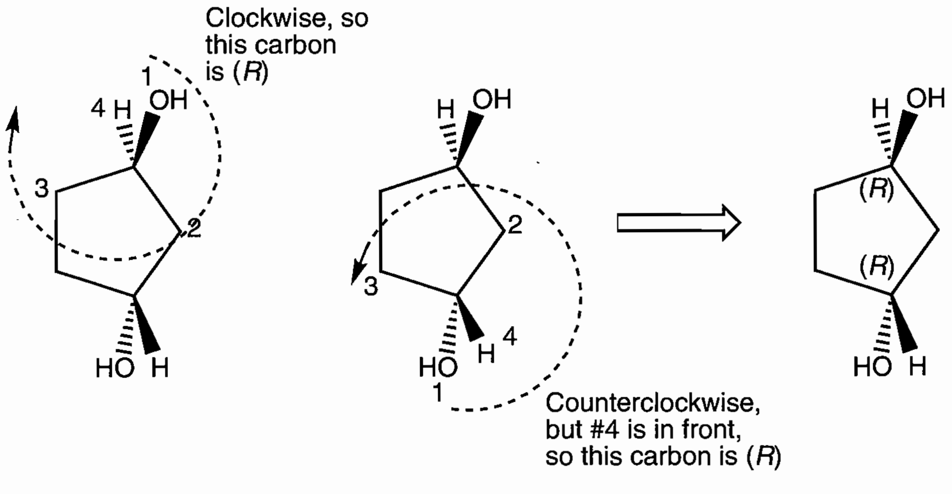


(b) Chiral. There is no plane of symmetry. By rotating the C(3)—C(4) bond 180°, you can see that the molecule lacks symmetry.

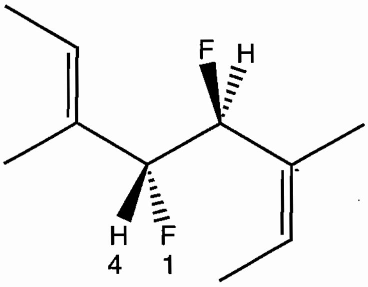


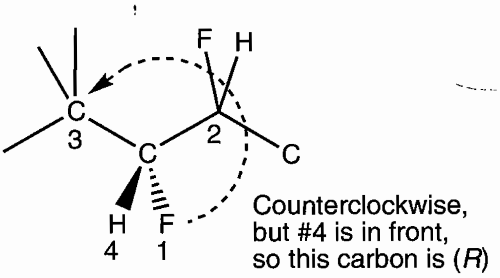
This molecule is (3*S*,4*S*)-3,4-dimethylhexane.

(c) Chiral. There is no plane of symmetry in this molecule. Let's determine the configuration of the two stereogenic carbons independently. On the left structure we see that the carbon with the OH group coming out at us has the (*R*) configuration. The middle structure shows the analysis of the carbon with the OH group going back. It has the lowest atomic number in front. The arrow from 1 to 2 to 3 is counterclockwise, but because number 4 is in front, this enantiomer is (*R*).

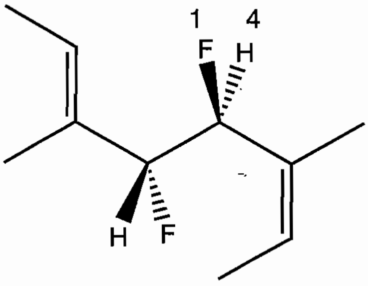


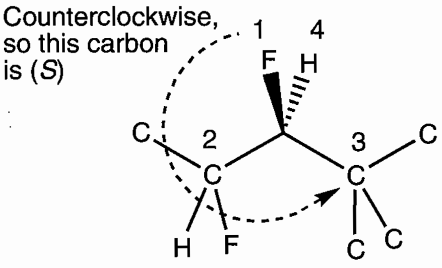
(d) Chiral. There is no plane of symmetry in this molecule. The two alkenes are different. The alkene on the left is (*E*) and the alkene on the right is (*Z*). Let's determine the configuration for the two stereogenic carbons separately. The carbon that has the attached fluorine going behind the plane of the paper has attachments of H, F, and two C's. The hydrogen is number 4. The fluorine is number 1. We have to compare the next attachments for the two carbons. This is shown on the second structure. The carbon on the right has (F, C, H). The carbon on the left has (C, C, C). We don't add the atomic numbers, we compare them. Because F is bigger than any carbon of (C, C, C), the number 2 designation goes to the group on the right. We can draw an arrow from 1 to 2 to 3 and see that it is counterclockwise, but the lowest atomic number is in front, so this an (*R*) configuration.





Now we can analyze the stereogenic carbon with the fluorine group coming out at us. The attachments are H, F, and two C's. The hydrogen is number 4. The fluorine is number 1. We can compare the next attachments for the two carbons as shown. The carbon on the left has (F, C, H). The carbon on the right has (C, C, C). Because F is bigger than any of the carbons of (C, C, C), the number 2 designation goes to the group on the left.



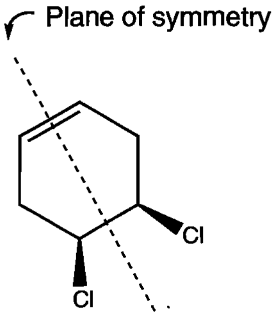


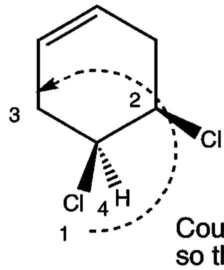
By the way, we know the IUPAC name for this molecule. It is (2*E*,4*R*,5*S*,6*Z*)-4,5-difluoro-3,6-dimethyl-2,6-octadiene.

(e) Achiral. There is a plane of symmetry through the middle of the cyclohexene. Even though the molecule is achiral, there are two stereogenic carbons. Let's analyze them separately. The carbon that is at the bottom of the cyclohexane has H, Cl, and two C's attached. The hydrogen is number 4 and the Cl is number 1. The two carbons need to be compared further. The carbon to the left has (C, H, H). The carbon to the right has (Cl, C, H). Because the Cl is the largest atomic number, the group to the right is number 2 and the group to the left is number 3. Drawing an arrow from 1 to 2 to 3 gives a counterclockwise direction, so this configuration is (*S*).

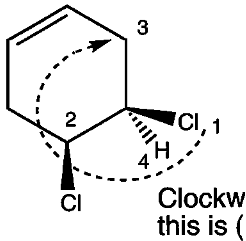
(continued)

Problem 4.43 *(continued)*





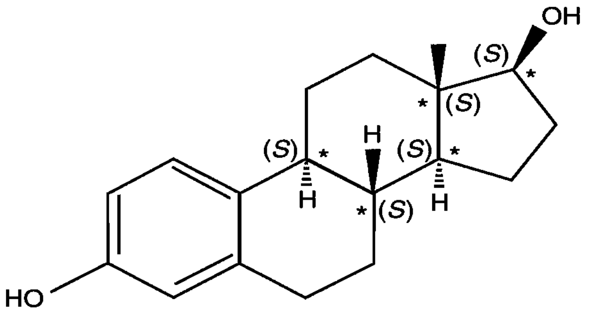
Counterclockwise, so this is (*S*)



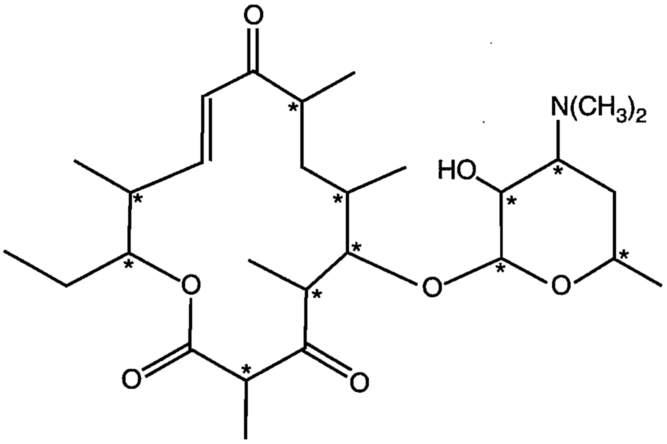
Clockwise, so this is (*R*)

Analysis of the other stereogenic carbon tells us that it is an (*R*) configuration. This molecule is (4*R*,5*S*)-4,5-dichlorocyclohexene. It is a meso compound. It is the same as (4*S*,5*R*)-4,5-dichlorocyclohexene.

Problem 4.44

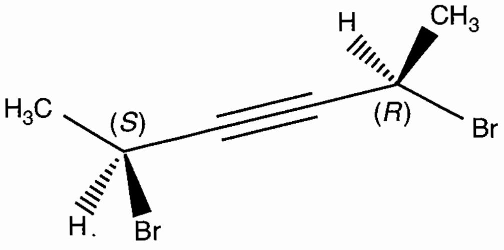


Problem 4.45 The asterisk shows the stereogenic carbons.

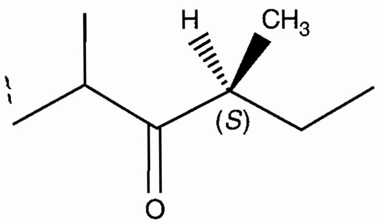


Problem 4.46 They are all chiral, except for (a), which is a meso compound.

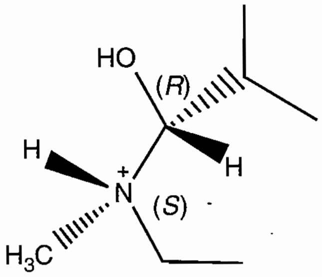
(a)



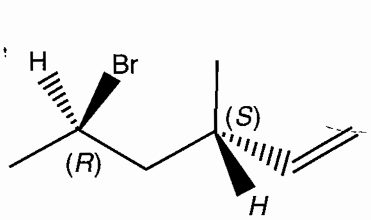
(b)



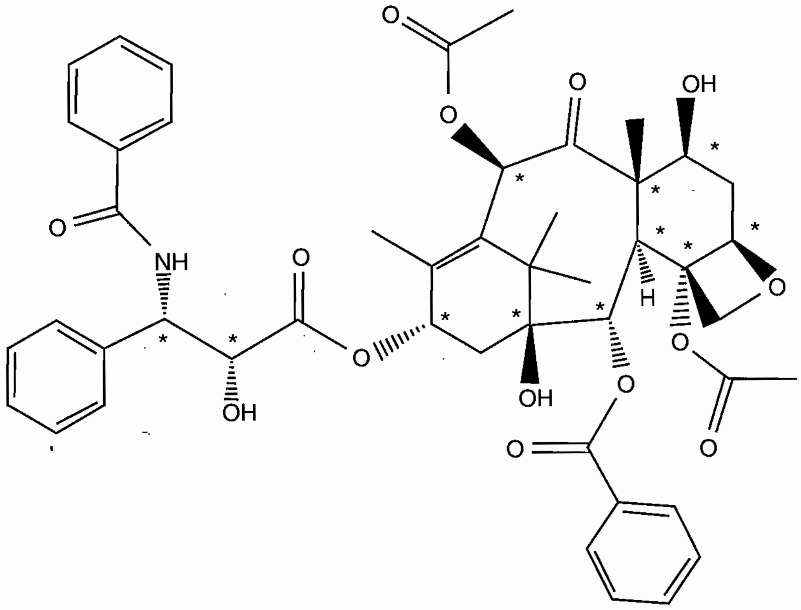
(c)



(d)

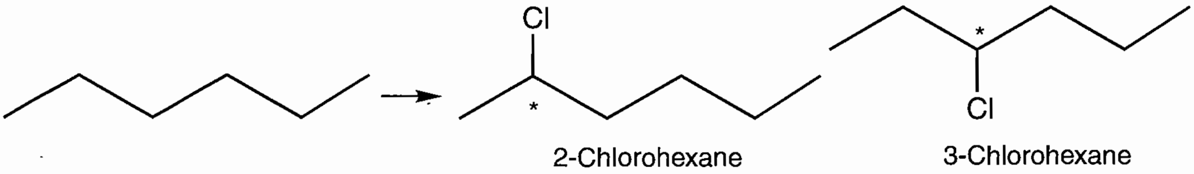


Problem 4.47



Problem 4.48 Two of the isomers formed from hexane are chiral.

From hexane,

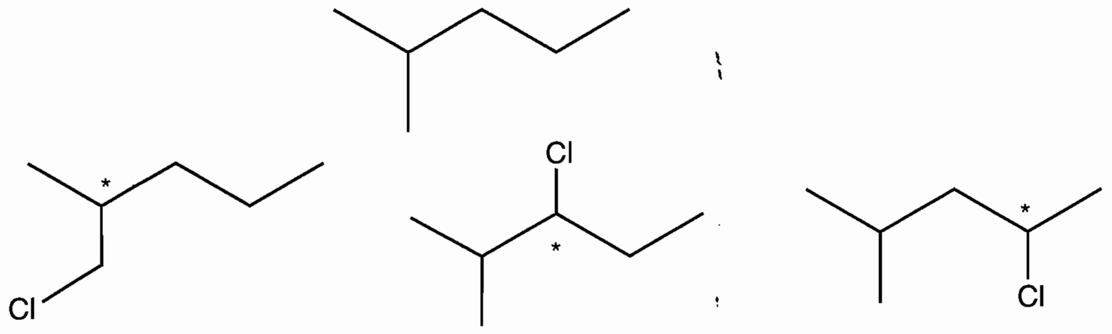


(continued)

Problem 4.48 *(continued)*

Three of the molecules formed from 2-methylpentane are chiral.

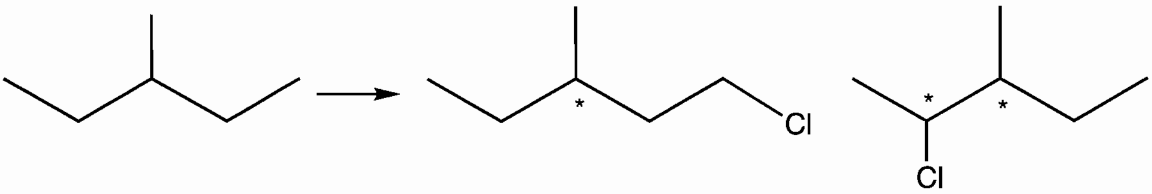
From 2-methylpentane,



1-Chloro-2-methylpentane 3-Chloro-2-methylpentane 2-Chloro-4-methylpentane

Two of the isomers formed from 3-methylpentane are chiral, and one isomer has two stereogenic carbons.

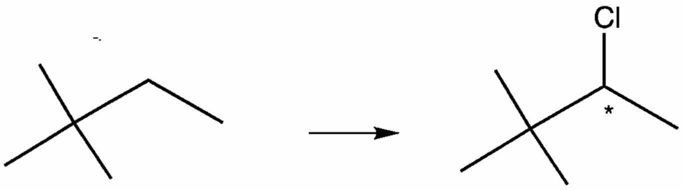
From 3-methylpentane,



1-Chloro-3-methylpentane 2-Chloro-3-methylpentane

Only one of the isomers from 2,2-dimethylbutane is chiral.

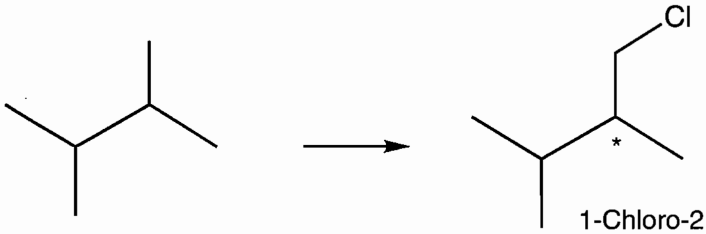
From 2,2-dimethylbutane,



3-Chloro-2,2-dimethylbutane

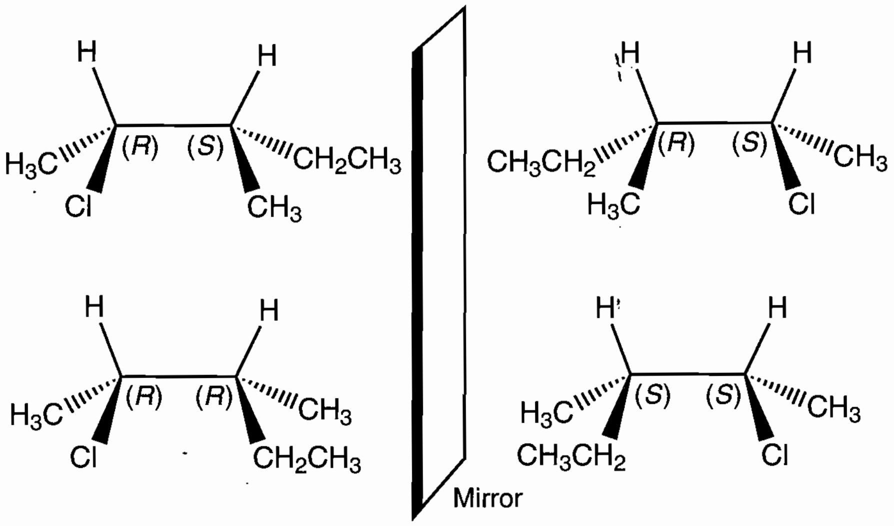
Similarly, only one of the isomers from 2,3-dimethylbutane is chiral.

From 2,3-dimethylbutane,

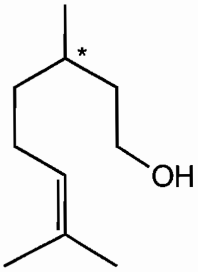


1-Chloro-2,3-dimethylbutane

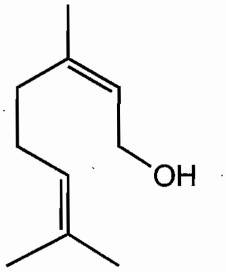
Problem 4.49 There is only one isomer to consider, 2-chloro-3-methylpentane. There will be four stereoisomers: two pairs of enantiomers.



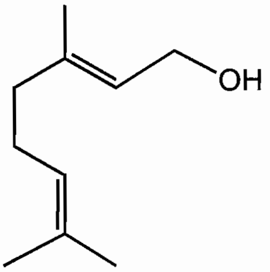
Problem 4.50 Only compound (b) can exist in (*E*) and (*Z*) forms. Compounds (a) and (d) have stereogenic carbon atoms:



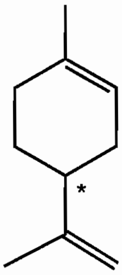
(a)



(b) (*Z*) Isomer



(b) (*E*) Isomer

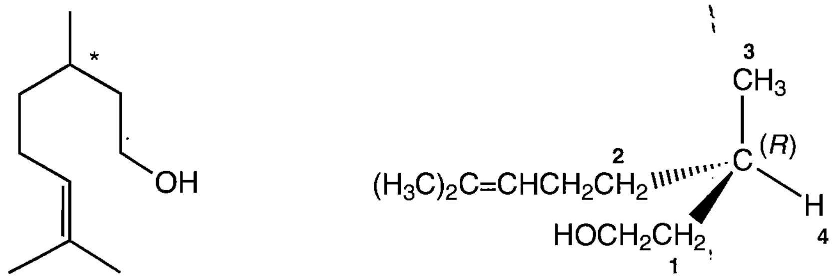


(d)

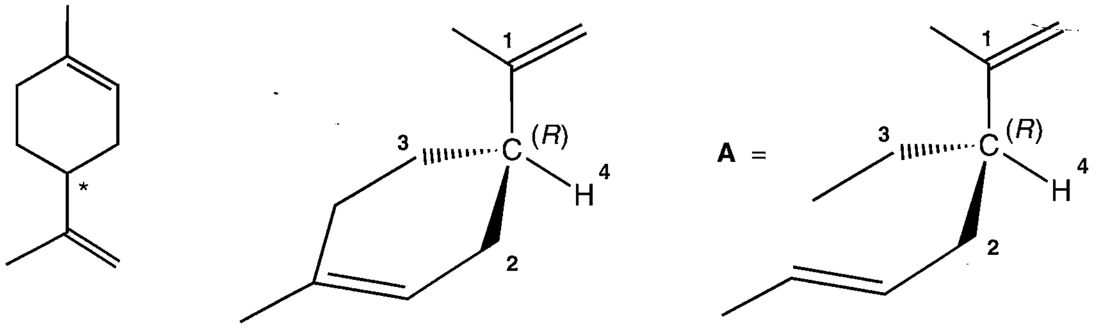
Technically, (d) could exist in (*E*) and (*Z*) forms. However, a trans double bond in a six-membered ring produces too much strain, and the isomer shown is the only one practically possible.

Problem 4.51 Base the tetrahedra on the stereogenic carbons. Determining priorities is certainly no problem in the acyclic molecules, but it may be more difficult in the cyclic species. *Remember*: The ring makes no special difference in this problem. For example, the priorities would be exactly the same in molecule **A** formed by eliminating a bond as shown. Why should anything be altered by closing the ring? It isn't.

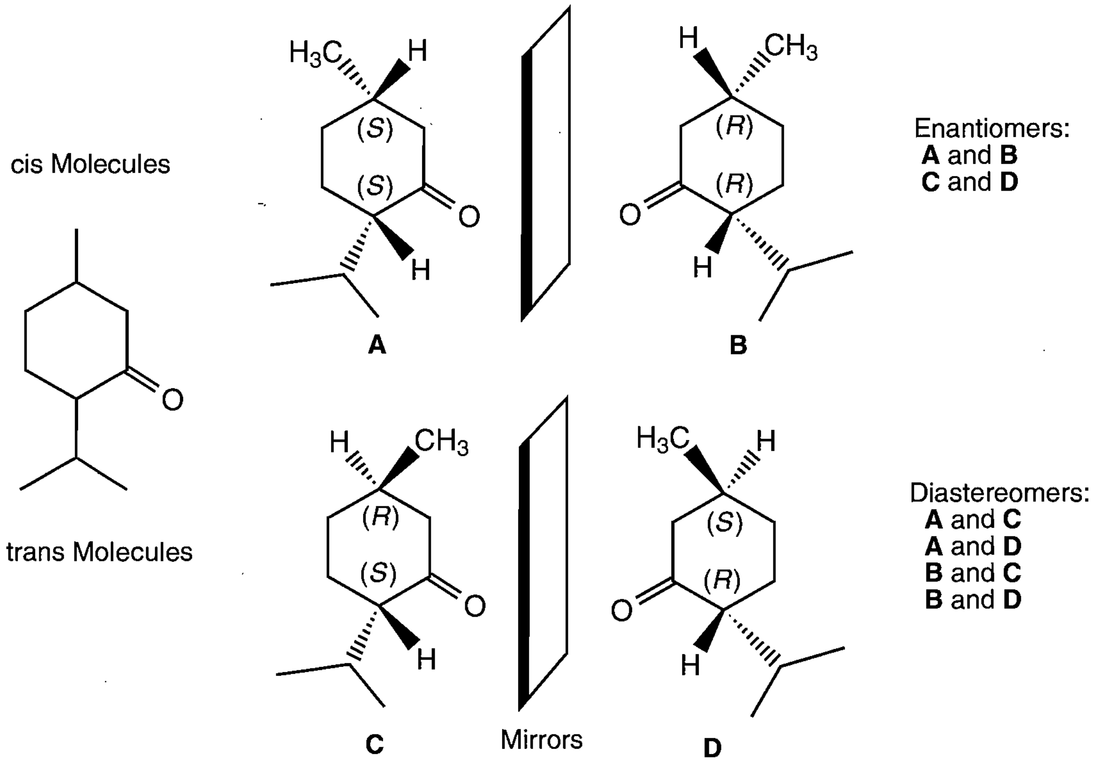
(a)



(d)



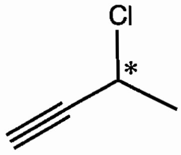
Problem 4.52 This molecule comes in cis and trans versions. In each case, there is a pair of enantiomers. There is a total of four stereoisomers, and the figure shows the enantiomeric and diastereomeric relationships.

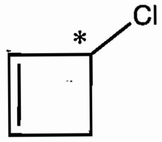


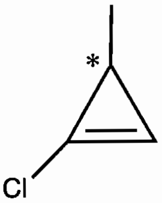
Problem 4.53 There are 2 degrees of unsaturation in C_4H_5Cl, which means we can have one of the following: two double bonds, a triple bond, a double bond and a ring, or two rings.

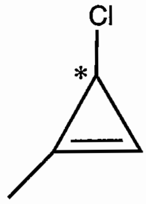
$$\text{Degrees of unsaturation} = \frac{\overbrace{(2 \times 4) + 2}^{\text{\# of hydrogens for } C_4} - \overset{\text{\# of H's and Cl in this molecule}}{6}}{2} = 2$$

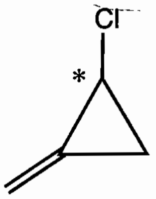
Here are five chiral molecules with this formula, with the stereogenic carbons indicated by an asterisk.



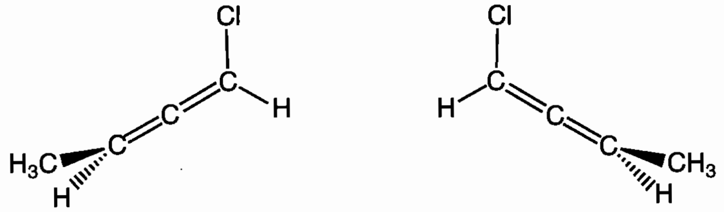






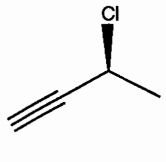


This is another chiral C_4H_5Cl molecule. It does not have a stereogenic carbon.

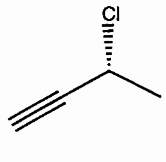


These two substituted allenes are nonsuperimposable mirror images

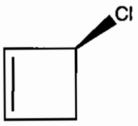
Problem 4.54



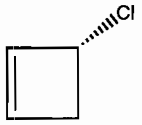
(*S*)-3-Chloro-1-butyne



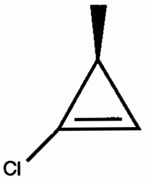
(*R*)-3-Chloro-1-butyne



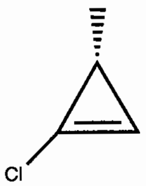
(*S*)-3-Chlorocyclobutene



(*R*)-3-Chlorocyclobutene



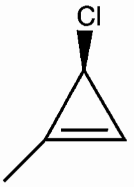
(*S*)-1-Chloro-3-methylcyclopropene



(*R*)-1-Chloro-3-methylcyclopropene

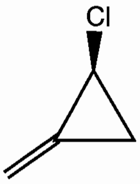
(continued)

Problem 4.54 *(continued)*

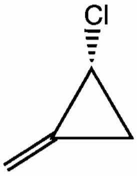


(*S*)-3-Chloro-1-methylcyclopropene

(*R*)-3-Chloro-1-methylcyclopropene

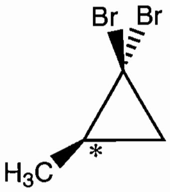


(*S*)-1-Chloro-2-methylenecyclopropane

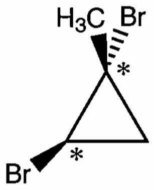


(*R*)-1-Chloro-2-methylenecyclopropane

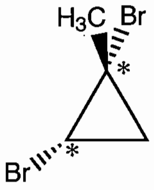
Problem 4.55 We have shown one of the enantiomers for each chiral dibromomethylcyclopropane. You might have drawn the other enantiomer, which is a completely correct answer.



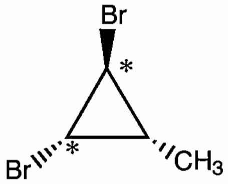
(*R*)-1,1-Dibromo-2-methylcyclopropane



(1*R*,2*R*)-1,2-Dibromo-1-methylcyclopropane

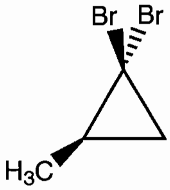


(1*R*,2*S*)-1,2-Dibromo-1-methylcyclopropane

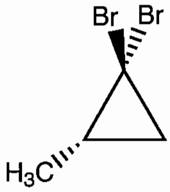


(1*S*,2*S*)-1,2-Dibromo-3-methylcyclopropane

Problem 4.56 The (*R*) configuration of 1,1-dibromo-2-methylcyclopropane was drawn in the answer key for Problem 4.55. Both enantiomers are shown here. There is only one stereogenic carbon. There are no diastereomers of this molecule.



(*R*)-1,1-Dibromo-2-methylcyclopropane



(*S*)-1,1-Dibromo-2-methylcyclopropane

Problem 4.57

(a) (2*R*,4*S*)-2,4-dibromo-4-chlorohexane

(b) 4,4-dimethyl-1-pentene

(c) (*E*,5*R*,8*S*)-5-ethyl-8-iodo-3-methyl-2-nonene

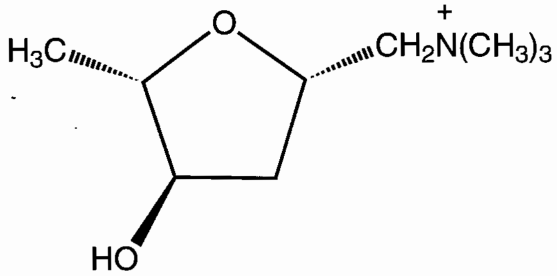
(d) (2*R*,6*R*)-2-chloro-6-fluoroheptane

(e) (*Z*)-3-bromo-4-methyl-3-hexene

(f) (*R*)-2,2-dichloro-3-ethylhexane

(g) (*Z*,4*R*)-4-bromo-2-pentene

Problem 4.58 Had the poison been gathered from nature, it would have been optically active. The sleuths got out their trusty polarimeter and determined that the poison was racemic—it could not have come from a mushroom. Lathom was hanged. He should have studied his orgo more.



Problem 4.59 The stereochemical outcome in each reaction is inversion. Because the carbon goes from one tetrahedral configuration to another, it must invert along the way.

Problem 4.60 The planar carbon is sp^2 hybridized. It has an unoccupied *p* orbital. If a stereogenic carbon underwent a reaction by losing a bromide, it would no longer be stereogenic. It would be flat, and the molecule would no longer be chiral (if the reacting carbon was the only stereogenic carbon in the molecule).

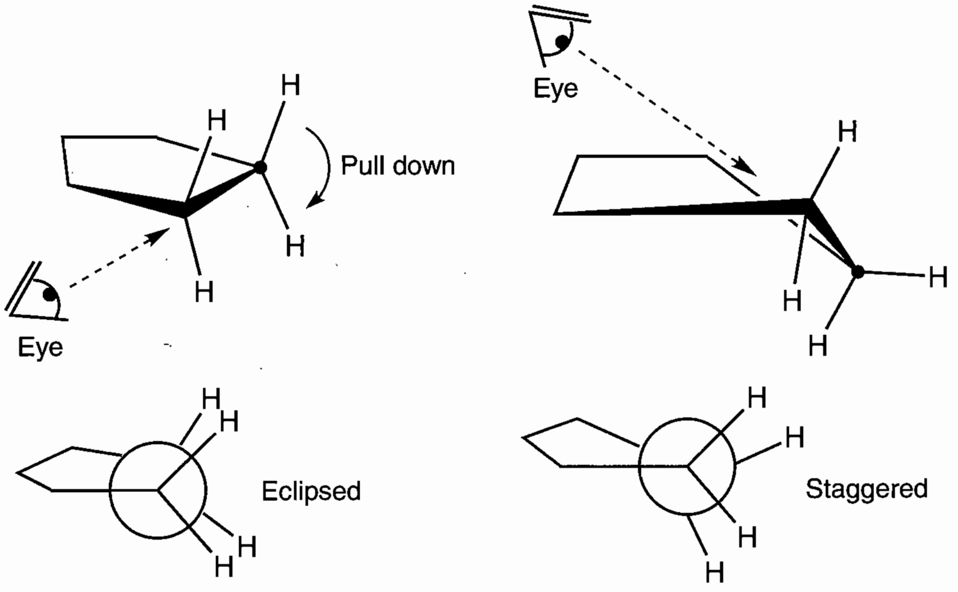
Problem 4.61 The hydrogen is anti to the bromide leaving group. This relationship is critically important. It is only the electrons of the anti C—H bond that can move into the available σ^* orbital at the backside of the C—Br bond.

Problem 4.62 Yes, the starting material is chiral. The configuration is (*S*). The product is achiral. This animation shows a chiral molecule undergoing a reaction that leads to an achiral product.

5

Rings

Problem 5.1 First look at planar cyclopentane in which the five top carbon–hydrogen bonds (as well as the bottom carbon–hydrogen bonds) are eclipsed. Once again, offset your eye just a bit so you can see the eclipsed bonds and atoms in the back. As in cyclobutane (Fig. 5.9), puckering of the five-membered ring relieves some of the eclipsing of the carbon–hydrogen bonds, and thus relieves torsional strain.



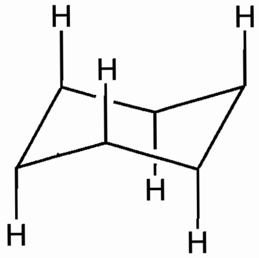
Planar
cyclopentane
dihedral angle = 0°

Envelope
cyclopentane
dihedral angle > 0°

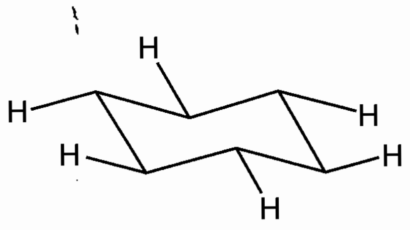
Note how puckering opens up the dihedral angle between the carbon–hydrogen bonds

Problem 5.3 There is only one kind of carbon in cyclohexane, and thus only one signal in the ^{13}C NMR spectrum. Get out your models and be sure you see that the six carbons are all equivalent.

Problem 5.4 The answer would seem at first to be "two signals": one for the set of six equivalent axial hydrogens and another for the set of six equivalent equatorial hydrogens.

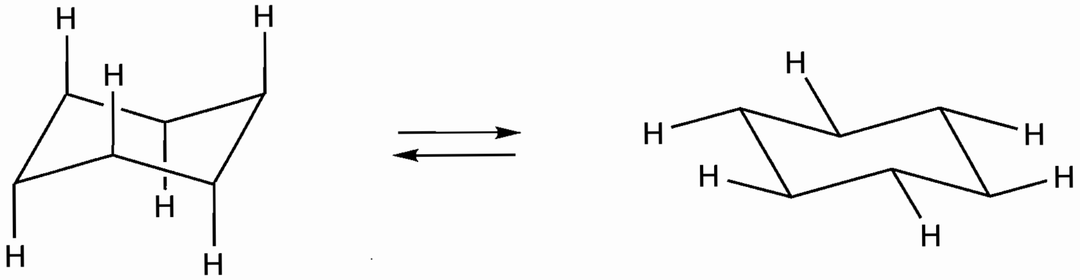


The set of six equivalent axial hydrogens



The set of six equivalent equatorial hydrogens

But if there is enough energy, these two sets interconvert, and there will be only one average signal in the ^{1}H NMR spectrum. In practice, at low temperature, two separate signals are observed, and at higher temperature (about room temperature), one averaged signal appears.



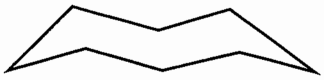
Problem 5.5 Presumably, taking the difference in heat of formation between two compounds that differ only by one methylene group will give the heat of formation of a single methylene. In practice, one takes the average of many such determinations. In this example, heptane ($\Delta H_f^\circ = -44.8$) – hexane ($\Delta H_f^\circ = -39.9$) gives –4.9; octane ($\Delta H_f^\circ = -49.8$) – heptane ($\Delta H_f^\circ = -44.8$) gives –5.0; nonane ($\Delta H_f^\circ = -54.5$) – octane ($\Delta H_f^\circ = -49.8$) gives –4.7; decane ($\Delta H_f^\circ = -59.6$) – nonane ($\Delta H_f^\circ = -54.5$) gives –5.1. The average of these determinations is –4.9 kcal/mol.

Problem 5.6 You might want to use your model set to help analyze this question. You will notice in column 4 of Table 5.1 that there is considerable strain associated with the small rings. Cyclopropane and cyclobutane have almost the same amount of strain (about 27 kcal/mol). Cyclopentane and cycloheptane have about 6.0 kcal/mol strain, but as you make a model, you will realize that this strain is not the same kind as in cyclopropane and cyclobutane. The 5- and 7-membered rings have very similar eclipsing interactions. The 8-membered to 12-membered rings (cyclooctane to cycloundecane), however, are higher in strain energy for a third reason. They have van der Waals strain. The 8-membered ring has 9.5 kcal/mol strain energy (see column 4 of Table 5.1). There is no ring strain for this ring size. The ring is sufficiently flexible to avoid eclipsing strain. Let's assume that most of the 9.5 kcal/mol is due to van der Waals strain. You should make a model, then you

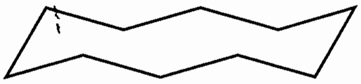
(continued)

Problem 5.6 *(continued)*

will see that there are many conformations for cyclooctane. It is very floppy. The best bond angles (fewest gauche interactions) are obtained with an extended chair-like structure, which has three pairs of CH_2 groups interacting across the ring from each other. If that is the only cause of strain, then each CH_2—CH_2 across the ring interaction produces about 3.2 kcal/mol of strain.



Cyclooctane

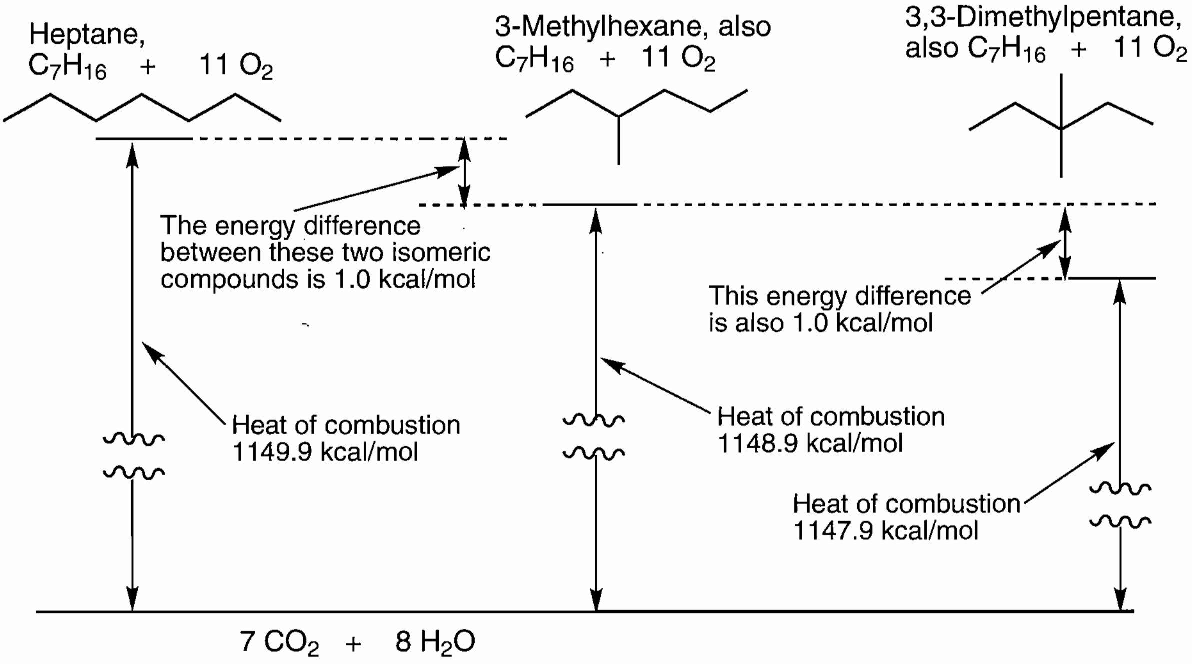


Cyclodecane

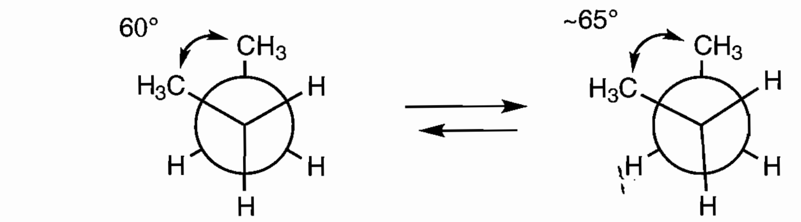
Now consider cyclodecane, which has four pairs of CH_2 groups interacting with each other. We see from column 4 that cyclodecane has 12.1 kcal/mol of strain. We would have predicted about 12.8 kcal/mol strain (four pairs of CH_2 groups at 3.2 kcal/mol per pair). This tells us that we aren't too far off.

Problem 5.7 This figure resembles Figure 5.21. The three isomeric alkanes all react with oxygen to give 7 CO_2 + 8 H_2O. The product of combustion of all three hydrocarbons is exactly the same. Therefore, the differences in their heats of combustion give the differences in their energies.

$$C_7H_{16} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O$$

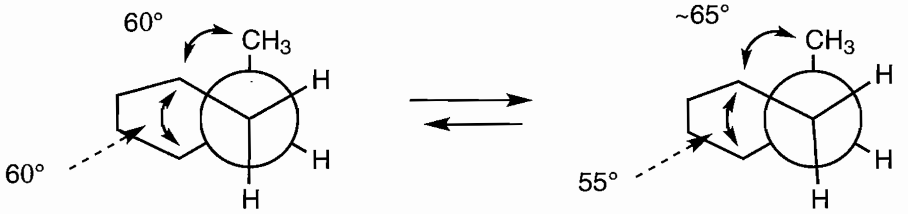


Problem 5.10 The gauche butane from Figure 5.28 has the ability to relieve some of the steric interactions by rotating the front carbon of the Newman projection slightly to counterclockwise, as shown below. The methyl–methyl interaction goes from having a 60° angle between the groups to something closer to a 65° angle.



Rotating the front carbon much further leads to the higher energy eclipsing conformation. But going from a 60° angle to about 65° is energetically favorable.

Now look at the Newman projection for axial methylcyclohexane. As we rotate the front carbon counterclockwise, we reduce the methyl-ring gauche interaction. But at the same time we are increasing the ring–ring gauche interaction. So there is no reduction of overall torsional strain for this system.

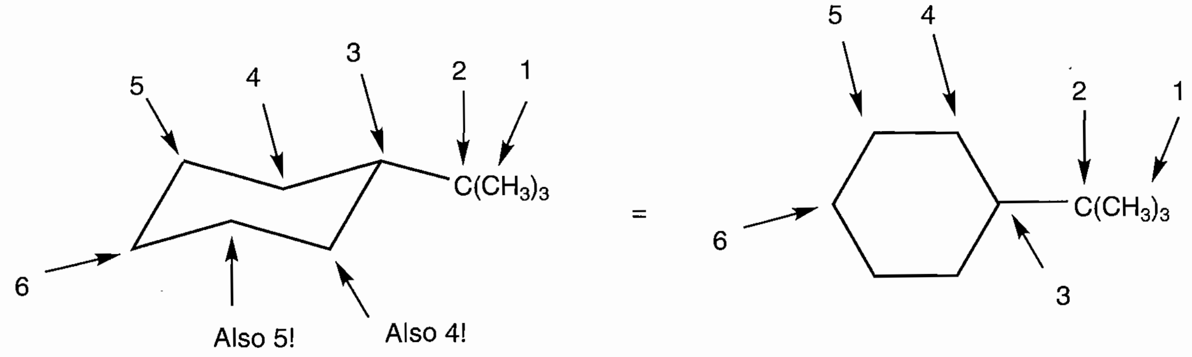


Problem 5.11 $\Delta G = -RT\ln K$, where R is about 2 cal/deg•mol, which is equal to about 0.002 kcal/deg•mol; $T = 25\ ^\circ\mathrm{C} = 298\ \mathrm{K}$; and $\Delta G = 2.8$ kcal/mol.

$2.8 = -(0.002)(298)\ln K$
$-4.70 = \ln K$
$9.1 \times 10^{-3} = K$

So, 2.8 kcal/mol translates into a mixture of products in which the ratio is 99.1: 0.9.

Problem 5.13 First of all, we have to draw the molecule and be careful to keep the *tert*-butyl group equatorial. There will be a negligible amount present of the chair with the *tert*-butyl group axial. The *tert*-butyl group has two different kinds of carbon, and there are four different ring carbons. So we will see a total of six signals in the ^{13}C NMR spectrum.

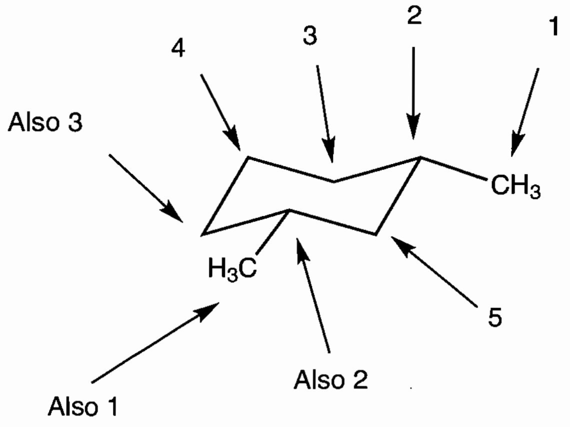


A three-dimensional view

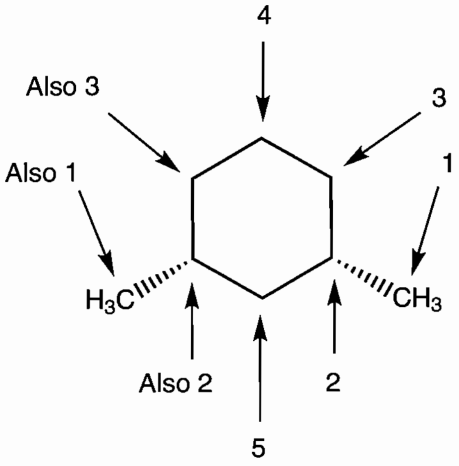
A schematic, "top" view

Problem 5.14 The analysis of *cis*-1,3-dimethylcyclohexane requires that we think about the preferred conformation. Although there will be some diaxial conformer at room temperature, we expect that most of the molecules will be in the diequatorial conformation at room temperature. The two methyl groups in the axial position would produce more than 3.5 kcal/mol of steric strain (see Problem 5.21). So we will use the diequatorial isomer in our NMR analysis.

cis-1,3-Dimethylcyclohexane is a bit challenging to analyze in the chair conformation. It is much easier to see the symmetry for this molecule in the perspective or "top" view. There is a plane of symmetry through the center of the molecule. As a result, the methyl groups are equivalent (labeled number 1). The carbons of the ring that are attached to the methyl groups are equivalent (labeled number 2). The carbons labeled number 3 are also equivalent. The result is five different carbons in *cis*-1,3-dimethylcyclohexane.



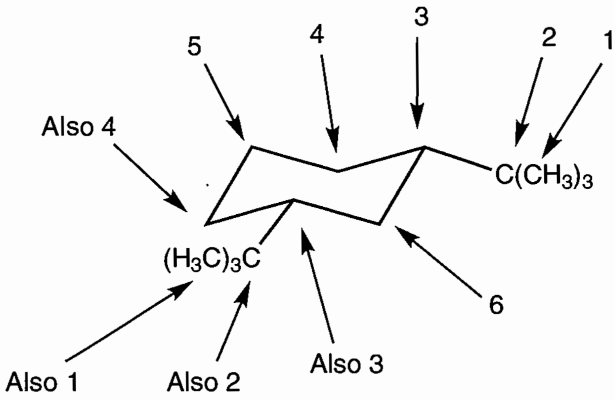
A chair conformation view



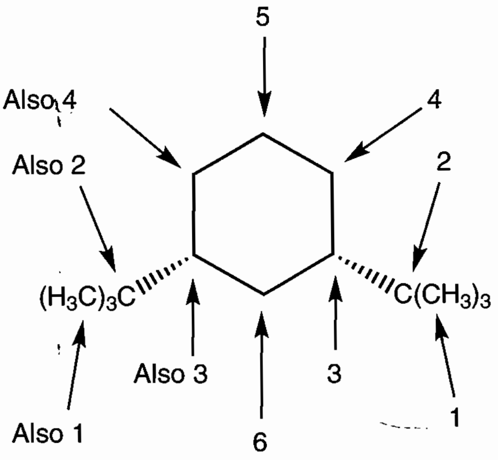
A "top" view with perspective

Analysis of *cis*-1,3-di-*tert*-butylcyclohexane is very similar. In this case there is no need to worry about the diaxial conformation. It is much higher in energy, and we won't see any evidence of its presence in the NMR spectrum of a sample at room temperature.

Once again, it is easier to see the symmetry of this molecule in the "top" view. The *tert*-butyl groups add only one new type of carbon to what we found in the dimethylcyclohexane. Therefore the answer is six carbon signals will be observed in the ^{13}C NMR spectrum of *cis*-1,3-di-*tert*-butylcyclohexane.

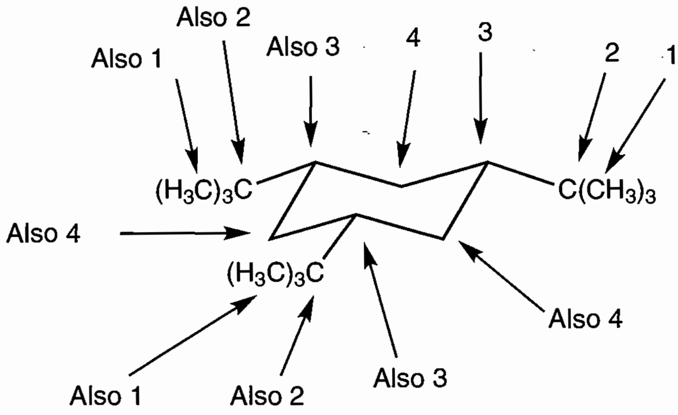


A chair conformation view

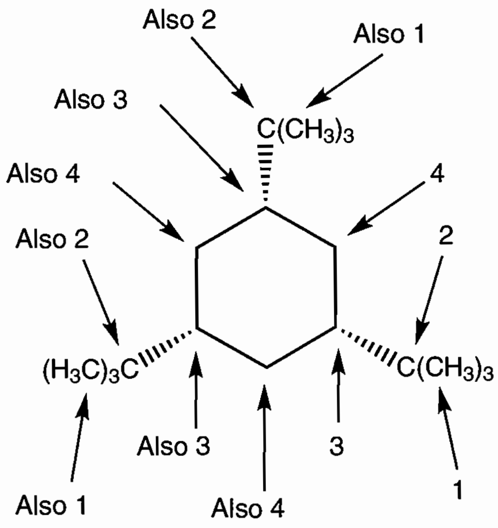


A "top" view with perspective

The all-*cis*-1,3,5-tri-*tert*-butylcyclohexane also has symmetry. The chair conformation view displays the symmetry fairly well. Perhaps you can see it better in the "top" view. You can see that there are only four different carbons in this molecule. So the ^{13}C NMR spectrum of all-*cis*-1,3,5-tri-*tert*-butylcyclohexane will have four signals.



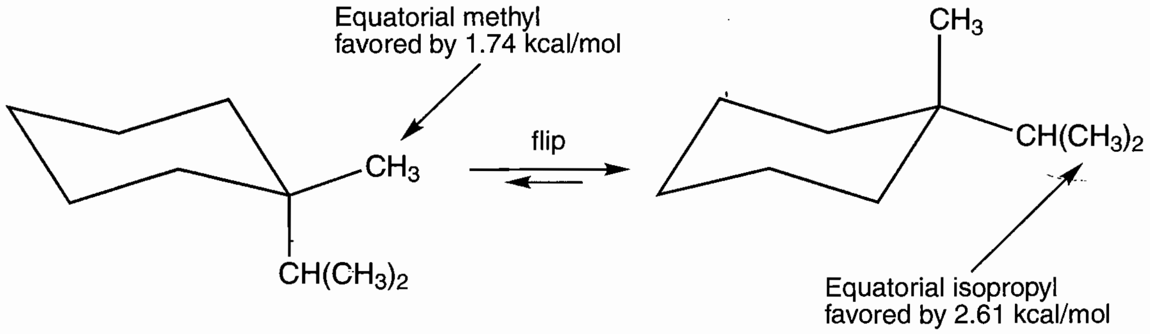
A chair conformation view



A "top" view with perspective

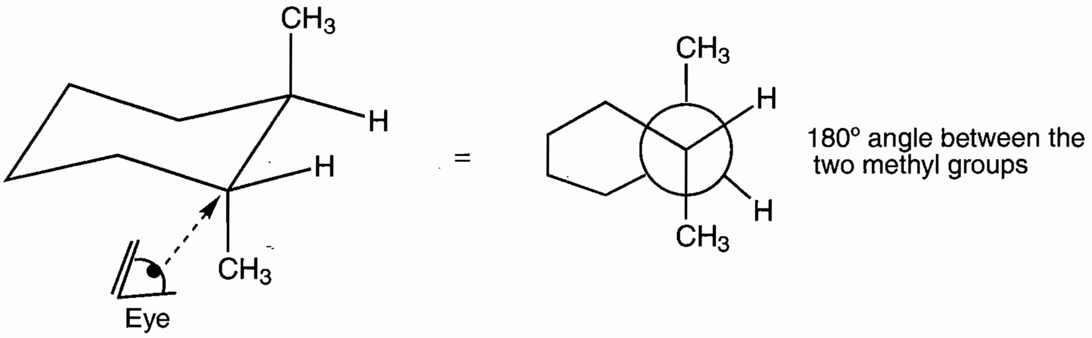
One point of this problem is to help you see the symmetry of the substituted cyclohexanes. You should also become comfortable twisting and turning the molecules so that the symmetry is easier to see.

Problem 5.15 In 1-isopropyl-1-methylcyclohexane, either the methyl or isopropyl group can be equatorial, but not both. Your intuition might tell you that the conformation with the larger isopropyl group equatorial will be preferred, but you will need to consult Table 5.3 to do the quantitative calculation. Table 5.3 tells us that a cyclohexane with an equatorial isopropyl group is more stable than a cyclohexane with an axial isopropyl group by 2.61 kcal/mol. Similarly, a cyclohexane with an equatorial methyl is 1.74 kcal/mol more stable than a cyclohexane with an axial methyl group. The ring flip of 1-isopropyl-1-methylcyclohexane involves the interconversion of equatorial and axial isopropyl and methyl groups.

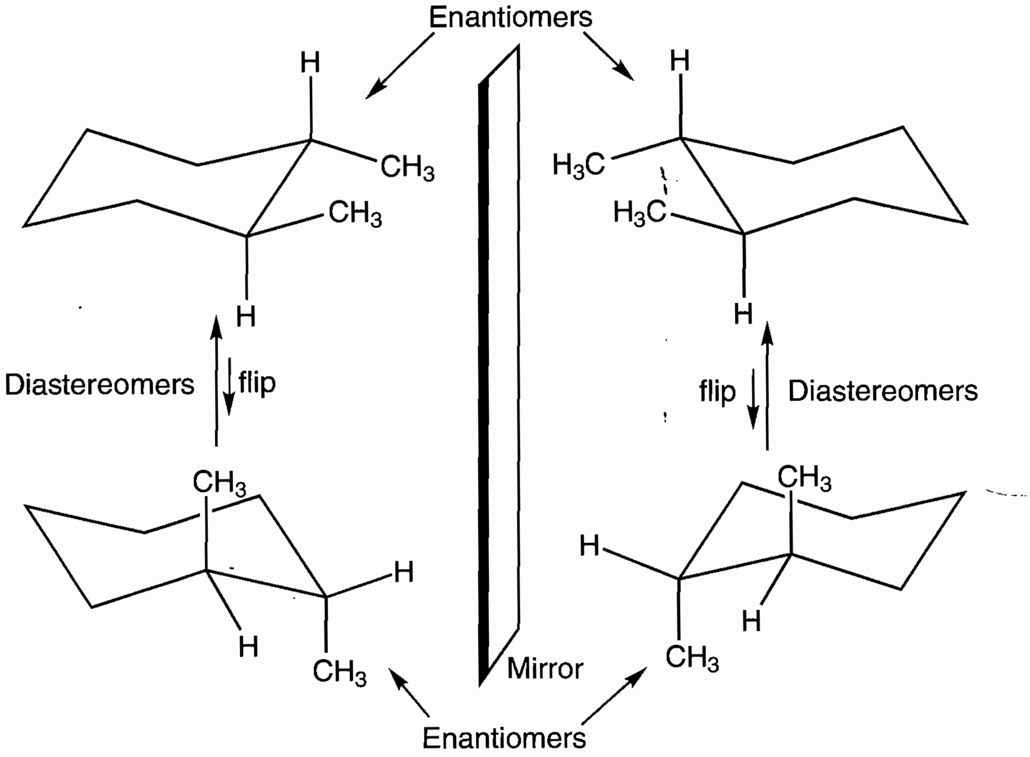


We calculate 2.61 – 1.74 = 0.87 kcal/mol in favor of the isomer with the equatorial isopropyl group.

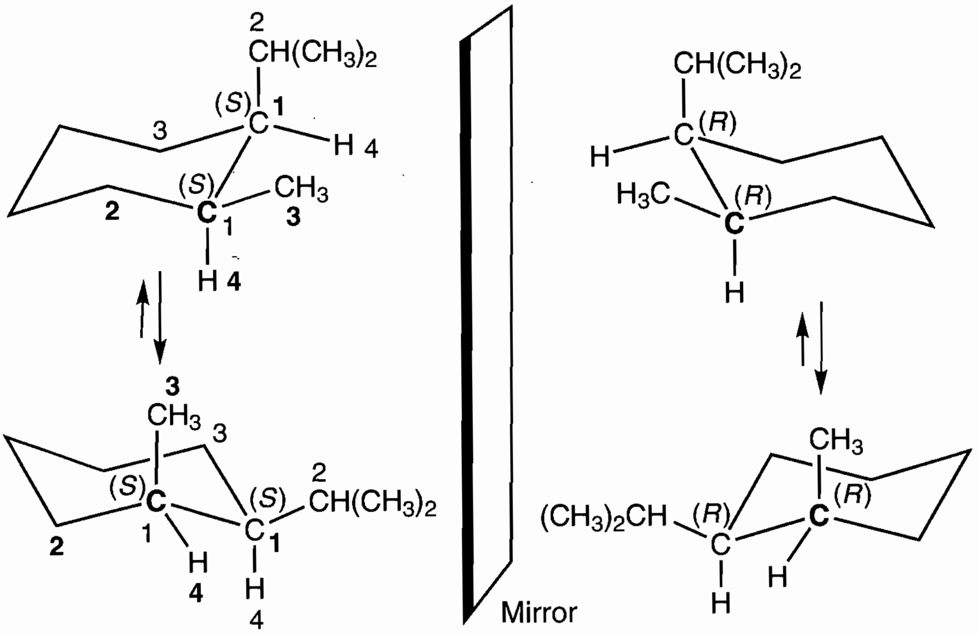
Problem 5.16 As the Newman projection shows, this dihedral angle is 180°.



Problem 5.17 In *trans*-1,2-dimethylcyclohexane, the ring flip converts the diequatorial stereoisomer into the diaxial form. These two molecules are conformational diastereomers, not enantiomers. There can be no racemization in this ring flip. Be certain you see the difference between this process and that shown in Figure 5.39 for similar ring flipping of *cis*-1,2-dimethylcyclohexane.

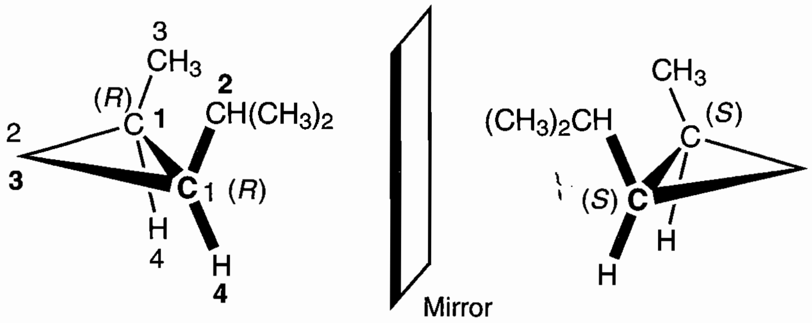


Problem 5.18 The two stereogenic carbons are shown in bold and lightface. The priorities used to determine (*R*) or (*S*) are also shown in bold and lightface, as is appropriate for each carbon.

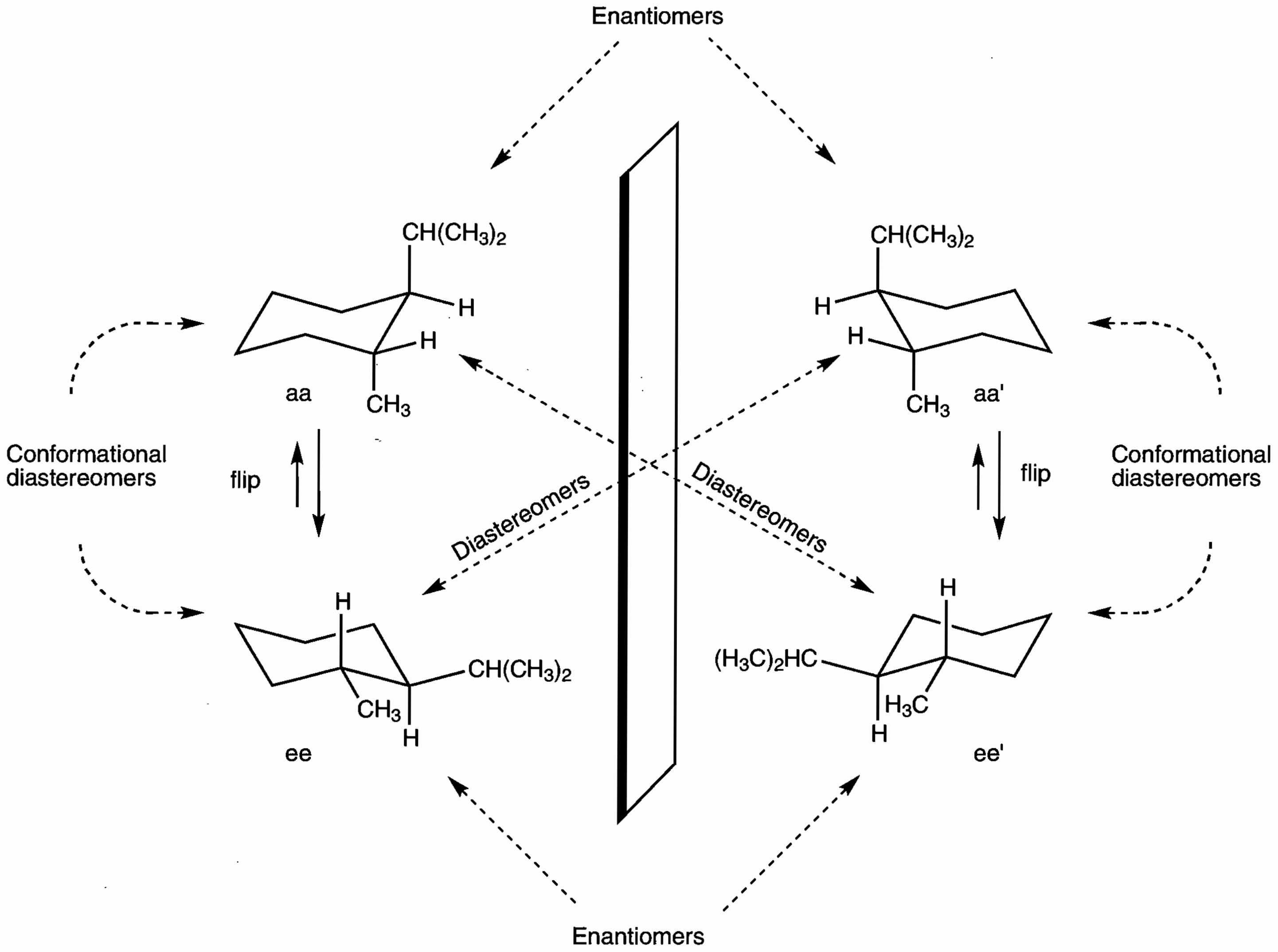


(continued)

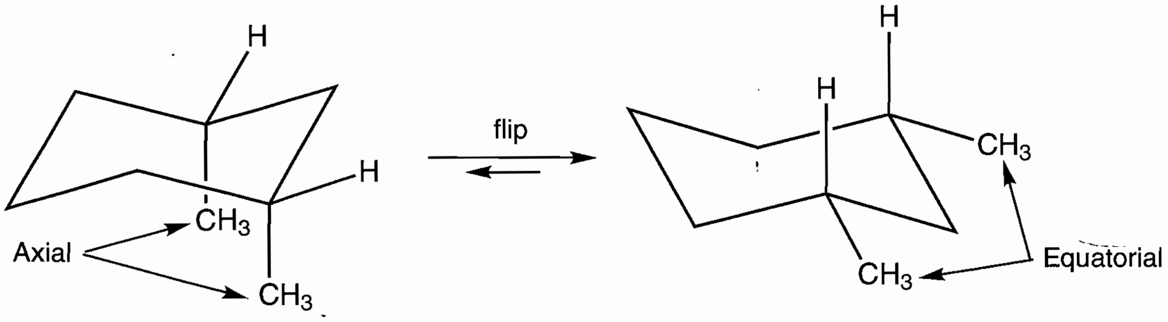
Problem 5.18 *(continued)*



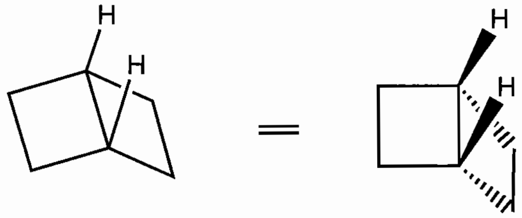
Problem 5.19 The axial, axial (aa) conformation of (1*S*,2*R*)-*trans*-1-isopropyl-2methylcyclohexane is chiral. Its enantiomer is the axial, axial (aa′) conformation of (1*R*,2*S*)-*trans*-1-isopropyl-2-methylcyclohexane. The diequatorial isomers (ee and ee′) are enantiomers. The aa and ee′ isomers are diastereomers, as are the aa′ and the ee molecules. Cyclohexanes aa and ee are diastereomers, but they can be interconverted by rotation around sigma bonds (ring flip). So they are conformational diastereomers. The aa′ and ee′ isomers are also conformational diastereomers for the same reason.



Problem 5.21 Table 5.3 shows that a cyclohexane with an equatorial methyl group is favored over a cyclohexane with an axial methyl group by 1.74 kcal/mol. In this ring flip, two equatorial methyl groups interconvert with two axial methyl groups. Accordingly, we expect the diequatorial isomer to be favored by at least 2 × 1.74 = 3.48 kcal/mol. There will be an additional serious destabilizing interaction between the two 1,3-diaxial methyl groups. The total energy difference between the two is about 5.5 kcal/mol.

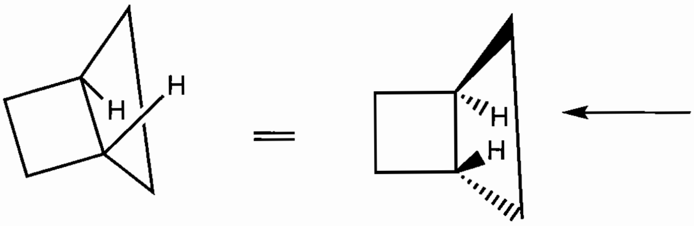


Problem 5.23 The *cis*-bicyclo[2.2.0]hexane can be represented without wedges and dashes or, perhaps more clearly, with the wedges and dashes.



cis-Bicyclo[2.2.0]hexane

The trans isomer is more difficult to represent. It certainly is painful to the mind's eye. Perhaps you can see why it has never been isolated. The connection between the two atoms coming off the ring is too stretched.



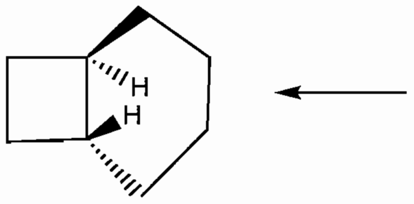
Trans connection requires a long bond between the two atoms coming off the ring

trans-Bicyclo[2.2.0]hexane

(continued)

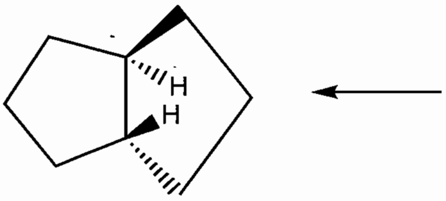
Problem 5.23 *(continued)*

There are two fused bicyclooctanes. One is *trans*-bicyclo[4.2.0]octane. It is a stable molecule because there are two additional carbons connecting the atoms that connect to the four-membered ring. This significantly reduces the ring strain.


Trans connection has two additional carbons between the two atoms coming off the ring

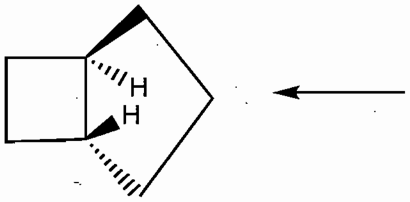
trans-Bicyclo[4.2.0]octane

The other bicyclooctane isomer is a [3.3.0] structure. The drawing of *trans*-bicyclo[3.3.0]octane shows that the extra carbon allows for an easier connection between the atoms coming off the ring.


Trans connection has an extra carbon between the two atoms coming off the ring

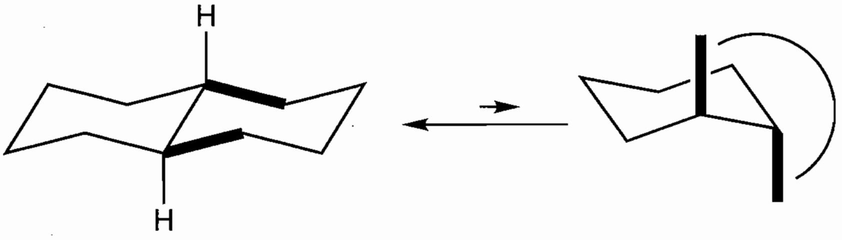
trans-Bicyclo[3.3.0]octane

A fused four-membered ring and five-membered ring gives bicyclo[3.2.0]heptane. The trans fused ring has the ability to make a connection between the trans atoms coming off the ring. This molecule is 24 kcal/mol higher in energy than its cis isomer. There is ring strain owing to the presence of the four-membered ring. But it has been isolated.


Trans connection has an extra carbon between the two atoms coming off the ring

trans-Bicyclo[3.2.0]heptane

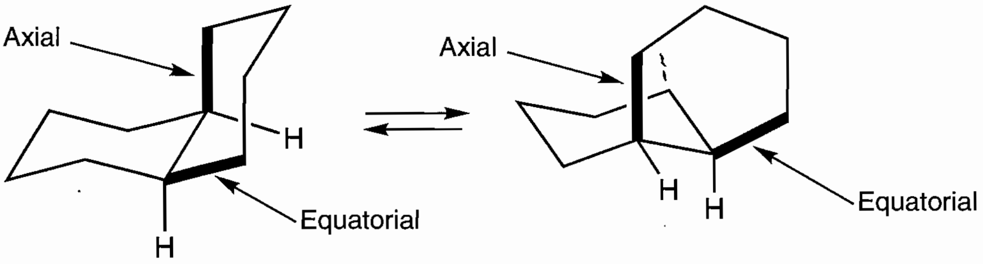
Problem 5.24 Get out your models! In the trans compound, ring flip requires that the second ring be connected through a pair of axial bonds. There are not enough atoms in the chain to do this.



Too long a distance to span

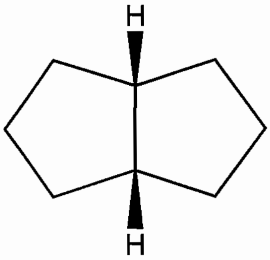
For this molecule to "flip," the two darkened bonds must become axial; it is not possible to connect the second ring in this way

By contrast, in the cis compound, the junction is made through one axial and one equatorial bond. Ring flip interchanges these two and is quite easy.

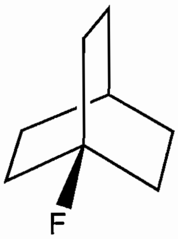


Problem 5.26 The directions for constructing bicyclic molecules are in the chapter. In (a), we connect the bridgeheads (always start with the bridgehead atoms) with two three-carbon bridges and one no-carbon bridge. In (b), all the bridges are the same, and in (c), there are a six-carbon bridge, a one-carbon bridge, and a no-carbon bridge. Be careful in this example to note that the bridge junction is trans. In (b), we place the fluorine at the 1-position, the bridgehead. In (c), we count around the longest bridge first, which makes the free cyclopropane position the 9-position.

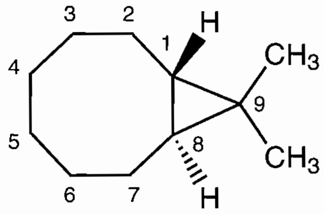
(a)



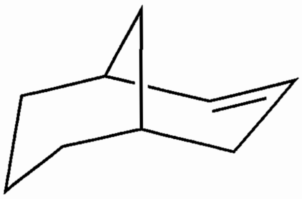
(b)



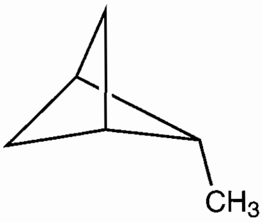
(c)



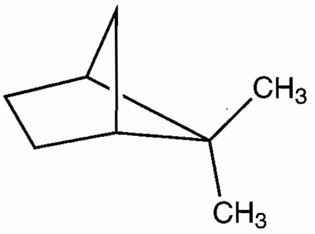
Problem 5.27



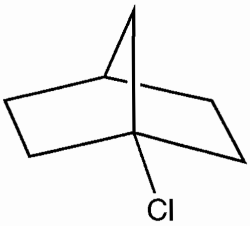
Bicyclo[3.3.1]non-2-ene



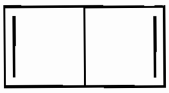
2-Methylbicyclo[1.1.1]pentane



5,5-Dimethylbicyclo[2.1.1]hexane

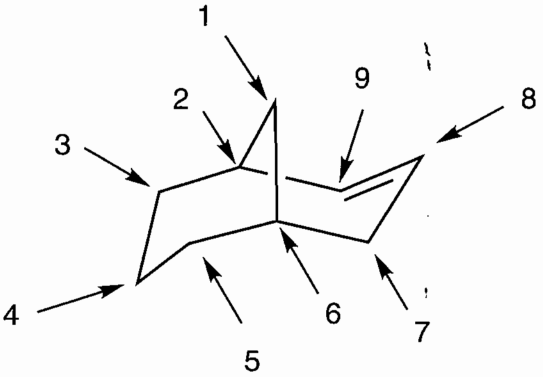


1-Chlorobicyclo[2.2.1]heptane

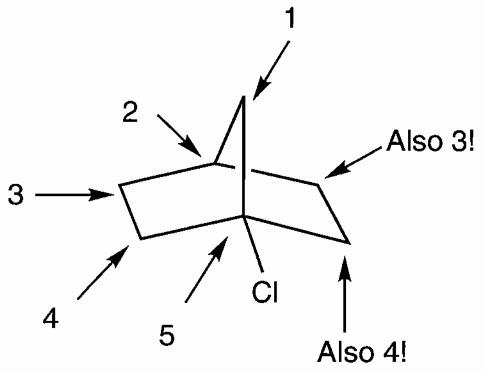


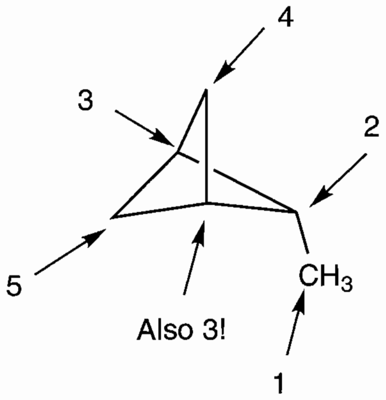
Bicyclo[2.2.0]hexa-2,5-diene

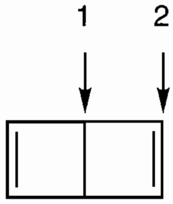
Problem 5.28 In the first molecule, all the carbons are different. There would be nine signals. If that double bond were not present, the situation would be very different. Then the molecule could be factored into two halves—there would be a plane of symmetry, and there would be only four signals.



That is essentially what happens in three of the other molecules. In each, there is at least one plane of symmetry, and several carbons appear in pairs of equivalent positions:



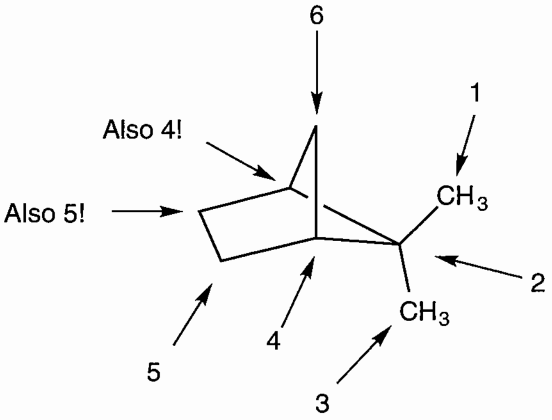




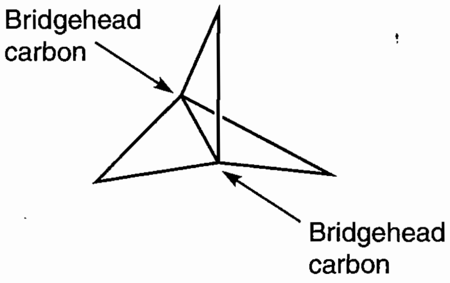
Notice how the presence
of the chlorine makes
2 and 5 and 3 and 4 different

Notice how the presence
of the methyl group
makes 4 and 5 different

The third molecule is the most difficult. The two methyl groups are different (one points toward a CH_2 and the other toward a CH_2—CH_2), but there is still a plane of symmetry, and four carbons appear as two equivalent pairs.

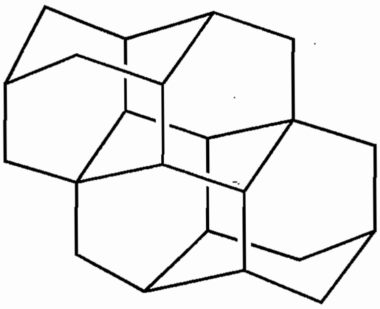


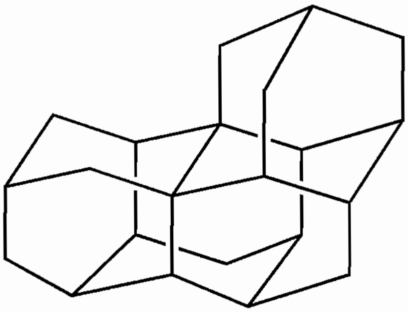
Problem 5.29 This molecule has all sorts of problems. Of course, it contains no fewer than three cyclopropane rings, and that alone will introduce severe strain. However, the factor that differentiates this molecule from the "merely" severely strained is that all four valences of the "bridgehead" carbons are aimed in the same direction! What kind of hybridization can be involved? That's no easy question, and the chemical world has spent quite some effort at puzzling out just why this molecule is as stable as it is. Although that's not a reasonable subject for an introductory book, two things about this problem are important. First, we can see why this molecule is so remarkable. Second, the isolation of this molecule shows how imperfect our understanding of chemistry still is! However, one must admit that it is a pleasure to see challenging curiosities continue to appear. There is much to learn, and many molecular marvels are still hiding from us.

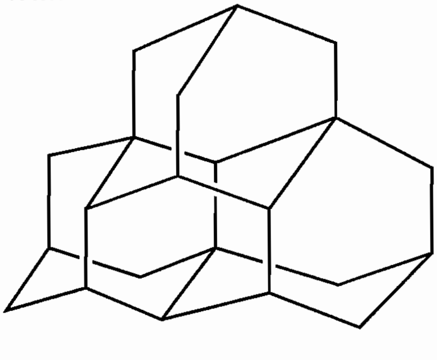


Problem 5.30 The empirical formula of diamond is C.

Problem 5.31 There are three possibilities for tetramantane. This problem is nearly impossible to do without models at this point in your career.


"anti" Form (this is another view of the isomer shown in Fig. 5.70)

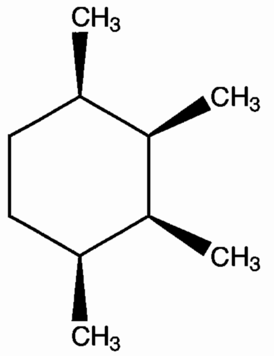

"skew" Form


"iso" Form

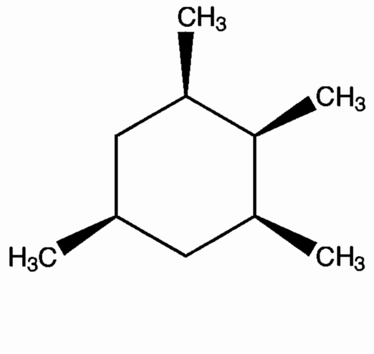
Additional Problem Answers

This chapter deals almost exclusively with the structures of ring compounds, and six-membered rings (cyclohexanes) are examined especially closely. The structural consequences of the ring flip of cyclohexanes (really just a series of rotations around carbon–carbon bonds) are emphasized, and the following problems should give you lots of practice in drawing, flipping, and evaluating substituted cyclohexanes.

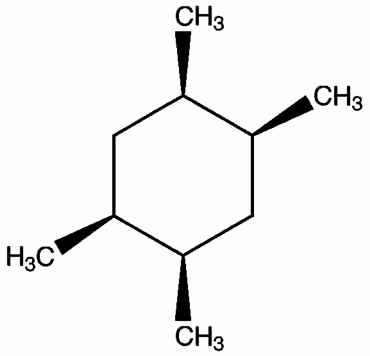
Problem 5.32 The three isomers of all-*cis*-tetramethylcyclohexane are found by trial and error. Start with the 1,2,3,4-tetramethylcyclohexane, then move one methyl group from C(4) to C(5). That gives 1,2,3,5-tetramethylcyclohexane. If we move the C(5) methyl to C(6), that will produce 1,2,3,4-tetramethylcyclohexane again. Next we can try moving two methyl groups. That gives 1,2,4,5-tetramethylcyclohexane.



All-*cis*-1,2,3,4-
tetramethylcyclohexane

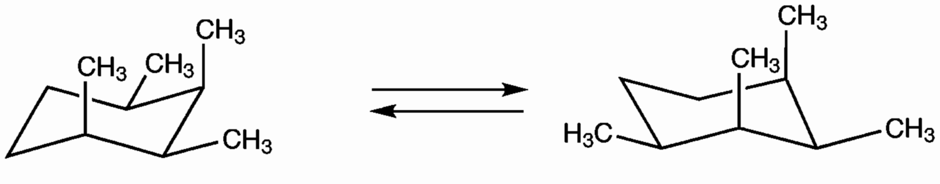


All-*cis*-1,2,3,5-
tetramethylcyclohexane

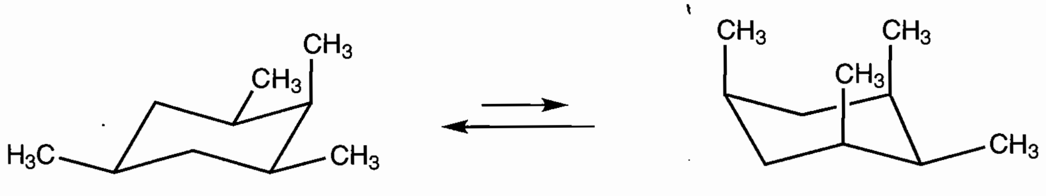


All-*cis*-1,2,4,5-
tetramethylcyclohexane

The chair structure for all-*cis*-1,2,3,4-tetramethylcyclohexane has two methyl groups axial and two methyl groups equatorial. The ring-flipped structure also has two groups axial and two groups equatorial. They have the same stability.

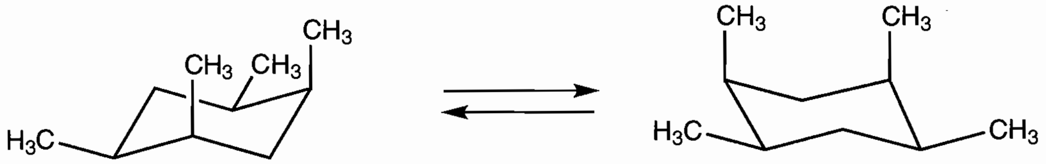


One of the chair structures of all-*cis*-1,2,3,5-tetramethylcyclohexane has three methyl groups equatorial and one methyl group axial. The ring-flipped structure would be much higher in energy because it has three methyls axial and one methyl equatorial.

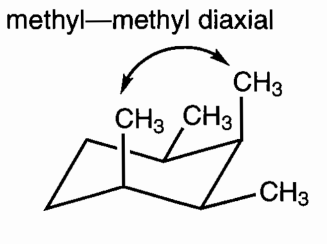


More stable conformation

The chair structures for the all-*cis*-1,2,4,5-tetramethylcyclohexane are also the same energy. Both chair conformations have two methyls axial and two methyls equatorial. They are identical structures.



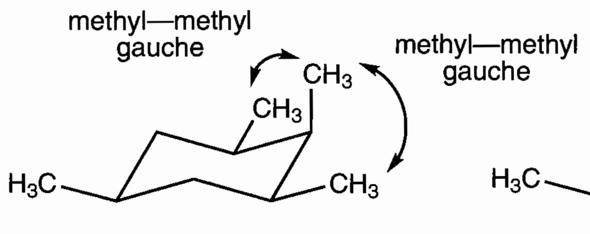
Problem 5.33 Both the 1,2,3,4-tetramethyl and the 1,2,4,5-tetramethyl isomers have two groups axial. The more stable isomer of the 1,2,3,5-tetramethylcyclohexane has only one methyl group axial. In addition, the methyl–methyl 1,3-diaxial interaction induces more van der Waals strain. Another consideration is the number of methyl–methyl gauche interactions. The 1,2,3,4-tetramethyl isomer has three methyl–methyl gauche interactions. Both the 1,2,3,5- and the 1,2,4,5-tetramethylcyclohexane isomers have two methyl–methyl gauche interactions. Therefore, the most stable isomer would be the all-*cis*-1,2,3,5-tetramethylcyclohexane.



two axial methyls

one methyl—methyl diaxial

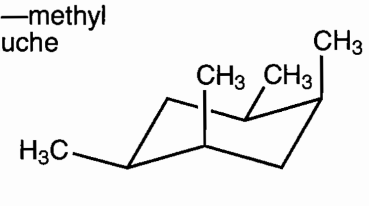
three methyl—methyl gauche



one axial methyl

no methyl—methyl diaxial

two methyl—methyl gauche

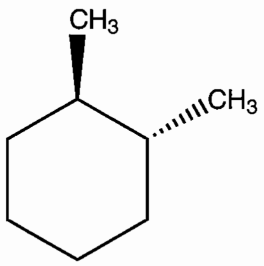


two axial methyls

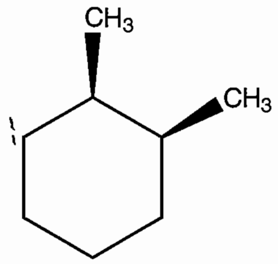
one methyl—methyl diaxial

two methyl—methyl gauche

Problem 5.34



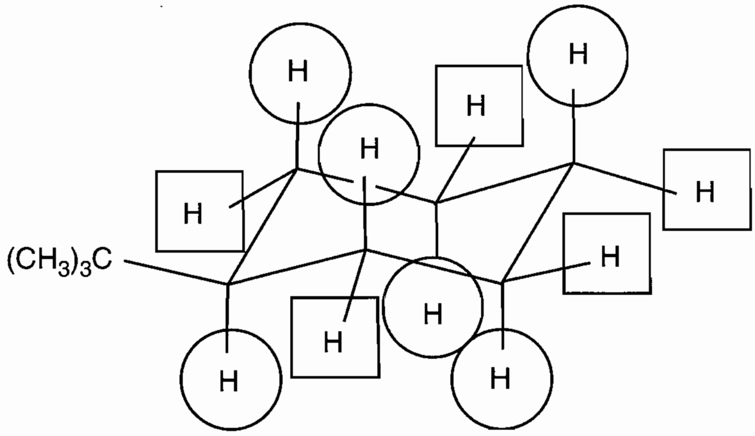
(*R*,*R*)-1,2-Dimethylcyclohexane



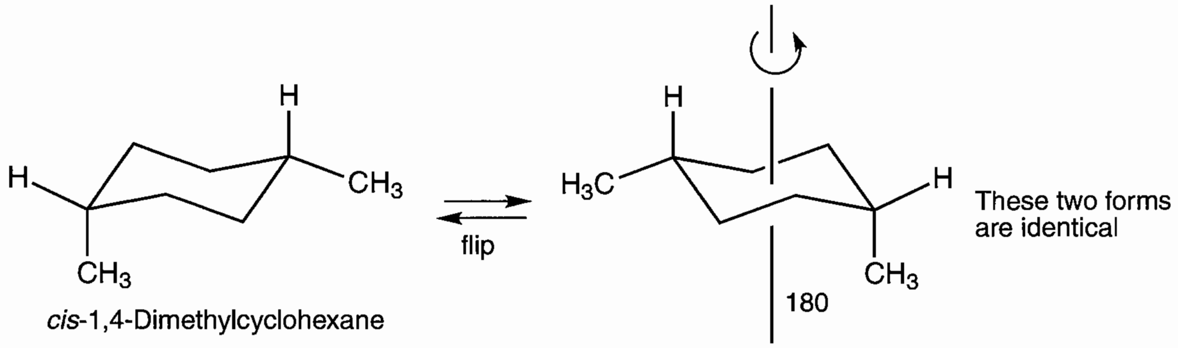
(*R*,*S*)-1,2-Dimethylcyclohexane

The bottle must contain (*R*,*S*)-1,2-dimethylcyclohexane because the (*R*,*R*) isomer would be optically active. The (*R*,*S*) isomer, however, is a meso molecule and therefore achiral. It would have no optical activity.

Problem 5.35



Problem 5.36 In the cis isomer, one methyl group must be equatorial and the other axial. Ring flip of one isomer produces an identical molecule. To see this, rotate the right-hand structure 180°, as shown.

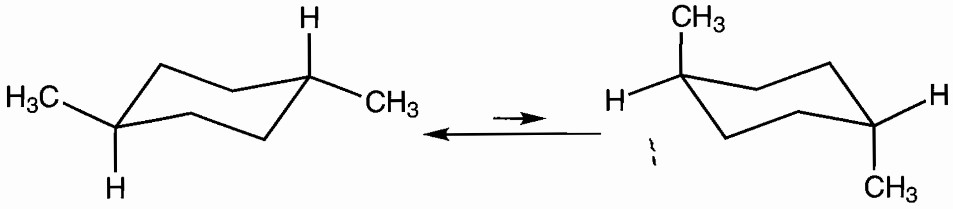


These two forms are identical

cis-1,4-Dimethylcyclohexane

In the trans isomer, both methyl groups are equatorial or both are axial. The molecule with the two groups equatorial will be far more stable.

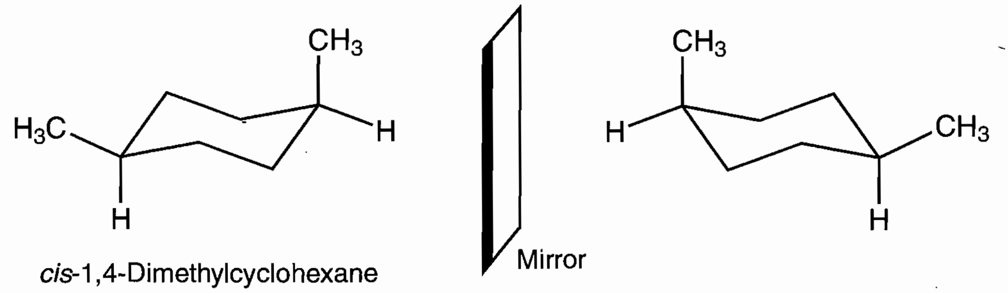
These two forms are diastereomers



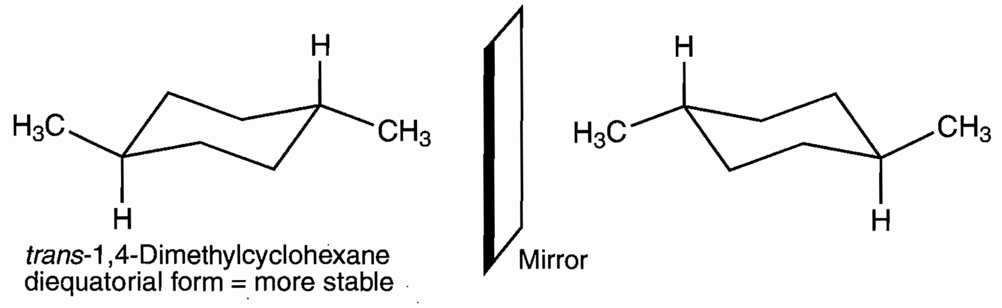
trans-1,4-Dimethylcyclohexane
diequatorial form = more stable

Diaxial form = less stable

Neither the cis nor trans compound is chiral. Both mirror images are superimposable on the original.



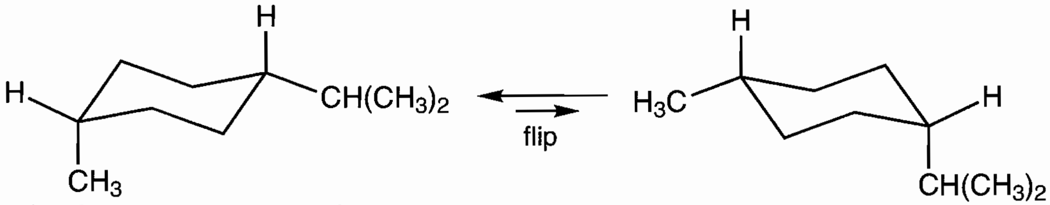
cis-1,4-Dimethylcyclohexane



trans-1,4-Dimethylcyclohexane
diequatorial form = more stable

Problem 5.37 In the cis form, it will be the diastereomer with the large isopropyl group equatorial that is favored.

These two forms are conformational diastereomers



cis-1-Isopropyl-4-methylcyclohexane
(more stable diastereomer)

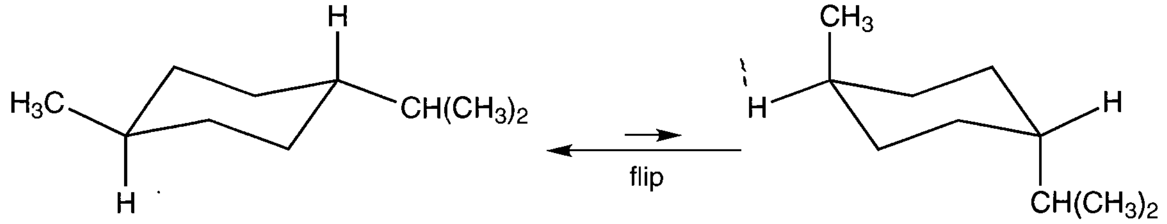
(less stable diastereomer)

(continued)

Problem 5.37 *(continued)*

Similarly, in the trans form, it is the diastereomer with both groups equatorial that is more stable.

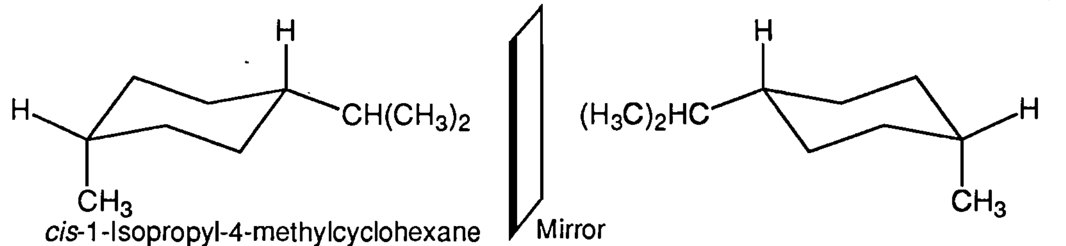
These two forms are conformational diastereomers



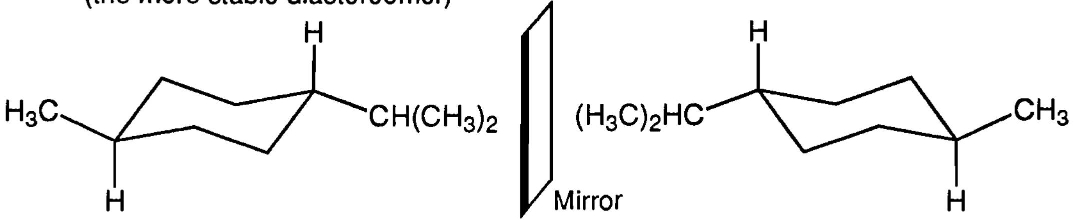
trans-1-Isopropyl-4-methylcyclohexane (more stable diastereomer)

This diaxial form is less stable

Once again, neither molecule is chiral, as in each case, the mirror image is superimposable on the original.

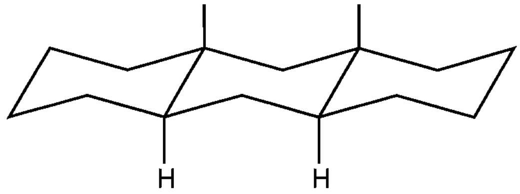


cis-1-Isopropyl-4-methylcyclohexane (the more stable diastereomer)

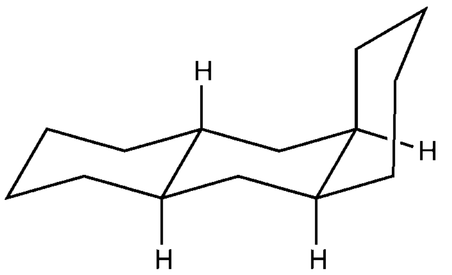


trans-1-Isopropyl-4-methylcyclohexane (the more stable diastereomer)

Problem 5.38



1



2

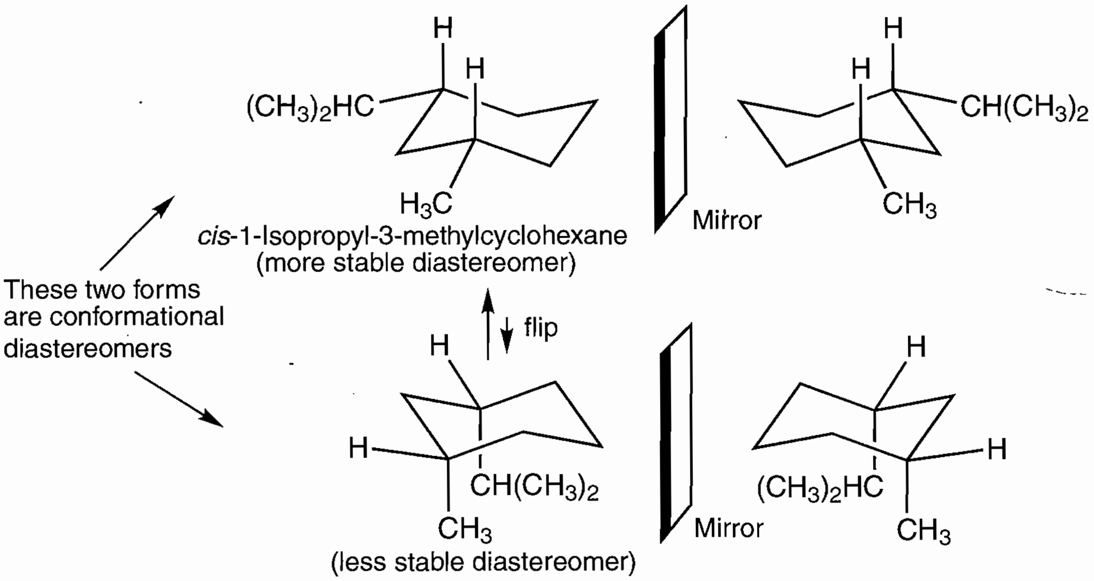
These molecules are diastereomers. There are four stereogenic carbons in each, and only one of the stereogenic carbons is switched (S to R) comparing compound **1** to compound **2**.

Isomer **1** is more stable than isomer **2** because isomer **1** has no axial groups. Isomer **2** has one carbon in an axial position.

Isomer **1** is achiral. It has a plane of symmetry. Isomer **2** is chiral. It has no plane or point of symmetry.

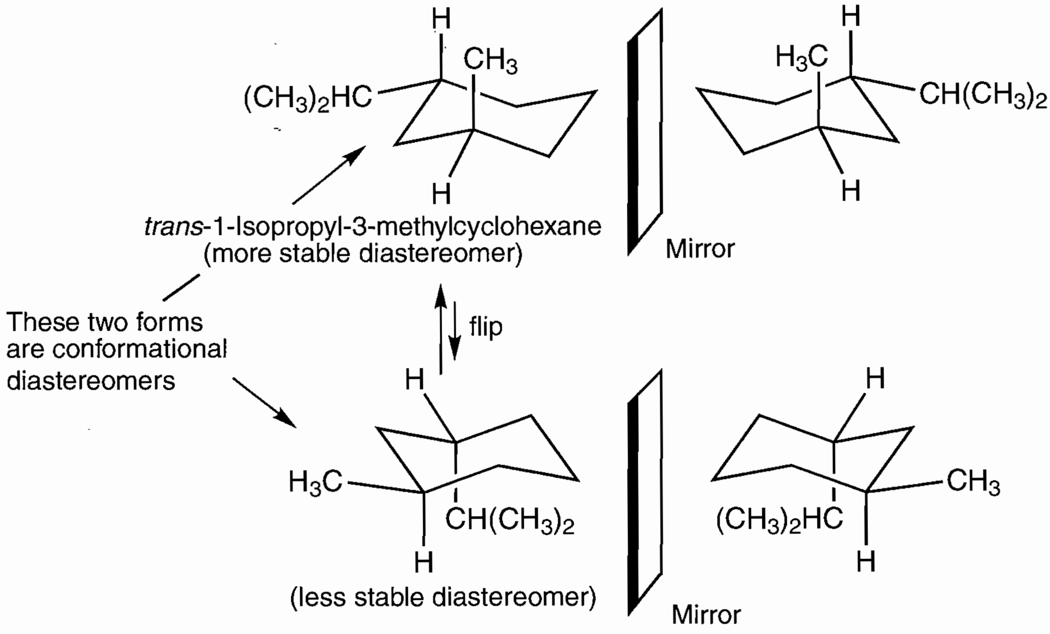
Problem 5.39 The more stable conformation of *cis*-1-isopropyl-3-methylcyclohexane is the one with the two alkyl groups equatorial. Ring flip generates the less stable conformation with the two alkyl groups axial. Each of these two diastereomers is chiral.

Neither mirror image is superimposable on the original—both diastereomers are chiral.



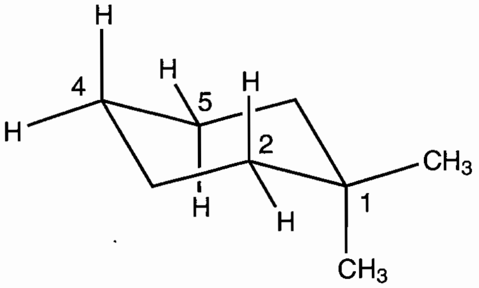
The situation is the same in the trans molecule. The more stable conformation has the large ispropyl group equatorial. Ring flip generates the less stable conformation with the large isopropyl group axial. Each of these two diastereomers is chiral.

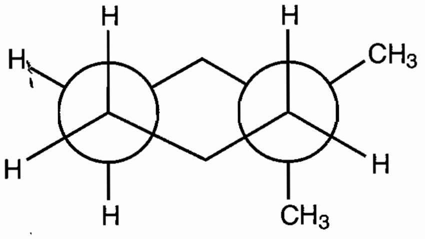
Neither mirror image is superimposable on the original—both diastereomers are chiral.



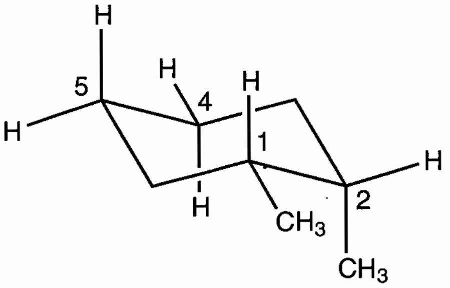
Problem 5.40

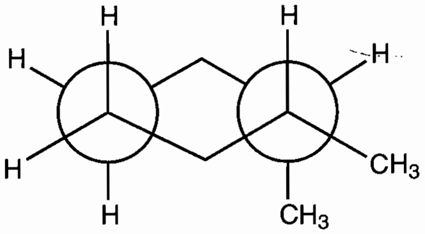
(a)



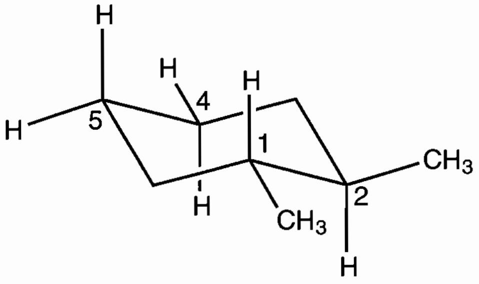


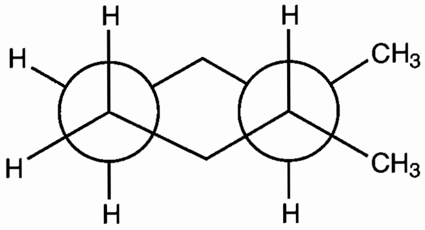
(b)



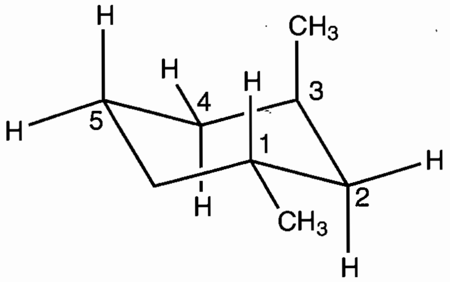


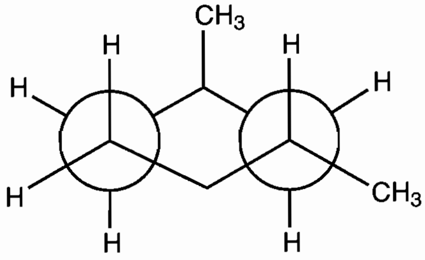
(c)





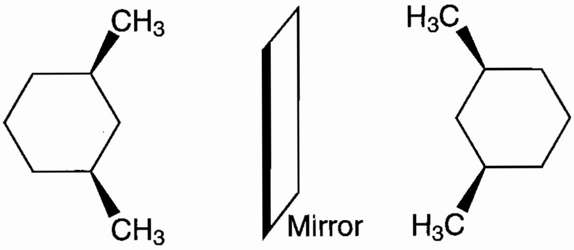
(d)



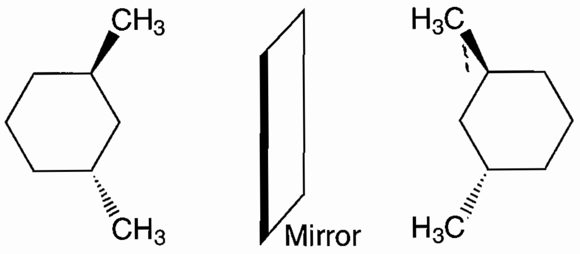


Problem 5.41

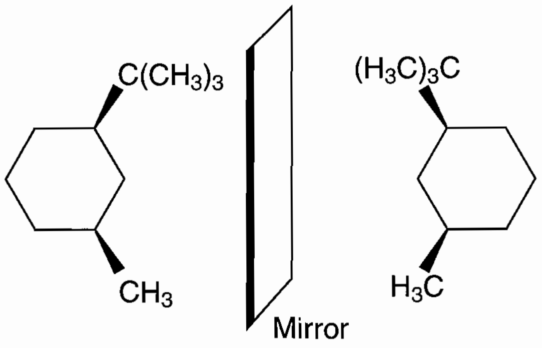
(a) This molecule is achiral as the mirror image is superimposable on the original.



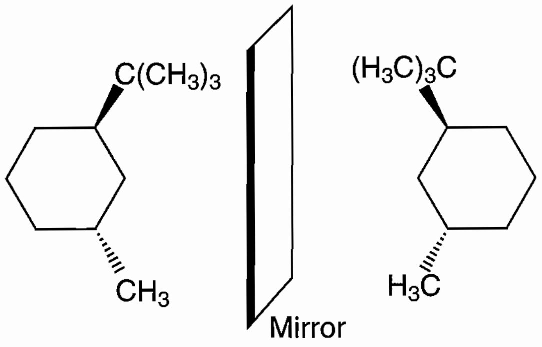
(b) This one is chiral—the mirror image is nonsuperimposable.



(c) This molecule is chiral. Its mirror image is nonsuperimposable. There is no plane of symmetry in the molecule.



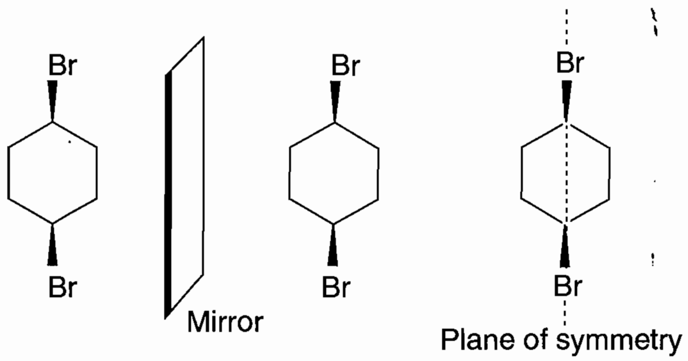
(d) This molecule is chiral. Its mirror image is nonsuperimposable. There is no plane of symmetry in the molecule.



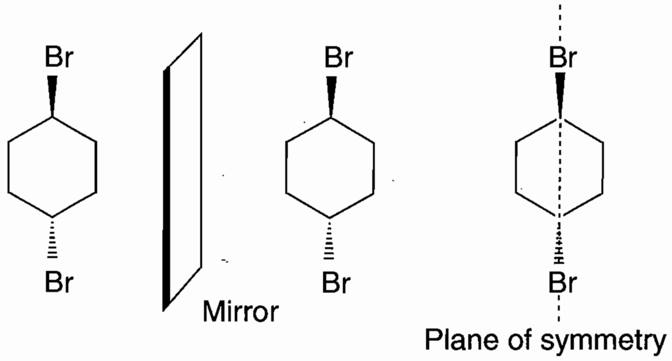
(continued)

Problem 5.41 *(continued)*

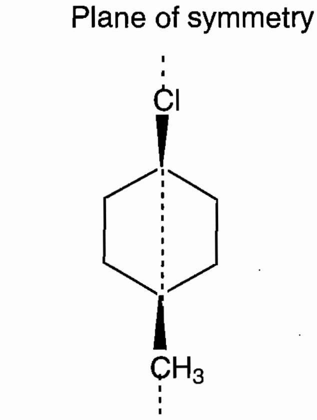
(e) *cis*-1,4-Dibromocyclohexane is achiral. Its mirror image is identical to the original. There is a plane of symmetry in the molecule.



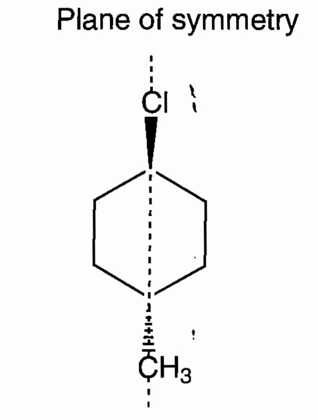
(f) *trans*-1,4-Dibromocyclohexane is achiral. Its mirror image is identical to the original. There is a plane of symmetry in the molecule.



(g and h) *cis*-1-Chloro-4-methylcyclohexane and *trans*-1-chloro-4-methylcyclohexane are both achiral. They both have a plane of symmetry in the molecule.



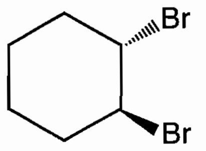
cis-1-Chloro-4-methyl cyclohexane

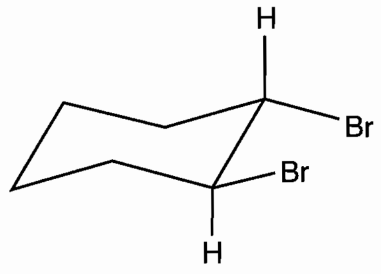


trans-1-Chloro-4-methyl cyclohexane

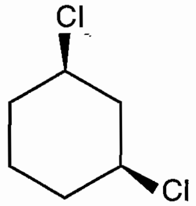
Problem 5.42

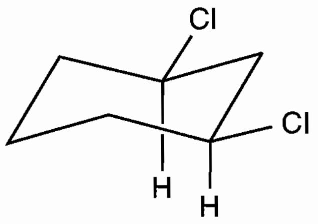
(a)



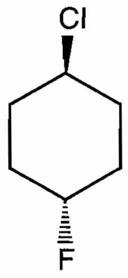


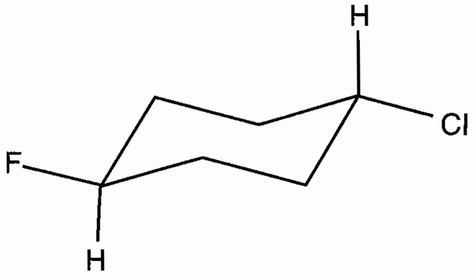
(b)





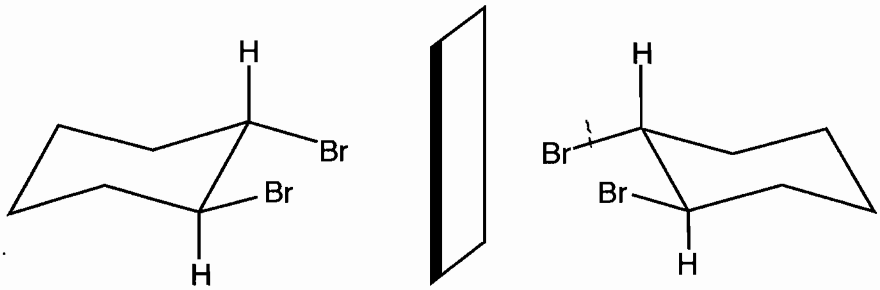
(c)





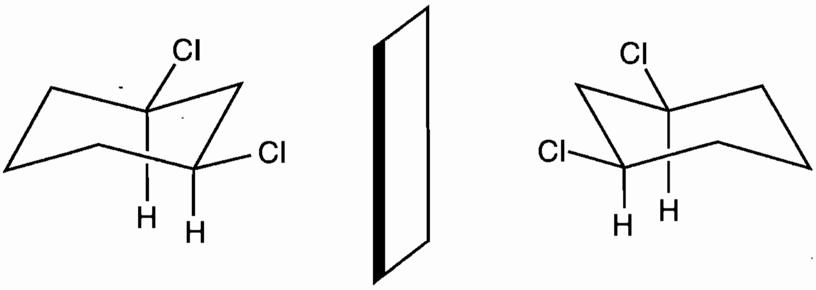
Problem 5.43

(a)



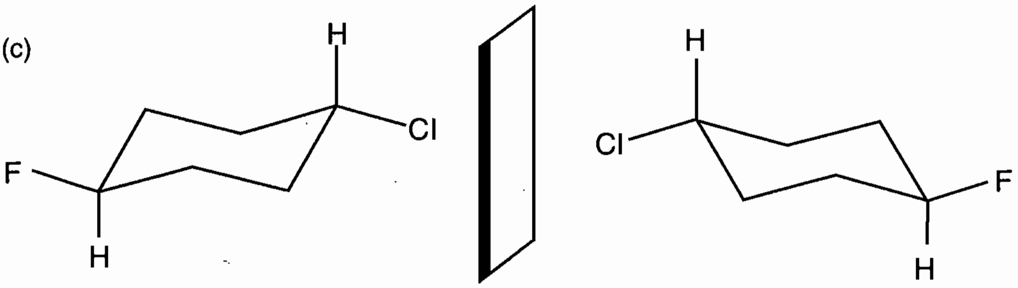
nonsuperimposable—chiral

(b)



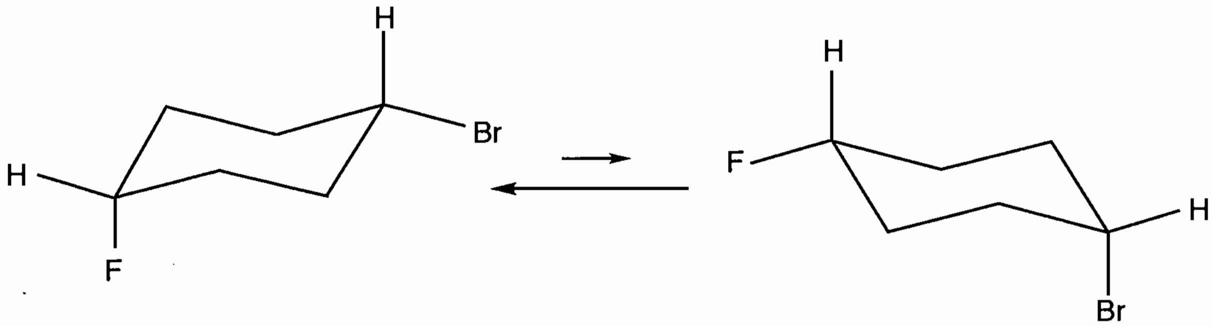
superimposable—achiral

(c)



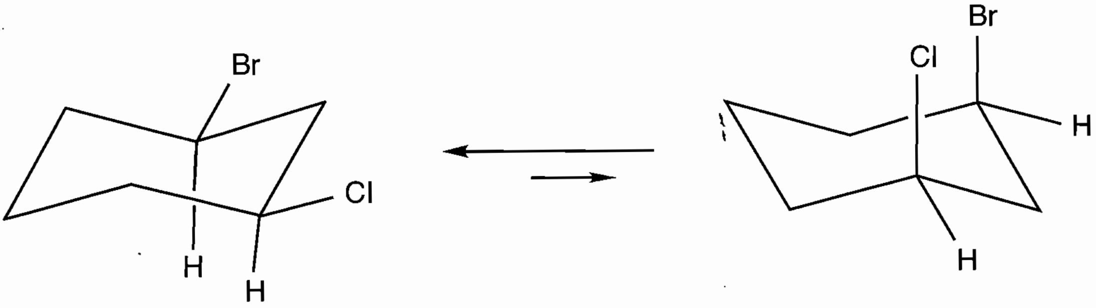
superimposable—achiral

Problem 5.44

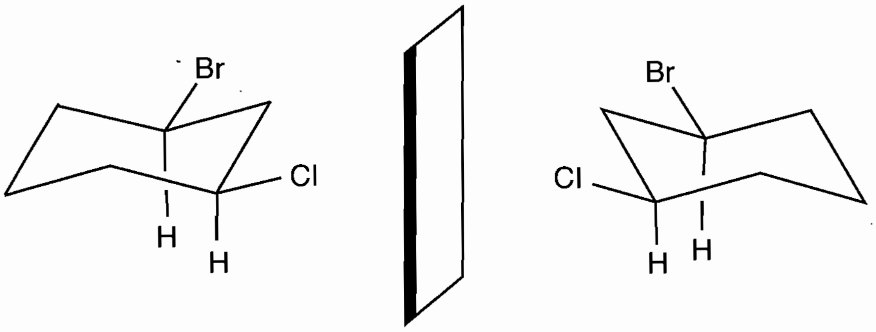


On the left, the larger Br is equatorial. Thus, this form is favored at equilibrium.

Problem 5.45

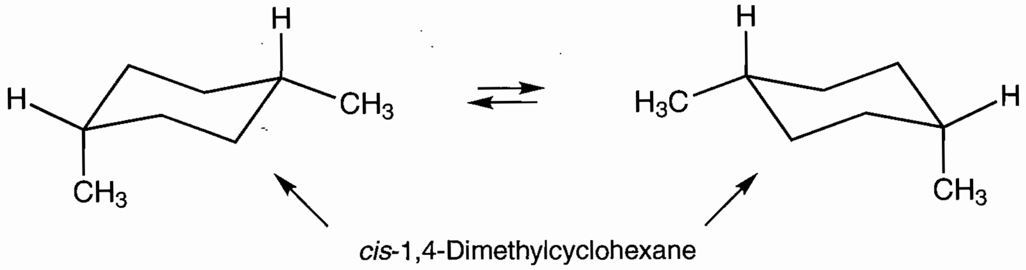


On the left, both large groups are equatorial, and this form is far more stable than the flipped form on the right. It is also chiral.

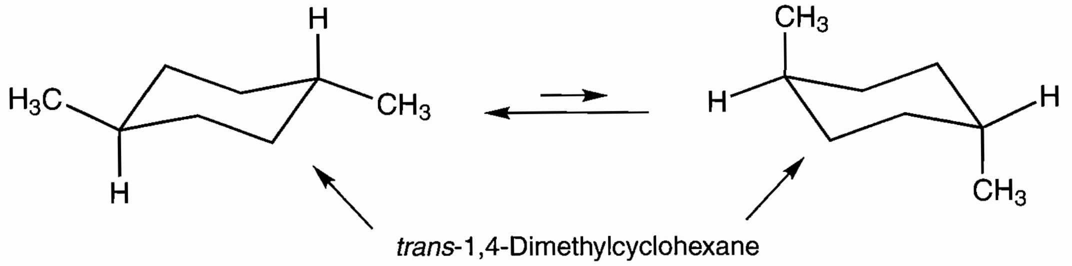


nonsuperimposable—chiral

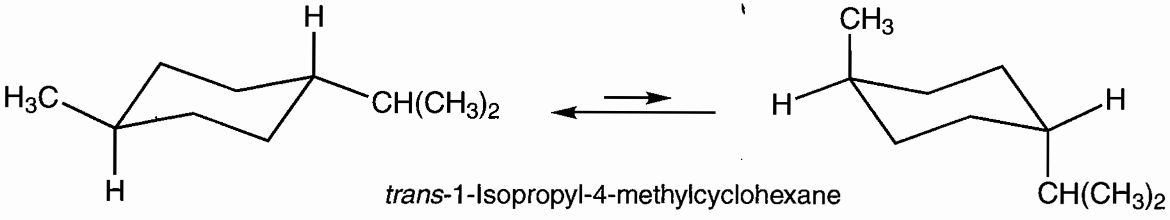
Problem 5.46 *cis*-1,4-Dimethylcyclohexane “flips” into itself. Thus there can be no energy difference between the two isomers.



In *trans*-1,4-dimethylcyclohexane, the molecule with two equatorial methyl groups will be more stable by twice the energy difference between equatorial and axial methylcyclohexane, or 2 × 1.74 = 3.48 kcal/mol (Table 5.3, p. 207).

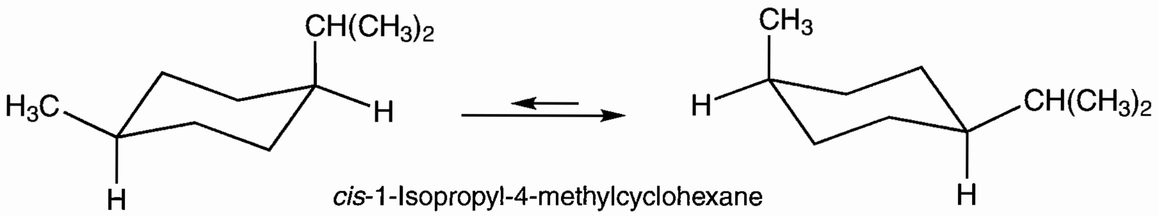


Problem 5.47 Let's do the trans compound first. In this molecule, both substituents are equatorial or both are axial. Table 5.3 tells us that an axial methyl group is destabilizing by 1.74 kcal/mol and that an axial isopropyl group is destabilizing by 2.61 kcal/mol. Accordingly, the chair with both groups equatorial will be more stable than the chair with both groups axial by the sum of these numbers, 4.35 kcal/mol.



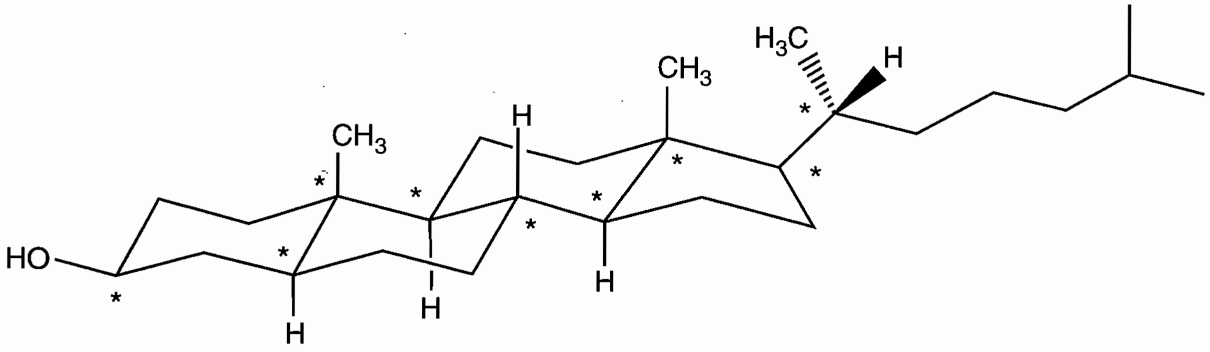
trans-1-Isopropyl-4-methylcyclohexane

In the cis isomer of 1-isopropyl-4-methylcyclohexane, one chair has the methyl group axial, and the other has the isopropyl group axial. The right-hand diastereomer will be more stable by 2.61 – 1.74 = 0.87 kcal/mol. It is energetically more favorable to have the larger isopropyl group equatorial.



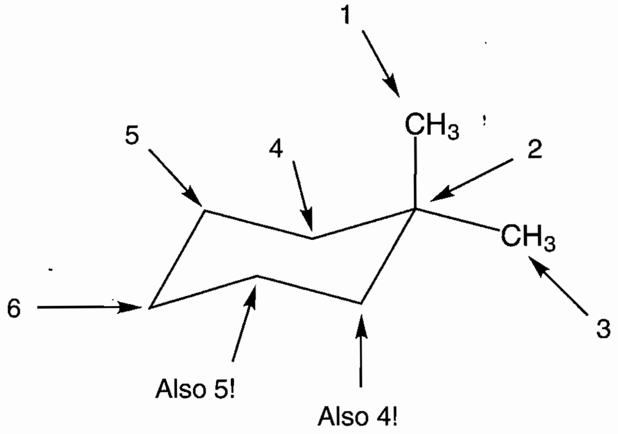
cis-1-Isopropyl-4-methylcyclohexane

Problem 5.48 Stereogenic atoms (nine, all carbons) are shown with an asterisk.

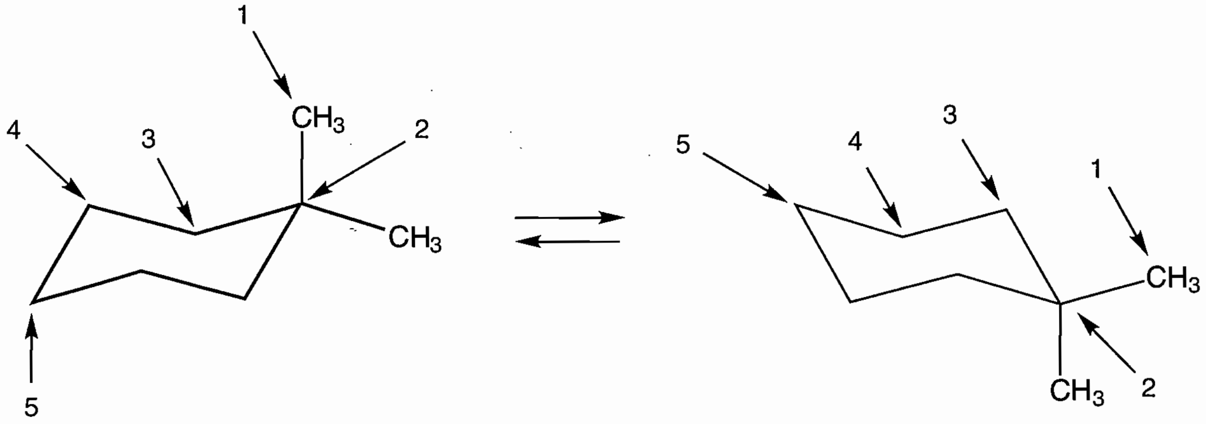


Problem 5.49 The question asks you to decide first what effect the increase in temperature can have. Cyclohexane chairs interconvert at room temperature and above, but the chair–chair flip can be stopped at low temperature. It would therefore seem that we must consider only one chair at low temperature and both chairs at high temperature.

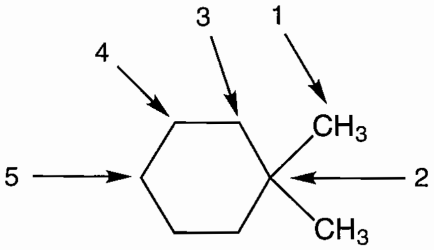
(a) Low temperature. The chair form will be as follows, and there will be two different methyl groups: one axial, the other equatorial. There will be a total of six signals for the six different carbons.



(b) High temperature. Now the two possible chairs will interconvert, and we must consider the averaged spectrum. There will now be only one methyl group, as the ring flip interconverts axial and equatorial positions.

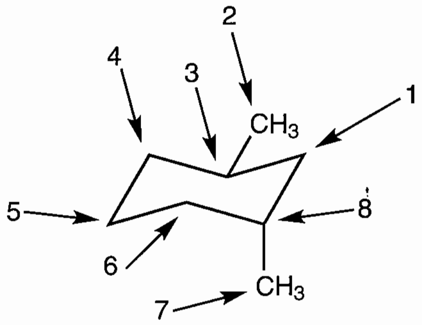


For our tally of different carbons, we can even use the averaged, flat structure:

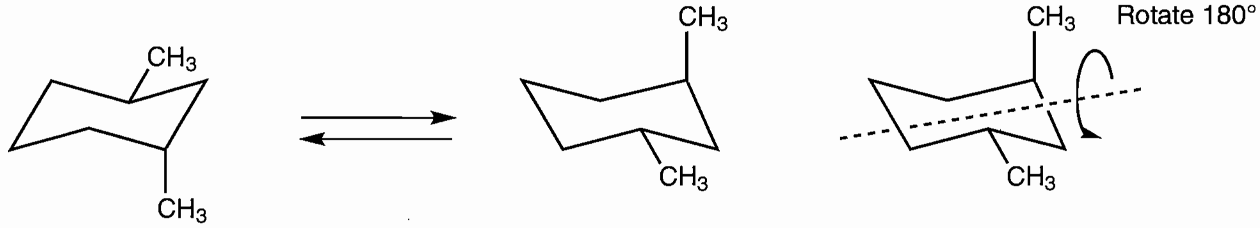


Problem 5.50

(a) *trans*-1,3-Dimethylcyclohexane will have eight different carbons at low temperature. Perhaps you can see that there are no two carbons that are equivalent when this molecule is "frozen" in one conformation. There is no symmetry.

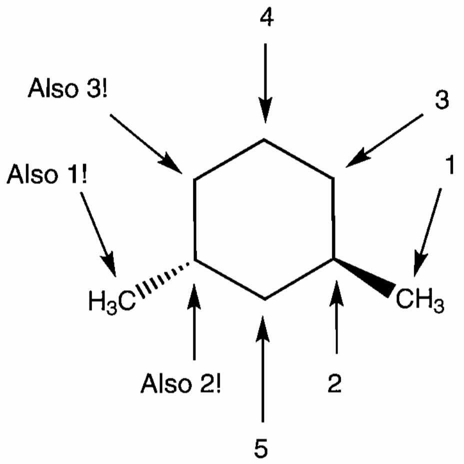


(b) At high temperature, the ring flipping will be fast, and that will make the methyl groups equivalent. If you look carefully at the two conformations **A** and **B** of *trans*-1,3-dimethylcyclohexane, you will see that they are identical. Rotate structure **B** 180° about the axis shown, and you will see that it is the same as **A**.

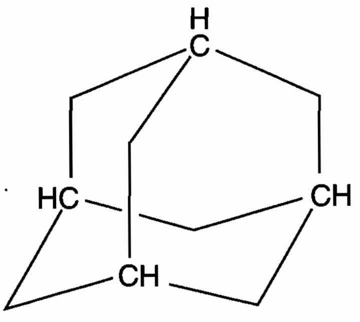


A **B** **B**

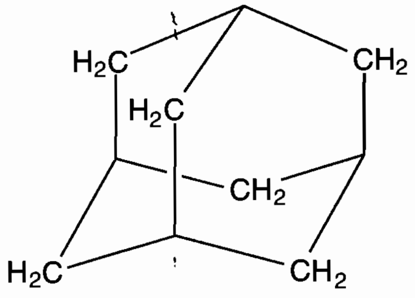
The drawing of the flat structure (top view with perspective) should make this point clearer. There will be five ^{13}C NMR signals at high temperature.



Problem 5.51 This one may also be hard to see. Adamantane has only two different carbons, the CH and the CH_2. Symmetry makes the four methine groups equivalent and the six methylene groups equivalent.



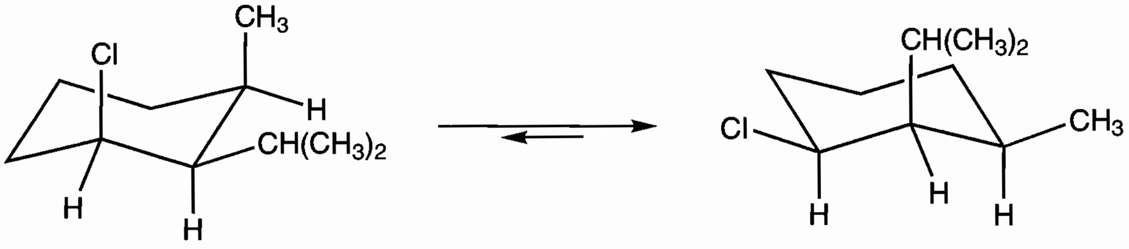
All CH groups
are the same



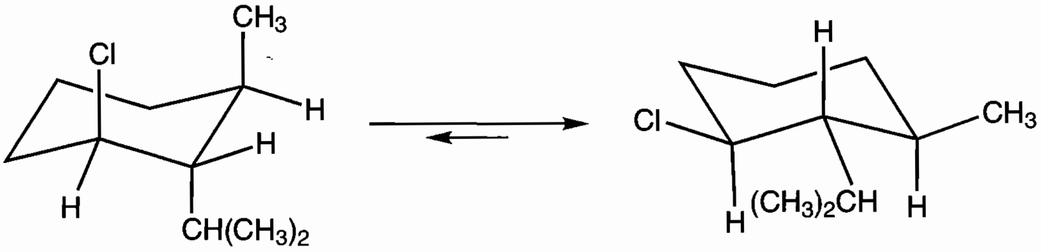
All CH_2 groups
are the same

Problem 5.52

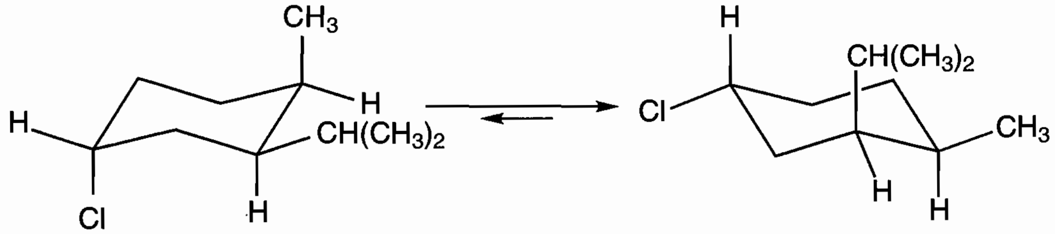
(a) We start with a tough call. The conformation with two groups equatorial (Cl and CH_3) is the more stable one, even though the largest group, isopropyl, must be axial.



(b) This one is easy. The conformation with all three groups equatorial is the more stable one.



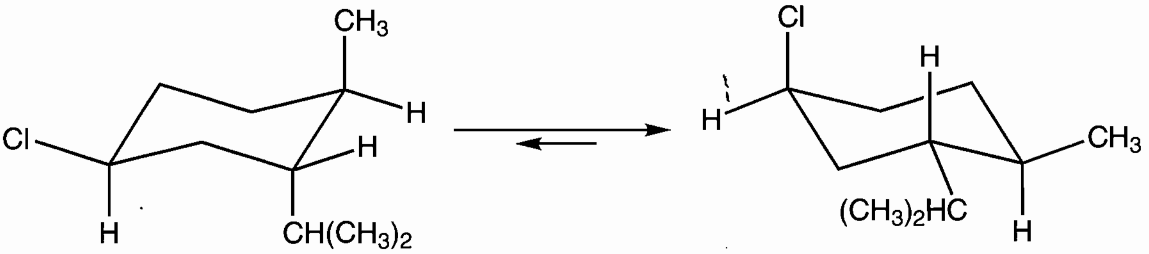
(c) Once again, the conformations with two groups equatorial are more stable than the conformations with two groups axial. Note that in (c), each conformational diastereomer has a gauche isopropyl–methyl interaction.



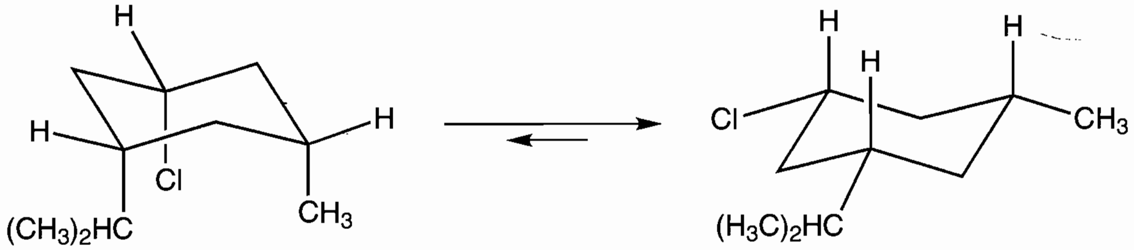
(continued)

Problem 5.52 *(continued)*

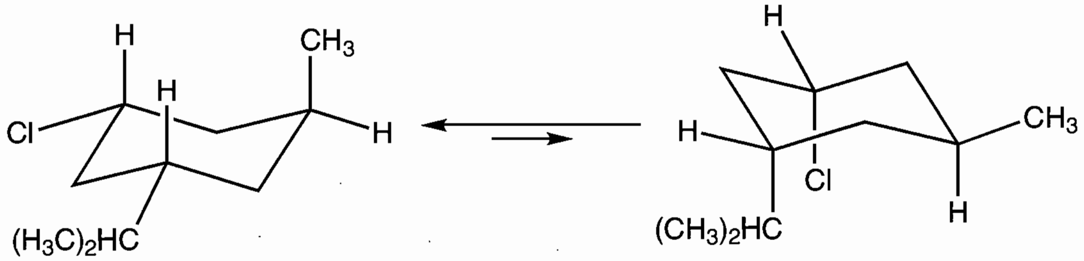
(d) Here the conformational diastereomer with isopropyl and methyl equatorial is favored, despite the gauche isopropyl–methyl interaction.



(e) The conformation with all three groups equatorial is the more stable one.



(f) The conformation with two groups equatorial is the more stable one.



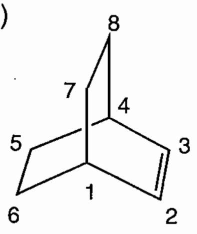
Problem 5.53

(a) All three bridges have two carbons, so the base name is bicyclo[2.2.2]octene. We start counting at the bridgehead and give the double bond the lowest possible number, so the final name is bicyclo[2.2.2]oct-2-ene.

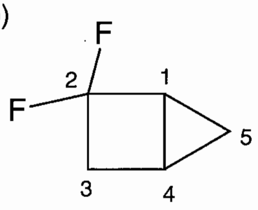
(b) We count first around the larger ring, so this compound is 2,2-difluorobicyclo[2.1.0]pentane.

(c) This compound is a bicyclo[3.1.1]heptene. We count around the largest bridge first and give the OH the lowest number. The molecule is bicyclo[3.1.1]hept-3-en-2-ol.

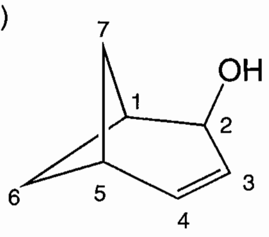
(a)



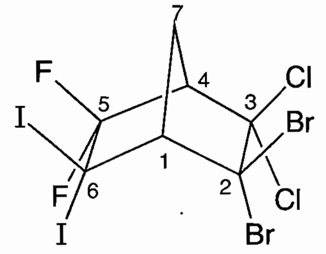
(b)

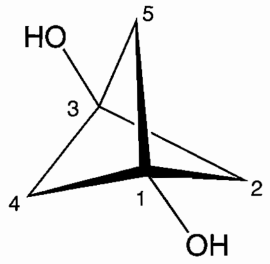


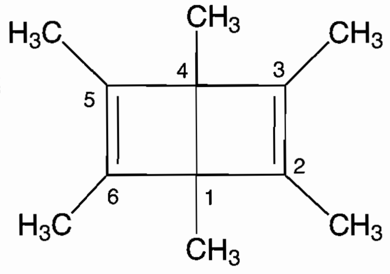
(c)



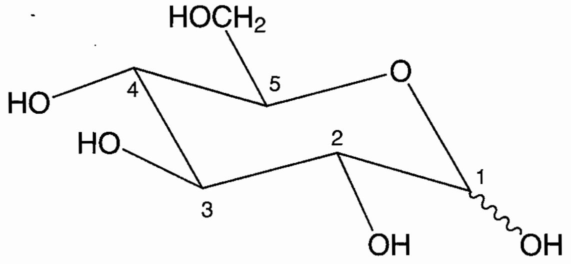
Problem 5.54 In (a), (b), and (c), remember to start counting at the bridgehead. In (c), no numbers are necessary for the methyl groups because this is the only possible hexamethyl compound.



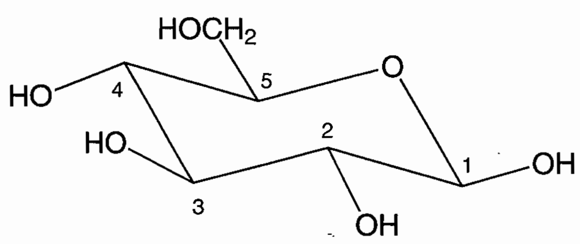


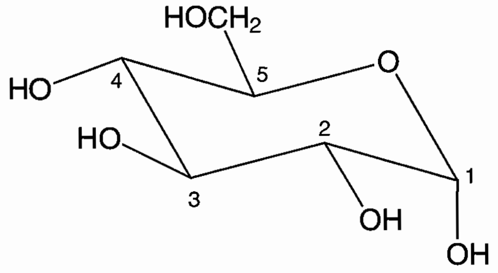


Problem 5.55 First, draw a chair with the oxygen taking the place of one of the ring carbons of cyclohexane. Then add the substituents, putting them all in the more favorable equatorial positions.

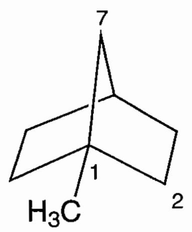


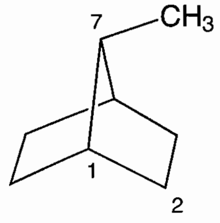
The OH at C(1) can be either "up," in the equatorial position, or "down," in the axial position.

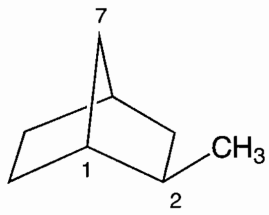




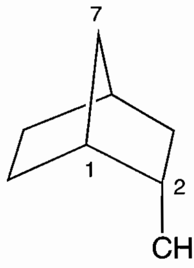
Problem 5.56 There are three different carbons in bicyclo[2.2.1]heptane, and a methyl group could be attached to each of them. At the 1- or 7-position, there is only one possible way of attaching a group, but at the 2-position, the methyl (or any group) could point toward the short bridge or the longer bridge. These positions are called "exo" and "endo," respectively. The endo and exo isomers are diastereomers.







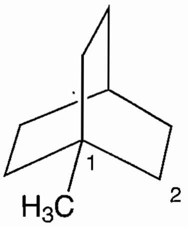
exo-2-Methylbicyclo-
[2.2.1]heptane



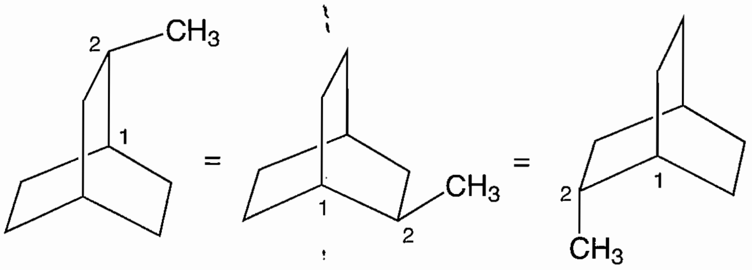
endo-2-Methylbicyclo-
[2.2.1]heptane

Problem 5.57

(a) No, there are no exo and endo forms here, as the two sides of the molecule are identical. There are only two structural isomers of methylbicyclo[2.2.2]octane.

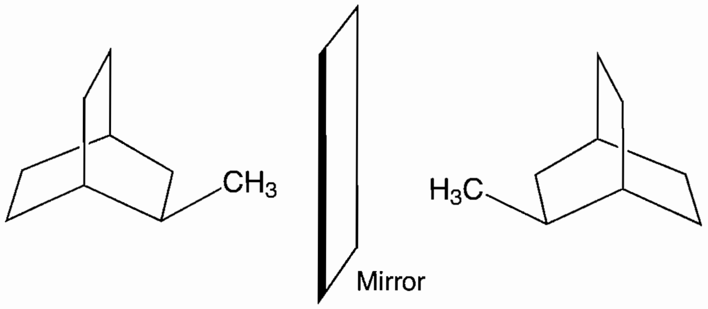


1-Methylbicyclo[2.2.2]octane

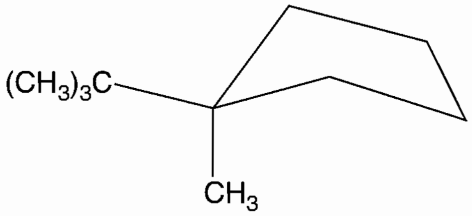


All three structures are 2-methylbicyclo[2.2.2]octane

(b) Yes, 2-methylbicyclo[2.2.2]octane is chiral. Its mirror image is not superimposable on the original.



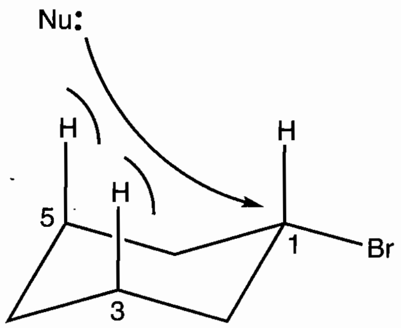
Problem 5.58



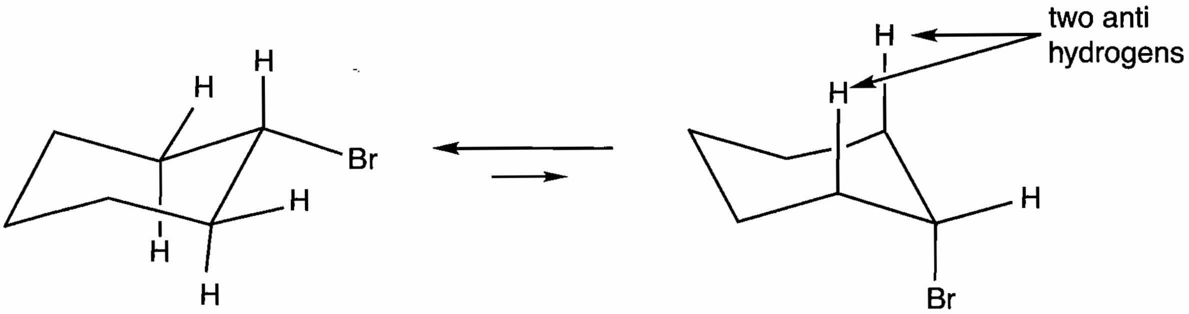
Problem 5.59 You will learn why this reaction is called S_N2 in Chapter 7. If you make a model of bromocyclopropane, you will find that the ring structure interferes less with the backside attack by a nucleophile compared to backside attack on 2-bromopropane. This phenomenon is referred to as a "tied-back" effect. The methyl groups don't block the backside as much if they are tied back, as they are in the ring compound. So, steric interactions are reduced. However, the ring carbon must go through an inversion in the S_N2 reaction. A carbon in a three-membered ring is already dealing with ring strain, and going through the sp^2-like transition state of the S_N2 reaction adds more strain. Thus, it is difficult to predict the correct answer. If you argue the S_N2 reaction for the bromocyclopropane is faster than for 2-bromopropane, then your reason is that the steric effects are greatly reduced as a result of the tied-back methyl groups. If you argue that the S_N2 reaction is going to be slower, then your reason is that ring strain in the transition state will be much higher for the bromocyclopropane.

Problem 5.60 The S_N2 reaction between axial bromocyclohexane and a nucleophile will undergo inversion to produce a product with the nucleophile in the equatorial position. In this reaction, the tied-back effect will reduce the steric interactions, and there is no added ring strain in the transition state. So it is likely that this displacement will be a faster reaction than the S_N2 reaction on 2-bromopropane.

Problem 5.61 The backside of the carbon–bromine bond for equatorial bromocyclohexane is not very accessible. This effect is much easier to see with a model set. It is difficult to get a nucleophile past the axial hydrogens that are on carbons 3 and 5. This reaction is slower than the S_N2 reaction on 2-bromopropane.



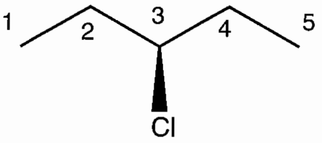
Problem 5.62 You will learn why this reaction is called an "E2" reaction in Chapter 8. You will notice that the hydrogen that is removed in the E2 reaction is on the adjacent carbon and in the anti position relative to the bromine. This geometry is a characteristic of all E2 reactions. Now look at the bromocyclohexane with the bromine in the equatorial position. Notice that there are no anti hydrogens on either of the adjacent carbons. So the E2 reaction cannot occur easily on this conformation of bromocyclohexane. The ring-flipped conformation has bromine in the axial position. Now there are anti hydrogens on carbon 2 and carbon 6. So this conformer undergoes the reaction easily.



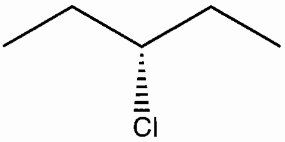
6

Substituted Alkanes: Alkyl Halides, Alcohols, Amines, Ethers, Thiols, and Thioethers

Problem 6.1 (a) This molecule is 3-chloropentane. Notice that there is no stereogenic carbon, even though the three-dimensional perspective is shown.

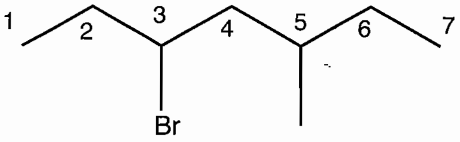


same as



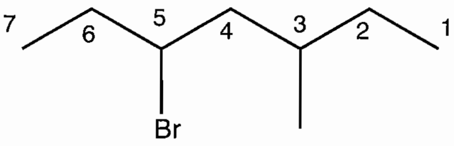
3-Chloropentane

(b) This molecule is 3-bromo-5-methylheptane. The longest carbon chain is seven carbons, so the root word is heptane. Numbering the longest chain from either end gives a 3,5-disubstituted system. So the alphabetical priority tells us the correct direction for numbering.



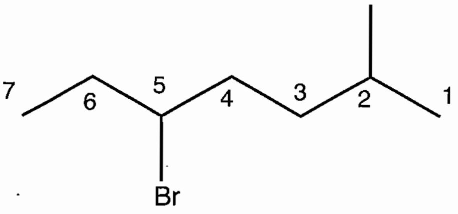
3-Bromo-5-methylheptane

not this numbering



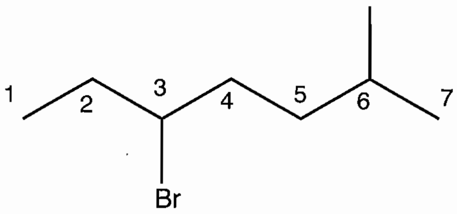
not 5-bromo-3-methylheptane

(c) This molecule is 5-bromo-2-methylheptane. The longest carbon chain is seven carbons, so the root word is heptane. We number from the right in order to be 2,5-disubstituted rather than numbering from the left, which would give us 3,6-disubstituted.



5-Bromo-2-methylheptane

not this numbering



not 3-bromo-6-methylheptane

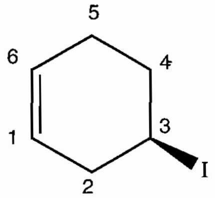
(d) This molecule is 1-fluorohexane. The longest carbon chain is six carbons, so we use the root word hexane. The only substituent is the flourine on carbon number 1.

(e) This molecule is 1,1,2-trichloroethene (or 1,1,2-trichloroethylene). There is no (*E*) or (*Z*) for this molecule because the carbon on one end of the alkene has two groups that are the same (two chlorines, in this case).

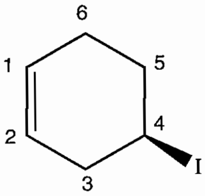
(f) This molecule is trichloromethane. Its common name is chloroform.

(g) This molecule is (*R*)-4-iodocyclohexene. The alkene is the priority group in this molecule. When we number a molecule containing a carbon–carbon double bond, the carbons of that double bond need to be numbered consecutively. That means this structure cannot be a 3-iodocyclohexene. That leaves us with two options. If we number counterclockwise, we obtain 4-iodocyclohexene. If we number the ring clockwise, we obtain 5-iodocyclohexene. Numbering counterclockwise results in a lower number for the only substituent.

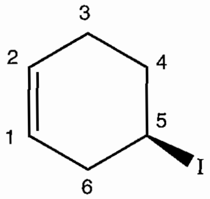
not this numbering



not 3-iodocyclohexene because the alkene carbons would be number 1 and number 6, which is not consecutive



4-Iodocyclohexene

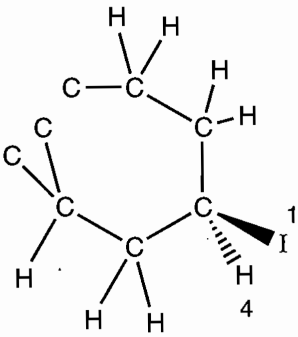


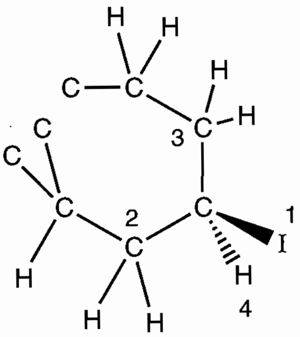
not 5-iodocyclohexene

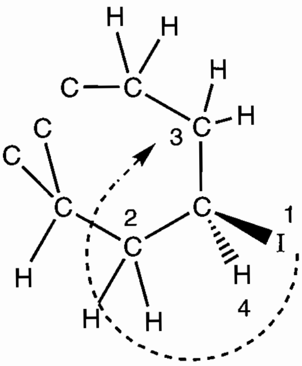
We don't need to indicate that this alkene is the (*Z*) isomer, although it would not be wrong to do so. The (*E*) cyclohexene is not a known molecule.

We also don't indicate that the priority group of the ring (the alkene in this case) is on carbon number 1. We would not call this molecule 3-iodo-1-cyclohexene. This is because the location of the priority group on a ring is defined as carbon number 1.

Finally, you noticed that there is a stereogenic carbon in the molecule. To determine the configuration, we can easily assign the highest and lowest atomic numbers. The iodo group on the stereogenic carbon is number 1 and the hydrogen on that carbon is number 4. The other two attachments are carbons. So we have to compare the next level of attachment. Both have (C, H, H). So we have to continue out to the next position on both lines. The line going to the left has (C, C, H) because of the double bond. That has a higher atomic number than the (C, H, H) of the other line. We can assign the number 2 and number 3 groups for this stereogenic carbon. We draw an arrow from group number 1 to number 2 to number 3 and see that the arrow is clockwise. This enantiomer is (*R*).



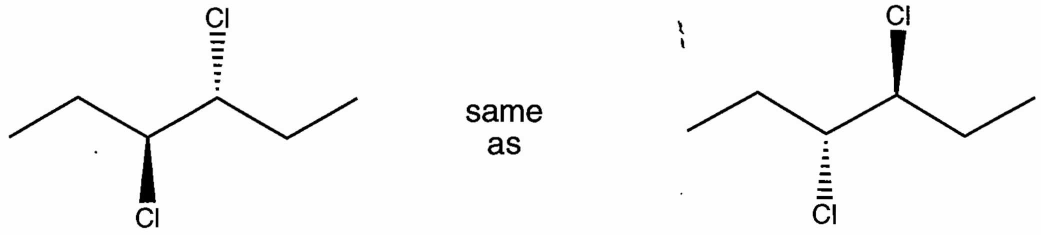




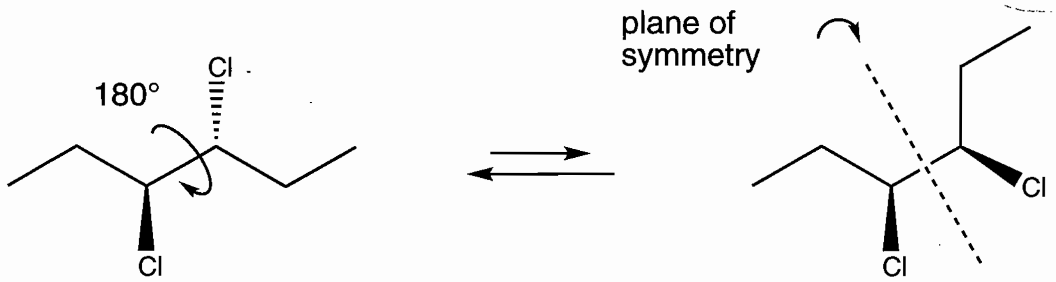
Problem 6.2

(a) (3*R*,4*S*)-Dichlorohexane

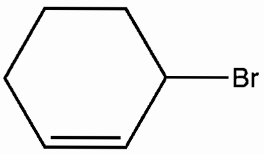
This molecule is meso. Its mirror image is identical. Either drawing is correct.



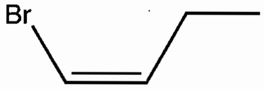
Rotation of 180° around the C(3)—C(4) bond allows you to see the plane of symmetry in the molecule.



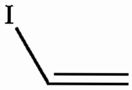
(b) 3-Bromocyclohexene



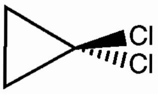
(c) (*Z*)-1-Bromo-1-butene



(d) Iodoethene

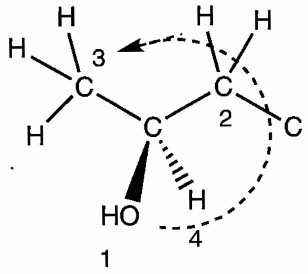


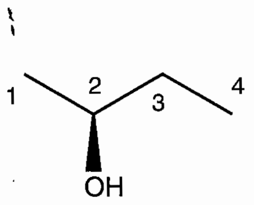
(e) 1,1-Dichlorocyclopropane



Problem 6.3

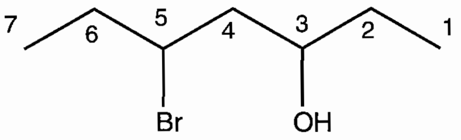
(a) This molecule is an alcohol. The longest chain is four carbons, which means butane is our root word. We drop the "-e" and add "-ol" for the suffix. We number from the left end in order to give the priority group the lowest possible number. This structure is 2-butanol. There is a stereogenic carbon with the three-dimensional information provided. We can determine the (*R*) or (*S*) configuration. The largest atomic number attached to the stereogenic carbon is oxygen and the lowest is hydrogen. The carbon to the right is attached to (C, H, H). The carbon to the left is attached to (H, H, H). Therefore the carbon to the right is number 2. The arrow from number 1 to number 2 to number 3 is counterclockwise. This molecule is (*S*)-2-butanol.





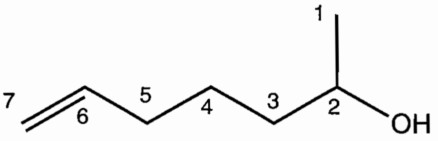
(*S*)-2-Butanol

(b) We recognize that the priority group in the molecule is the alcohol. We find the longest chain that includes the carbon attached to the priority group and use the appropriate root word (heptane, in this case). We drop the "-e" and add "-ol" in the suffix to give us heptanol. We number the chain from the end closest to the priority group so that the priority group gets the lowest possible number. This molecule is 5-bromo-3-heptanol.

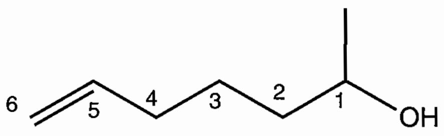


5-Bromo-3-heptanol

(c) The alcohol has a higher priority than an alkene. We find the longest chain that includes the carbon attached to the priority group, a heptane. Because there is a double bond in the chain, it is heptene. We have no prefix for an alkene in the IUPAC system. We drop the "-e" and add "-ol" to give heptenol. We number the chain from the end closest to the priority group so that the priority group gets the lowest possible number. (Don't forget to include the whole chain. It is a common error to number this incorrectly. The 1-methyl is part of the chain.) We must put the locating number for the alcohol next to the "-ol" in order to avoid confusion. This molecule is 6-hepten-2-ol.



6-Hepten-2-ol



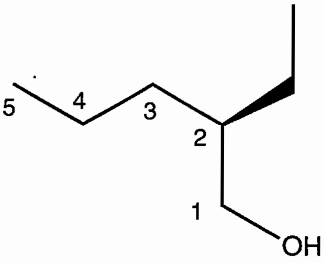
not 1-methyl-5-hexen-1-ol

(d) The alcohol is the priority group. The longest chain that includes the carbon attached to the priority group is five carbons. This structure is a pentane. We drop the "-e" and add "-ol" to get pentanol. We number the chain from the end closest to the priority group so that the priority group gets the lowest possible number. There is an ethyl group on carbon number 2. You also notice that there is a stereogenic carbon with the three-dimensional perspective shown. That means we need to indicate whether this is the (*R*) or the (*S*) enantiomer. The stereogenic carbon is attached to three carbons and one hydrogen. The hydrogen gets number 4. The carbon attached to the alcohol has (O, H, H), and oxygen is a larger atomic number than (C, H, H) that the other two carbons have

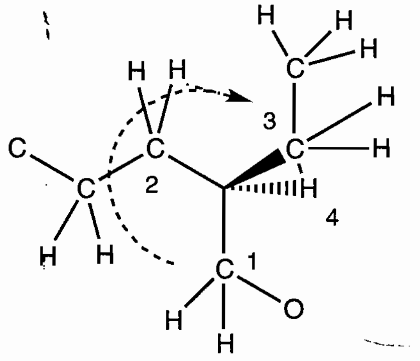
(continued)

Problem 6.3 *(continued)*

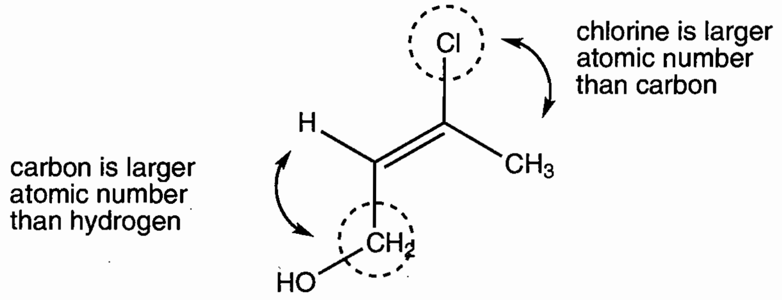
for attachments. The carbon attached to oxygen is number 1. Comparing the carbon at the next level of attachment for the remaining two lines, we have (C, H, H) compared to (H, H, H). The propyl group is number 2 and the ethyl group is number 3. The arrow from number 1 to number 2 to number 3 is clockwise. This structure is (*R*)-2-ethyl-1-pentanol.

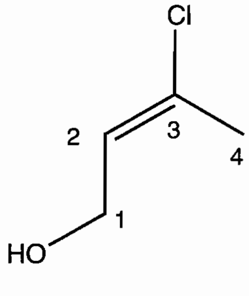


(*R*)-2-Ethyl-1-pentanol



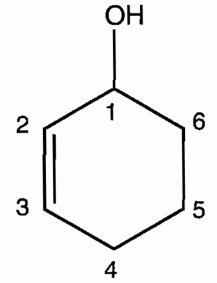
(e) This molecule has an alcohol as the priority group. The longest chain is four carbons and contains an alkene. The root word is butene. We drop the "-e" and add "-ol", which gives us butenol. We number the chain so that the priority group gets the lowest possible number. This process gives us 3-chloro-2-buten-1-ol. We aren't finished. The double bond could be (*E*) or (*Z*). Because the atoms with the higher atomic numbers attached to each end of the alkene are on opposite sides of the alkene, this molecule is (*E*)-3-chloro-2-buten-1-ol.





(*E*)-3-Chloro-2-buten-1-ol

(f) The priority group is the alcohol. There is also an alkene. This molecule is a cyclohexenol. As is always the case for a ring, carbon number 1 is the carbon bearing the priority group, which means that the only number needed in the name is the location of the alkene. This structure is 2-cyclohexenol.

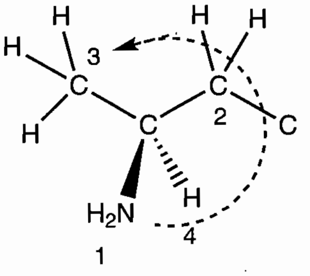


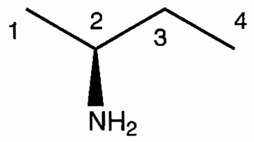
2-Cyclohexenol

(g) This molecule is 2,3-butanediol.

Problem 6.4

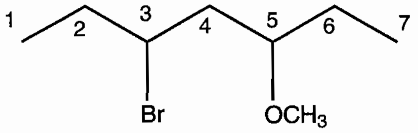
(a) The priority group is the amine. The longest chain including the carbon attached to the priority is a four-carbon chain. This molecule is a butane. Because it is an amine, we drop the "-e" and add "-amine" in the suffix. We number from the left end in order to give the priority group the lowest possible number, giving us 2-butanamine. There is a stereogenic carbon with the three-dimensional information provided. The largest atomic number attached to the stereogenic carbon is nitrogen and the lowest is hydrogen. The carbon to the right is attached to (C, H, H). The carbon to the left is attached to (H, H, H). Therefore the carbon to the right is number 2. The arrow from number 1 to number 2 to number 3 is counterclockwise. This molecule is (*S*)-2-butanamine.





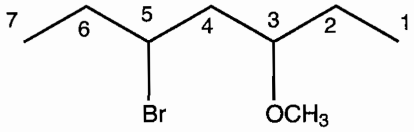
(*S*)-2-Butanamine

(b) There are no priority groups in this molecule. The longest chain is seven carbons, which means this structure is a heptane. Because there is no priority group, we don't change the suffix. We have a bromo group and a methoxy group on the chain. Numbering the chain from either end gives a 3,5-disub-stituted system. So the alphabetical rule tells us the correct direction for numbering. This molecule is 3-bromo-5-methoxyheptane.



3-Bromo-5-methoxyheptane

not this numbering



not 5-bromo-3-methoxyheptane

(c) The alkene is the priority group in this molecule. An ether is a subordinate group (see the inside front cover of the textbook). The longest chain containing the priority group is seven carbons. This structure is a heptene. We number the chain from the left end in order to give the priority group the lowest possible number. The only substituent on this chain is the ethoxy group on carbon number 6. This molecule is 6-ethoxy-1-heptene.

(continued)

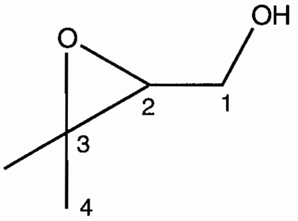
Problem 6.4 *(continued)*

(d) The alcohol is a higher priority group than an amine. The longest carbon chain is four carbons long. This is a butanol. We number the chain so that the priority group gets the lowest possible number. This molecule is a 1-butanol. The substituents are a methoxy group on carbon number 3 and an amino group on carbon number 4. This structure is 4-amino-3-methoxy-1-butanol.

(e) The priority group in this molecule is the amine. The longest chain is four carbons and it includes a double bond. This structure is a butene, we drop the "-e" and add "-amine" to give butenamine. We number the chain so that the lowest possible number is given to the priority group, and we must indicate the location of the alkene. That means the location of the amine will need to be connected to the amine in order to avoid confusion. This structure is a 2-buten-1-amine. There is a methyl group on carbon number 3. Because the attachments to carbon number 3 (one end of the alkene) are the same, there is no (*E*) or (*Z*) for this molecule. This molecule is 3-methyl-2-buten-1-amine.

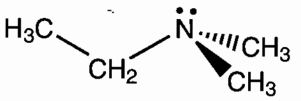
(f) The priority group in this molecule is the amine. It is attached to a five-carbon ring, which means this is a cyclopentanamine. The carbon attached to the amine must be carbon number 1 because it is the priority group. There is a methyl group on the nitrogen and a methyl group on carbon number 2 of the ring. This molecule is *N*,2-dimethylcyclopentanamine.

(g) The priority group in this molecule is the alcohol. The longest chain that includes the carbon with the priority group is four carbons. This is a butanol. We number from the right side to give the priority group the lowest possible number. This molecule has a methyl on carbon number 3 and an epoxy group, which is an ether, a subordinate group. The way to name an epoxide is to use epoxy as the prefix with the location indicating the two carbons that are attached to the group. This molecule is 2,3-epoxy-3-methyl-1-butanol.

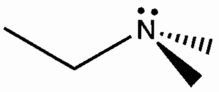


Problem 6.5 Angle and hybridization are intimately connected; if you know one, you know the other. The angle in methyl alcohol is almost exactly the tetrahedral angle, and oxygen must be almost exactly hybridized sp^3. We know the angle by comparison to water, for example.

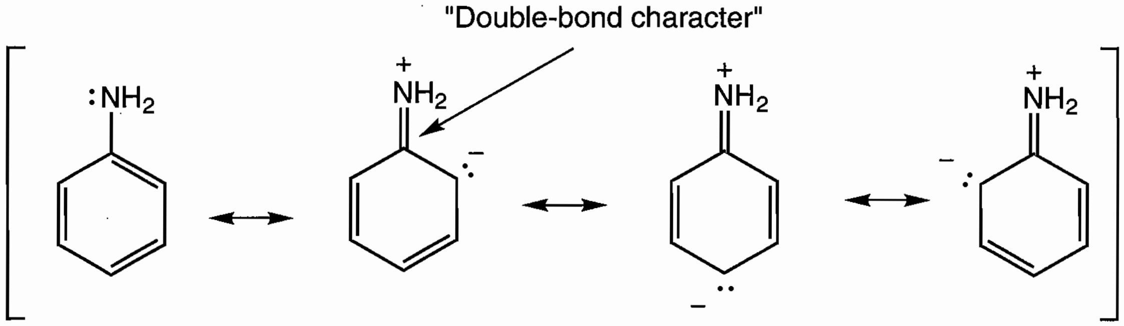
Problem 6.6



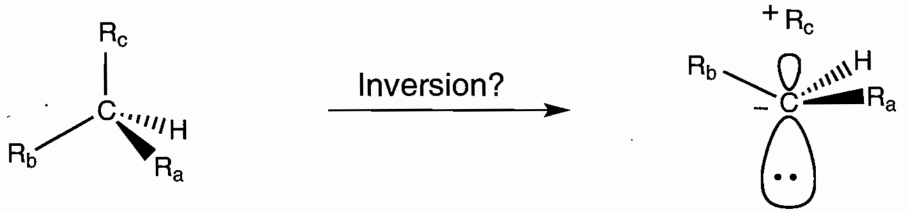
or



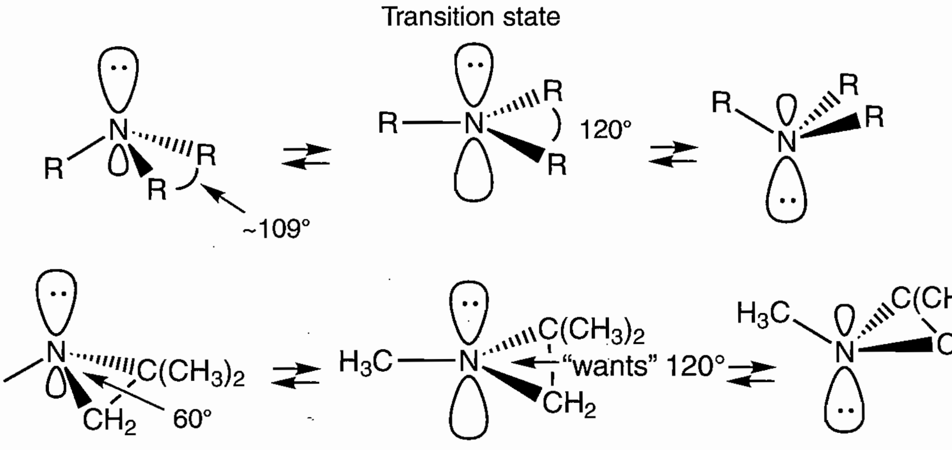
Problem 6.7 First of all, the carbon–nitrogen bond in aniline is an sp^2/sp^2 bond and will be shorter than the sp^3/sp^3 bond of methylamine. Second, in aniline there is overlap between the orbital containing the two nonbonding electrons on nitrogen and the orbitals of the ring. The resonance forms show this well. The result is double-bond character in the bond attaching the nitrogen to the ring. As double bonds are shorter than single bonds, double-bond character leads to a shortening of the carbon–nitrogen bond distance compared to that in alkylamines, in which there is no resonance effect.



Problem 6.8 A stereogenic carbon has four bonds. There is no lone pair on such a carbon, so no inversion is possible. Bonding occurs because it is stabilizing. Remember the orbital interaction diagrams that show the lower energy bonding molecular orbitals. Doing an inversion on a carbon with four bonds would require breaking a bond and leaving atoms charged. There could be no mixing between the orbitals.



Problem 6.9 In aziridines, there is more angle strain in the transition state than there is for noncyclic amines. In an amine, the most favorable angle is approximately the tetrahedral angle, about 109°. In the sp^2-hybridized transition state, this angle is expanded from about 109° to 120°. One might say that there is approximately 11° worth of angle strain. In an aziridine, in which one angle is restricted to 60° through incorporation into the three-membered ring, the transition state is very highly strained. Now there is 60° of angle strain. Accordingly, it is much more difficult to reach the transition state for inversion in aziridines than it is in acyclic amines.

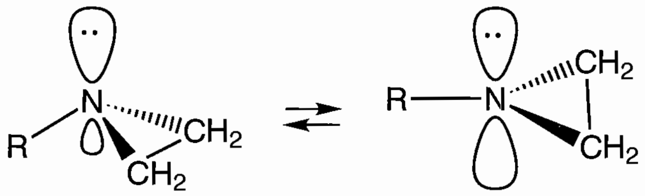


120 − 109 = 11°
angle strain in going
from starting material
to transition state

120 − 60 = 60°
angle strain in going
from starting material
to transition state

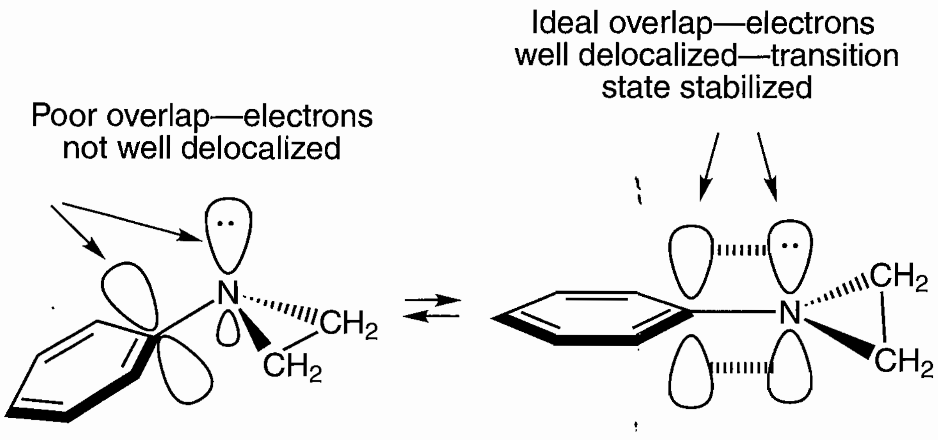
Problem 6.10 A subtle, tough question. In the starting aziridine, there is relatively poor overlap between the hybrid orbital on nitrogen containing the nonbonding electrons and the orbitals of the phenyl ring. There is some overlap, but the connection between the unsymmetrical hybrid and the $2p$ orbital on carbon is not ideal. In the transition state, the nitrogen is hybridized sp^2, and now there is excellent overlap, and hence good delocalization of the nonbonding electrons into the benzene ring. The transition state is stabilized, is lowered in energy, and becomes easier to reach from starting material.

Starting material Transition state

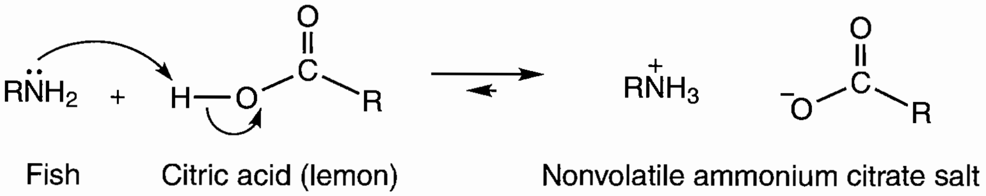


(continued)

Problem 6.10 *(continued)*



Problem 6.11 Citric acid (lemon) acts as a Brønsted acid toward the Brønsted base, the amine (fish odor), in a proton-transfer reaction to form a salt. Unlike the amine, the salt is not volatile and cannot easily be detected by our sense of smell. The fish has been deodorized by the acid–base reaction.



Problem 6.12 Conjugate acids and conjugate bases are related through the gain or loss of a single proton. The conjugate acids of the molecules shown are always "the molecule plus one proton."

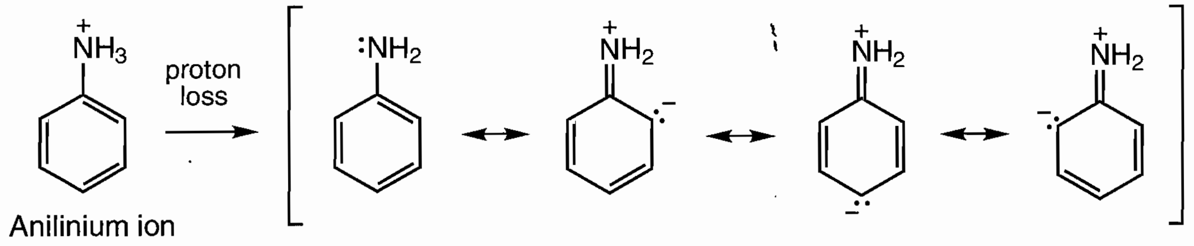
(a) $H_3\overset{+}{O}$ (b) HOH (c) $\overset{+}{N}H_4$ (d) $CH_3\overset{+}{O}H_2$ (e) $H_2C{=}\overset{+}{O}H$ (f) CH_4

Sometimes there are choices to be made as to where to put the proton in making the conjugate acid. In this set, only $H_2C{=}O$ really presents such a choice. Another conjugate acid is $H_3C{-}O^+$, although this molecule is much less stable than the one shown above. (Why?)

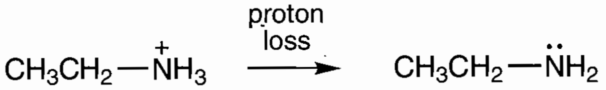
Problem 6.13 The conjugate bases of these molecules will always be "the molecule less one proton."

(a) HO^- (b) O^{2-} (c) $^-NH_2$ (d) CH_3O^- (e) $^-CH_3$ (f) $^-OSO_2OH$ (g) $^-OSO_2O^-$

Problem 6.16 The anilinium ion (pK_a = 4.6) is a much stronger acid than the ethyl ammonium ion (pK_a = 10.6) because the conjugate base of the anilinium ion, aniline, is stabilized by resonance, whereas the conjugate base of the ethyl ammonium ion, ethylamine, is not. Moreover, the electron-withdrawing benzene ring destabilizes adjacent electron deficiency.



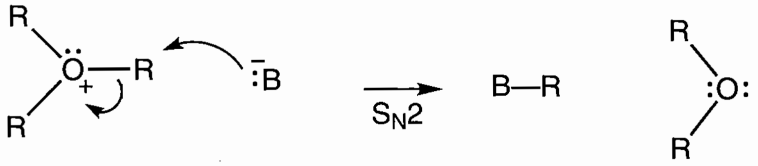
Resonance stabilization lowers the energy of aniline and makes deprotonation of the ammonium ion relatively easy



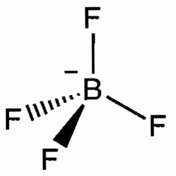
$$CH_3CH_2-\overset{+}{N}H_3 \xrightarrow{\text{proton loss}} CH_3CH_2-\ddot{N}H_2$$

In this case, neither reactant nor product is stabilized by resonance

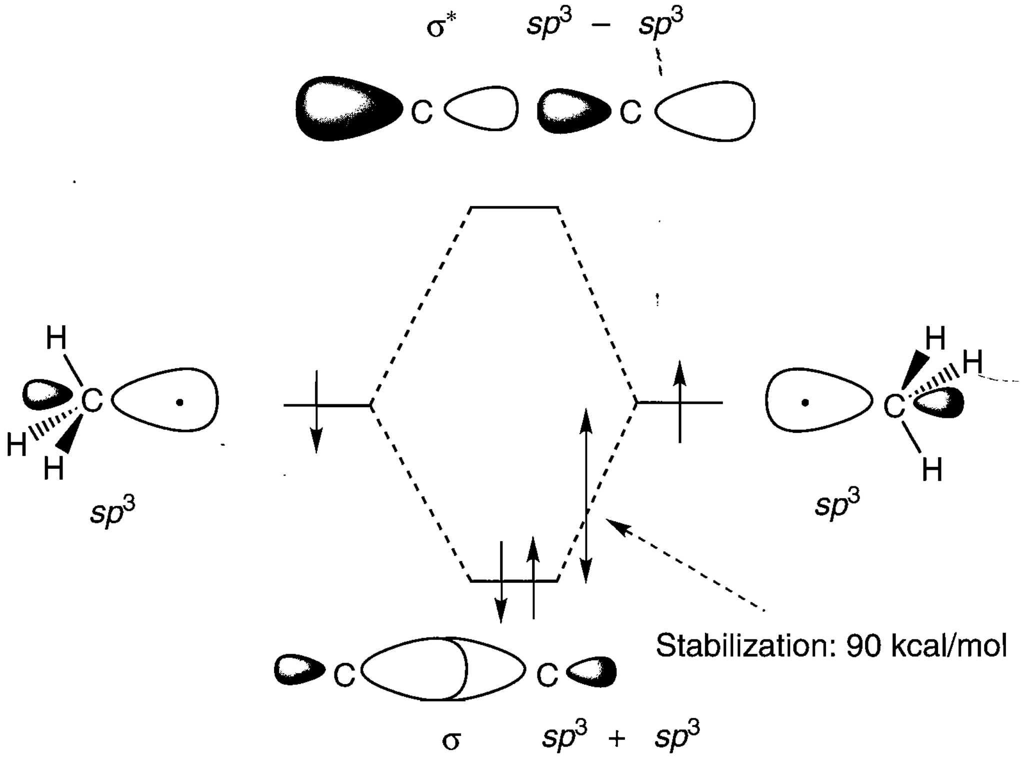
Problem 6.17 Oxonium ions are destroyed by nucleophiles through an S_N2 alkylation process.



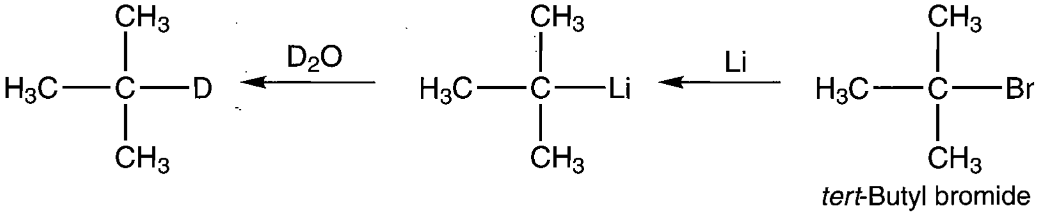
Most negatively charged counterions are nucleophiles, but $^-BF_4$ is an exception. There is no lone pair of electrons on boron and therefore no possible nucleophilicity.



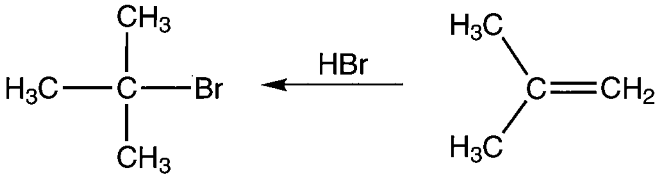
Problem 6.18 Basically, the problem asks you to build ethane, or at least the carbon–carbon sigma bond. Here is the diagram. Because you know the bond strength of ethane (Ch. 2, p. 72), you know the stabilization of the two electrons in σ.



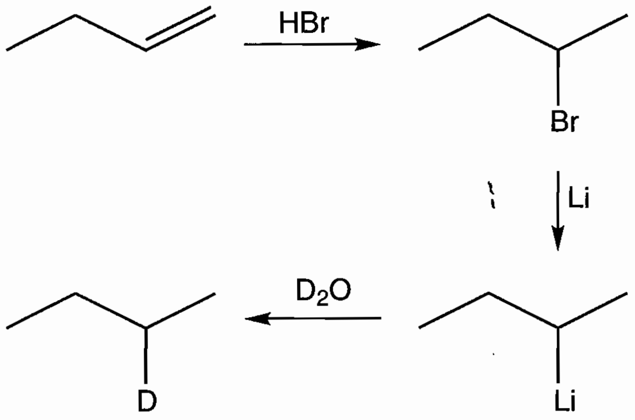
Problem 6.19 Let's work backward. Given the previous paragraph in the text, certainly the final step is the quenching of an organometallic reagent with D_2O. The organolithium or Grignard reagent is made from the bromide and either lithium or magnesium.



Now, the only remaining question is how to convert the alkene into the bromide. For this you must remember material in Chapter 3. Simple addition of HBr to isobutene gives *tert*-butyl bromide (Chapter 3, p. 136).



Basically, the second part of this problem involves the same chemistry as the first part. Add HBr to 1-butene to give 2-bromobutane, make the organometallic reagent, and quench with D_2O.



Problem 6.20

(a) This one is right out of the text. Treat the thiol with Raney nickel.

(b) Make the Grignard, then add water: 1. Mg, 2. H_2O.

(c) Just convert cyclohexene into bromocyclohexane (add HBr) and proceed as in part (b): 1. HBr, 2. Mg, 3. H_2O. There is a much simpler way, but you don't know it yet.

Additional Problem Answers

Problem 6.21

(a) 3-Methyl-1-butanol

(b) 3-Methyl-2-butanol

(c) 2-Methyl-2-butanol

(d) 2-Methyl-1-butanol

(e) 2-Fluoro-1-pentanol

(f) 4-Phenyl-1-pentanol

(g) *trans*-1,2-Cyclobutanediol
or (1*R*, 2*S*)-1,2-Cyclobutanediol

(h) 4-Penten-1-ol

(i) (*E*)-3-Penten-1-ol

(j) *cis*-3-Ethoxycyclohexanol
or (1*S*, 3*R*)-3-Ethoxycyclohexanol

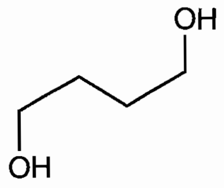
(k) 1,3-Propanediol

(l) Propanethiol (propyl mercaptan)

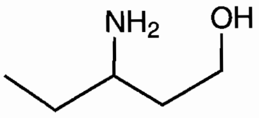
(m) Dipropyl sulfide

Problem 6.22

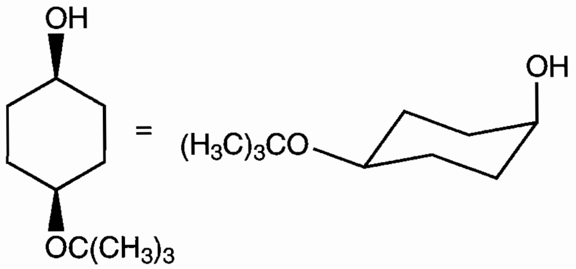
(a)



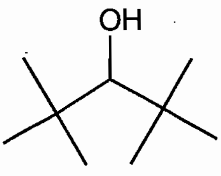
(b)



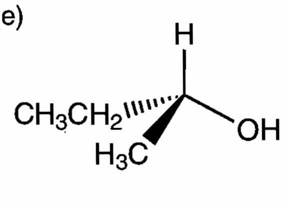
(c)



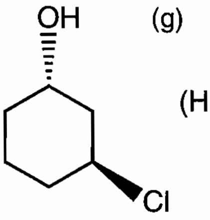
(d)



(e)

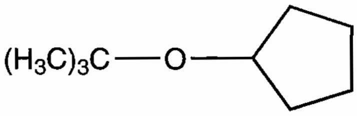


(f)



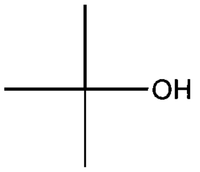
(or its enantiomer)

(g)

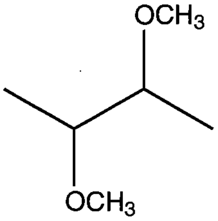


Problem 6.23 This problem includes some common names. It is worth memorizing these common names. There are systematic names for each one, of course, but you are likely to encounter the common names in the future.

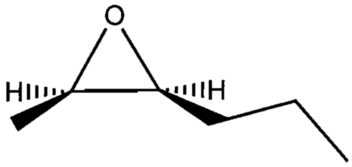
(a) *tert*-Butyl alcohol is a common name; the IUPAC name is 2-methyl-2-propanol.



(b)

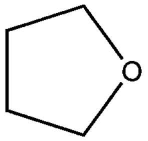


(c)

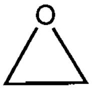


(or its enantiomer)

(d) Tetrahydrofuran (THF) is a common name; the IUPAC name is oxolane. A more systematic IUPAC name is 1,4-epoxybutane.

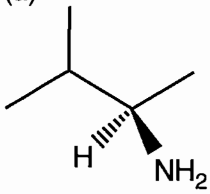


(e) Ethylene oxide is a common name; the IUPAC name is oxirane. A more systematic IUPAC name is 1,2-epoxyethane.

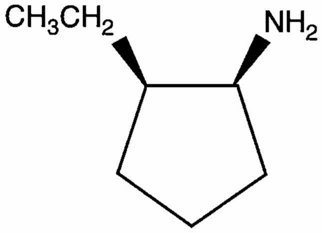


Problem 6.24

(a)

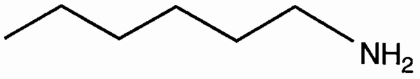


(b)

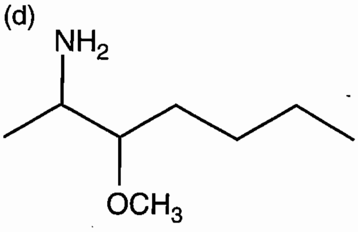


(or its enantiomer)

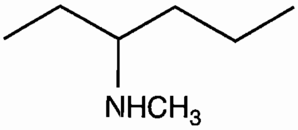
(c)



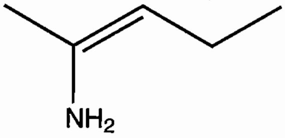
(d)



(e)

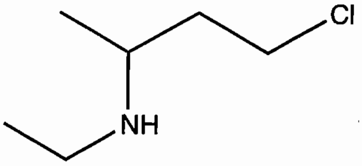


(f)

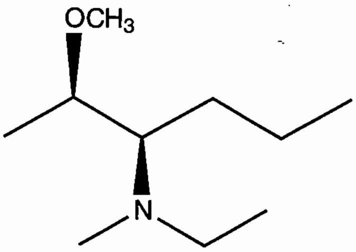


Problem 6.25

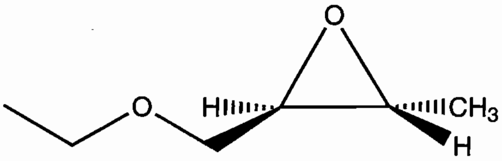
(a)



(b)

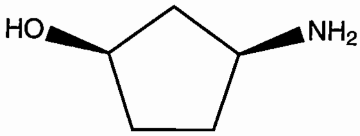


(c)



(or its enantiomer)

(d)

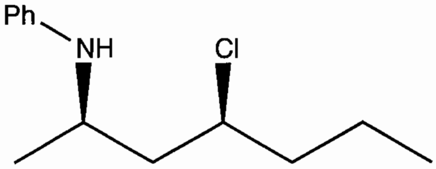


(or its enantiomer)

(continued)

Problem 6.25 *(continued)*

(e)



Problem 6.26

(a) Cyclohexanamine

(b) (*S*)-4-Methyl-2-pentanamine

(c) (3*S*, 5*S*)-Heptanediamine

(d) 2-Amino-4,5-dimethyl-1-hexanol

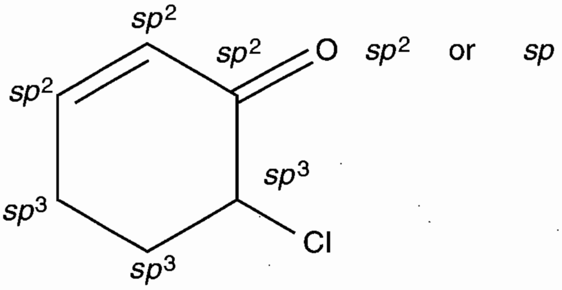
(e) 6-Methoxy-2-heptanamine

Problem 6.27

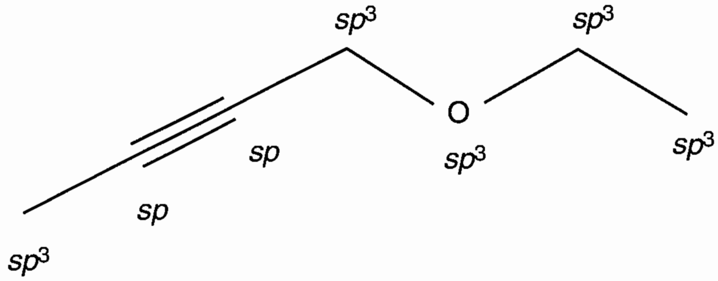
(a) All C, N, O sp^3.

(b) All ring C and N sp^2. CH_2 and O are sp^3.

(c)



(d)

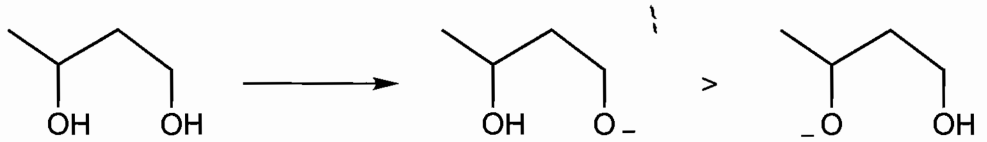


(e) Ring Cs and N are all sp^2.

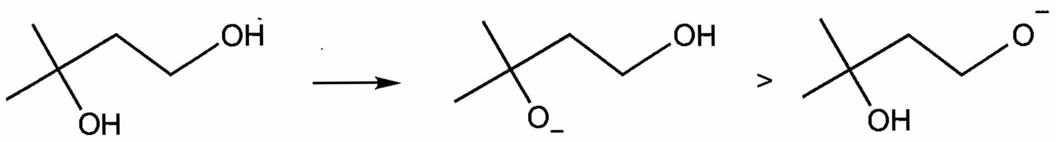
Problem 6.28 All the molecules in Problem 6.27 can hydrogen bond to water. Molecules (a), (b), and (e) can hydrogen bond to themselves.

Problem 6.29

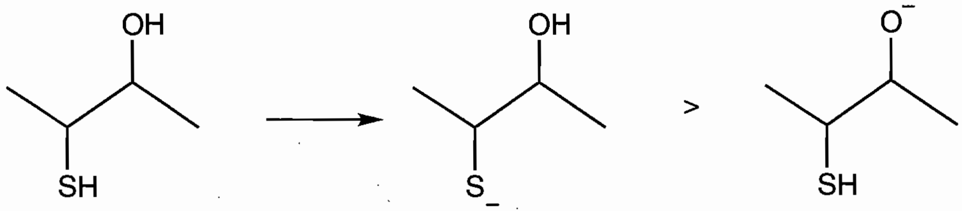
(a) In solution, at least, ethyl alcohol is a stronger acid than isopropyl alcohol (Table 6.6, p. 246). So we would expect that the primary alcohol would be the stronger acid here.



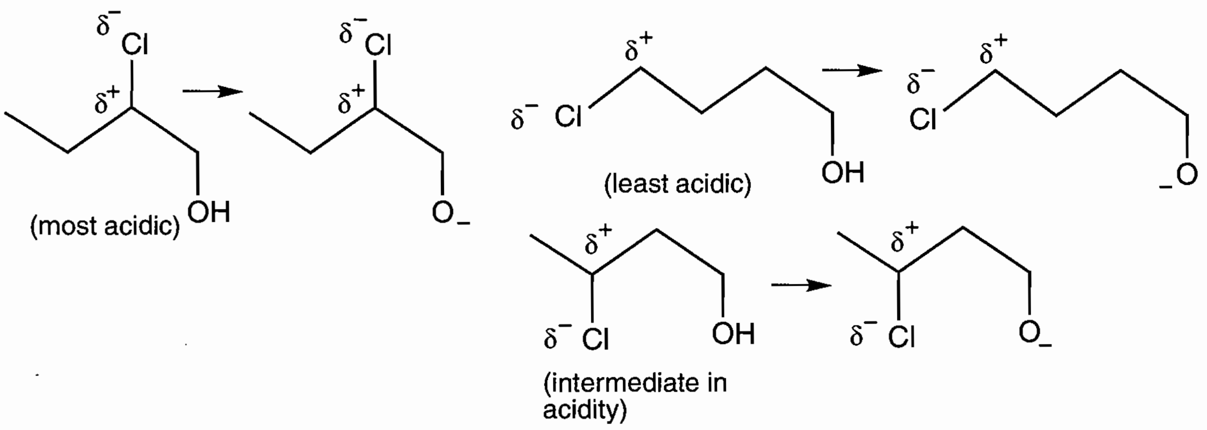
(b) In the gas phase, the acidity order for alcohols is the reverse of what obtains in solution. So in this case, it will be the tertiary alkoxide that will be preferentially formed.



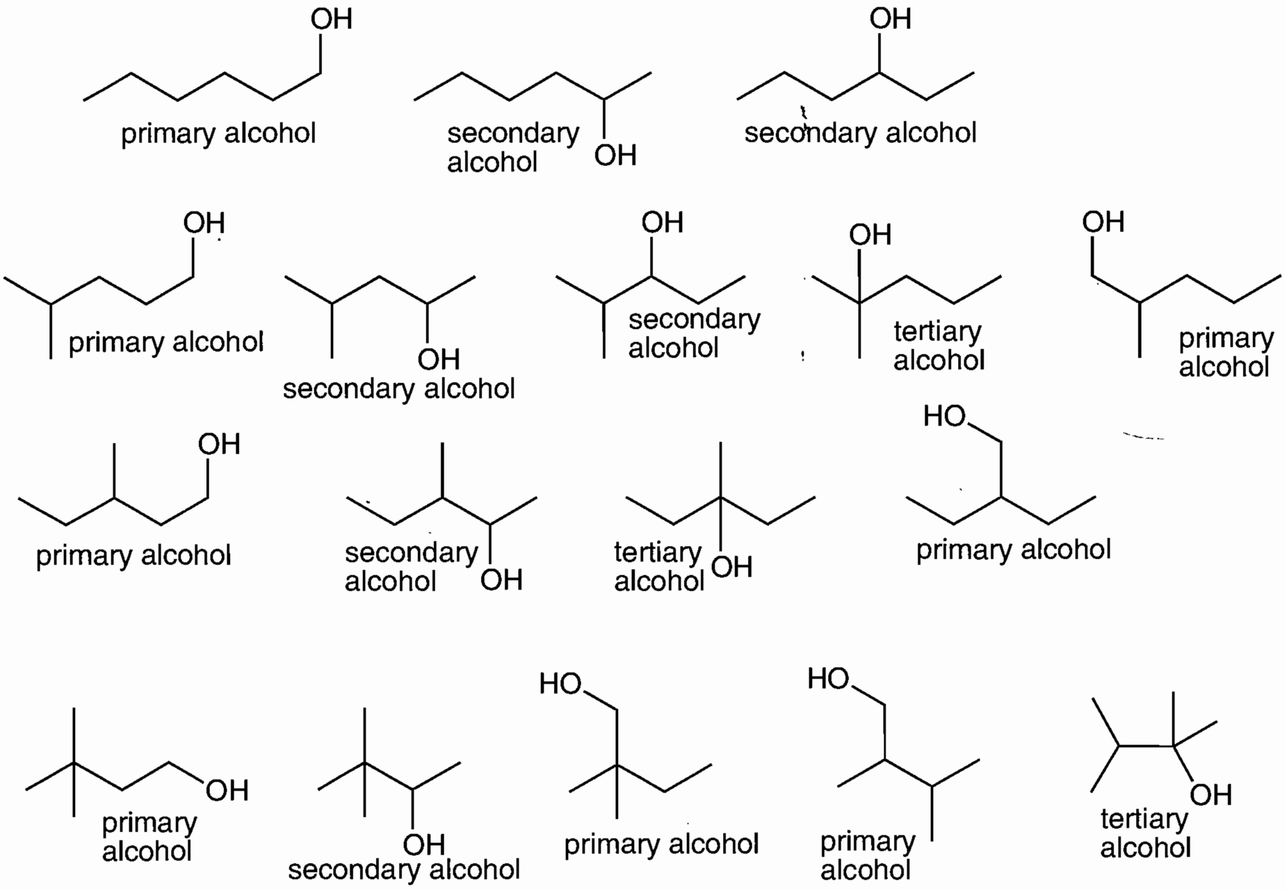
(c) Thiols are stronger acids than alcohols, so the SH will be preferentially deprotonated.



Problem 6.30 The carbon–chlorine bond is strongly polarized, with the negative end of the dipole on chlorine. There is a partial positive charge on carbon. That δ^+ will be stabilizing to a neighboring anion. The closer it is, the greater the stabilization. Accordingly, the stability of the related alkoxide, and thus the acidity order of the alcohols, is in the following order:



Problem 6.31 We think this is all of the possible isomeric alcohols of formula $C_6H_{14}O$.



Problem 6.32

(a) Primary amine: 2-pentanamine or 2-aminopentane.

(b) Secondary amine: *N*-pentyl-1-pentanamine or dipentylamine.

(c) Tertiary amine: *N,N*-dipentyl-1-pentanamine or tripentylamine.

(d) Primary amine: 3-fluoro-2-pentanamine.

(e) Quaternary ammonium ion: tetrapentylammonium iodide.

(f) Both amines are primary: 1,3-pentanediamine or 1,3-diaminopentane.

Problem 6.33

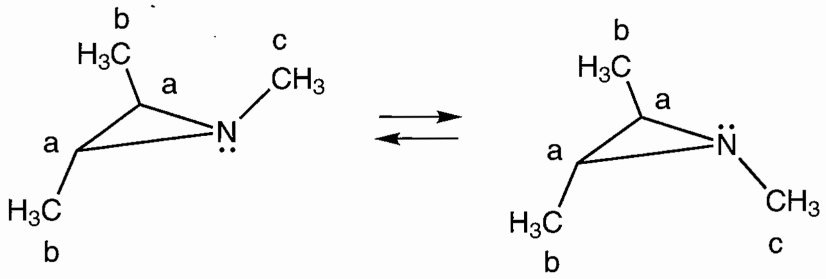
(a) Primary amine: 3-buten-2-amine.

(b) Tertiary amine: ethylmethylphenylamine or *N*-ethyl-*N*-methylaniline or *N*-ethyl-*N*-methylbenzenamine.

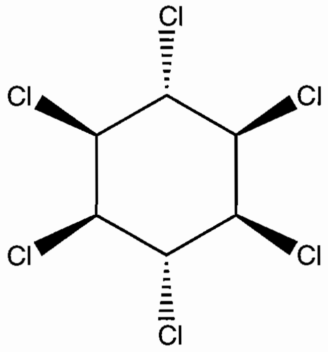
(c) Primary amine: 2-propyn-1-amine or propargylamine.

(d) Primary amine: 3-amino-2-butanol.

Problem 6.34 At low temperature, what you see is what you get. There are five different carbons in the molecule and, of course, five different signals in the ^{13}C NMR spectrum. At higher temperature, amine inversion sets in, and the two carbon-attached methyl groups and the two ring carbons become equivalent. There are now only three different carbons (shown as a, b, and c in the figure) and three signals in the ^{13}C NMR spectrum.



Problem 6.35 Lindane is 1,2,3,4,5,6-hexachlorocyclohexane. It is the stereoisomer shown. Lindane has been used as an insecticide, most often for fruit trees and seed crops. It has been banned from agricultural use in most countries since 2009, including the United States. There is a plane of symmetry in lindane. It is achiral.

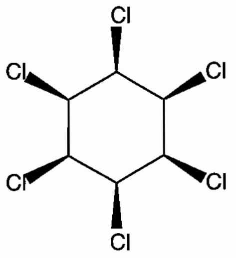


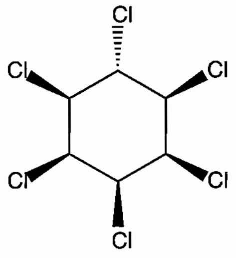
Lindane

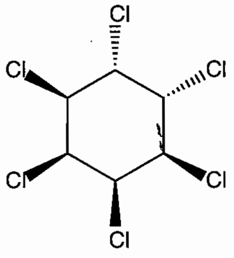
(continued)

Problem 6.35 *(continued)*

Diastereomers of lindane are


achiral


achiral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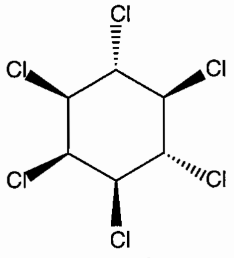
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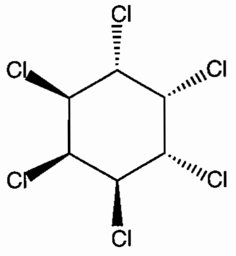
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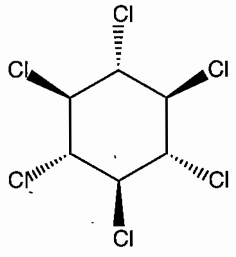
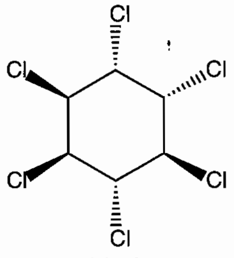
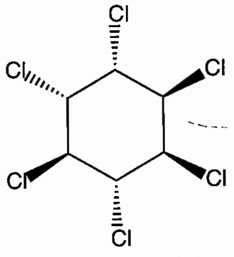
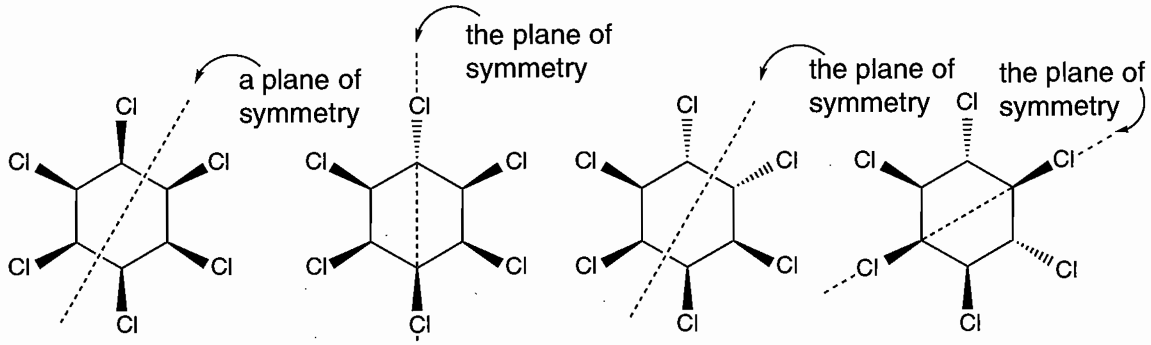
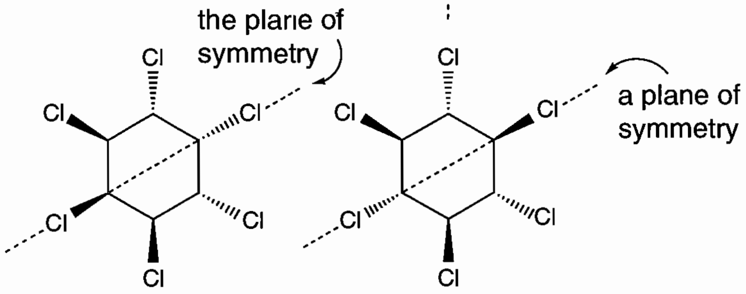
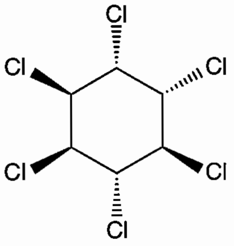

achiral


chiral

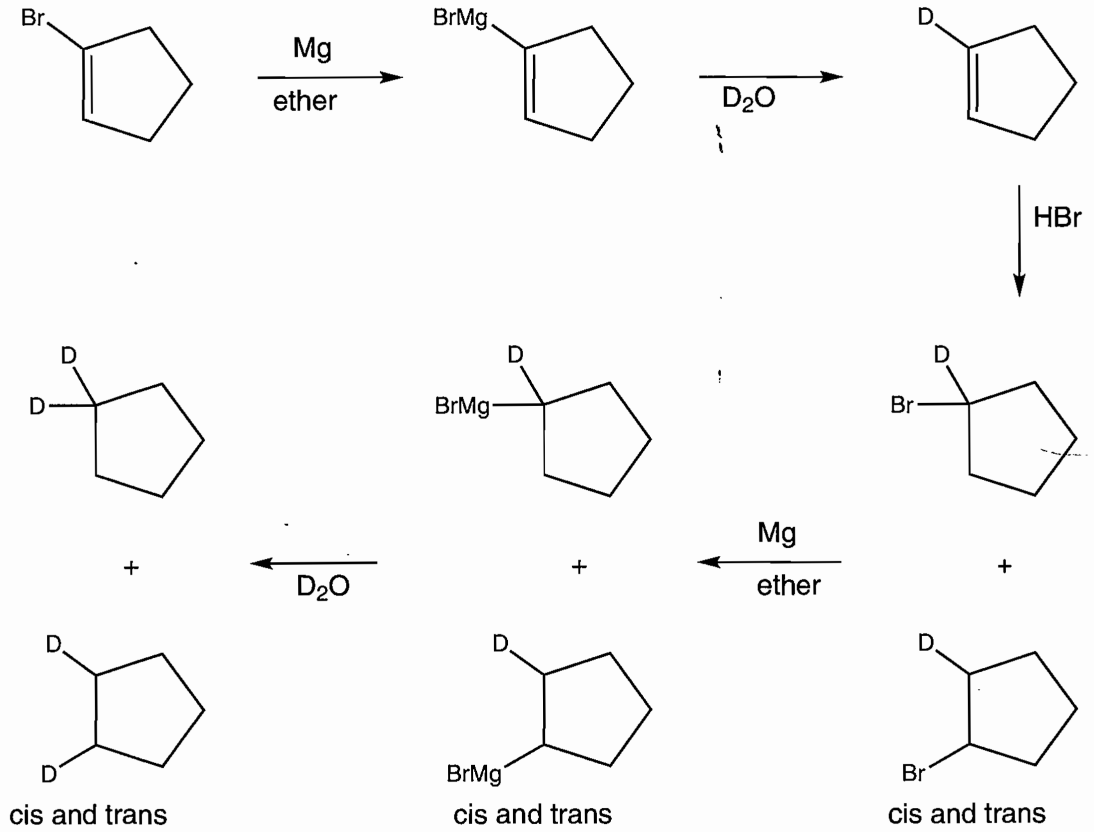

enantiomer of the one chiral diastereomer of lindane



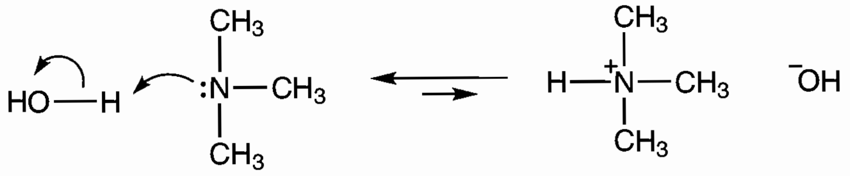



chiral
no plane of
symmetry

Problem 6.36



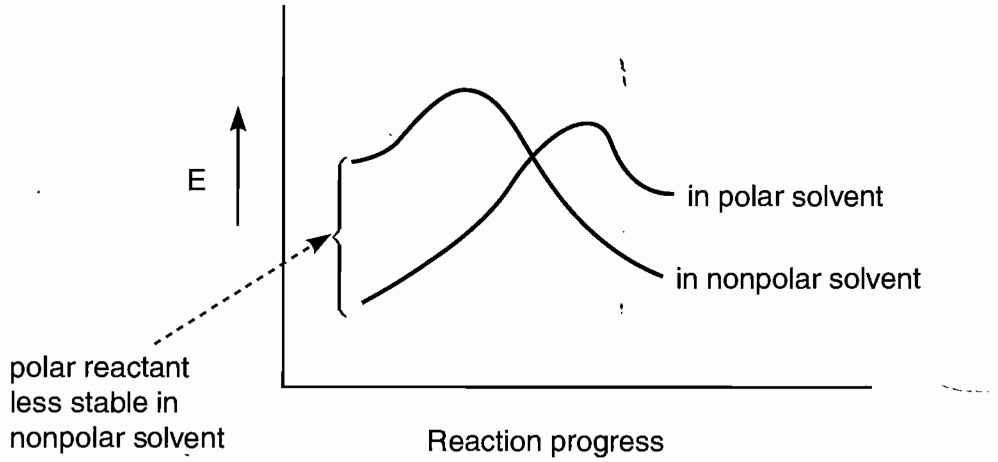
Problem 6.37 The lower the pK_b, the greater the base strength. So, methylamine is a stronger base than ammonia, and dimethylamine is a (slightly) stronger base still. Yet trimethylamine is a weaker base than the other methylated species and almost as weak a base as ammonia itself. Indeed, we might well have been disturbed at the small difference between methylamine and dimethylamine as the two are almost of equal base strength. The problem is one of solvation. Each methyl group increases base strength but decreases the possibilities for solvation of the charged intermediates (and the transition states leading to them). So, for trimethylamine, each methyl group stabilizes the intermediate by helping to disperse the charge, but, at the same time, it interferes with the stabilizing effects of solvation. It's a balancing act. See the discussion of these effects in terms of the pK_a values of the conjugate acids in this chapter (p. 250).



Each methyl group helps to disperse the charge, but also interferes with stabilization of the ions by solvent

Problem 6.38 None of the above. The Hofmann elimination reaction requires a quaternary ammonium ion.

Problem 6.39 A polar solvent would stabilize the very polar starting materials. The products are relatively nonpolar. So, one would predict that the reaction would be slower in a polar solvent, because the transition state leading to products would be a higher barrier.



Problem 6.40 One might guess that the alkene or the amine is the best nucleophile. We have seen both functional groups behave as nucleophiles. We know that an alkene will react with electrophiles, but the alkene will not undergo the S_N2 reaction with the alkyl halide, whereas an amine will react well with the alkyl halide. So, we might conclude that the amine is a better (or more reactive) nucleophile. The calculated HOMO supports this idea. It shows that the amine has more available electrons than does the alkene.

Problem 6.41 According to the energy diagram, the most stable intermediate is the protonated alcohol that is formed first. The least stable intermediate is the secondary carbocation.

The process that is occurring in the first step of the reaction is called a protonation. The alcohol oxygen is being protonated by one of the acidic protons on the H_2SO_4. The first step occurs because the pK_a of sulfuric acid is about −3. The pK_a of the conjugate acid of the alcohol is about −2 (see Table 6.6). The equilibrium for this process lies to the right.

$$\mathrm{ROH} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{R\overset{+}{O}H_2} + \mathrm{HSO_4^-}$$

7

Substitution Reactions: The S_N2 and S_N1 Reactions

Problem 7.2 The HOMO is the filled 1*s* orbital on hydrogen and the LUMO is the empty 2*p* orbital of the methyl cation.

Problem 7.5 Here is a simple, plug-in-the-numbers problem. This problem is designed to help you to develop a feeling for the relationship between ΔG and K so that you can make quick estimates in either direction.

$\Delta G° = -2.3RT \log K$; at 25 °C, $2.3RT = 1.364$ kcal/mol
    if $K = 7$, $\Delta G° = -(1.364) \log 7 = -1.15$ kcal/mol
    if $K = 14$, $\Delta G° = -(1.364) \log 14 = -1.56$ kcal/mol

Problem 7.6

(a) Bonds broken:		Bonds formed:	
H—Br	87.5 kcal/mol	C—H	101.1 kcal/mol
C=C	<u>66 kcal/mol</u>	C—Br	<u>72.1 kcal/mol</u>
	153.5 kcal/mol		173.2 kcal/mol

Difference in $H°$ = 173.2 – 153.5 = 19.7 kcal/mol
Products more stable than starting materials

(b) Bonds broken:		Bonds formed:	
H—OH	118.8 kcal/mol	C—H	101.1 kcal/mol
C=C	<u>66 kcal/mol</u>	C—OH	<u>92.1 kcal/mol</u>
	184.8 kcal/mol		193.2 kcal/mol

Difference in $H°$ = 193.2 – 184.8 = 8.4 kcal/mol
Products more stable than starting materials

(c) Bonds broken:		Bonds formed:	
H—F	136.3 kcal/mol	C—H	101.1 kcal/mol
C=C	<u>66 kcal/mol</u>	C—F	<u>115 kcal/mol</u>
	202.3 kcal/mol		216.1 kcal/mol

Difference in $H°$ = 216.1 – 202.3 = 13.8 kcal/mol
Products more stable than starting materials

(continued)

Problem 7.6 *(continued)*

(d) Bonds broken:		Bonds formed:	
H—Cl	103.2 kcal/mol	C—H	101.1 kcal/mol
C=C	66 kcal/mol	C—Cl	83.7 kcal/mol
	169.2 kcal/mol		184.8 kcal/mol

Difference in $H°$ = 184.8 – 169.2 = 15.6 kcal/mol
Products more stable than starting materials

Problem 7.7 In every case, the reaction is $R—H \longrightarrow R\bullet + \bullet H$. There can be no difference in the energy of the hydrogen atom formed in every reaction, and the differences must lie in the R• partner, the radical. As it takes less energy to form the more substituted radical (R•), the more substituted radicals must be more stable than the less substituted radicals. One can even make a very rough estimate as to the amount of the increased stability.

$H—CH_3 \longrightarrow H\bullet + \bullet CH_3 \quad \Delta H° = 105.0$ kcal/mol

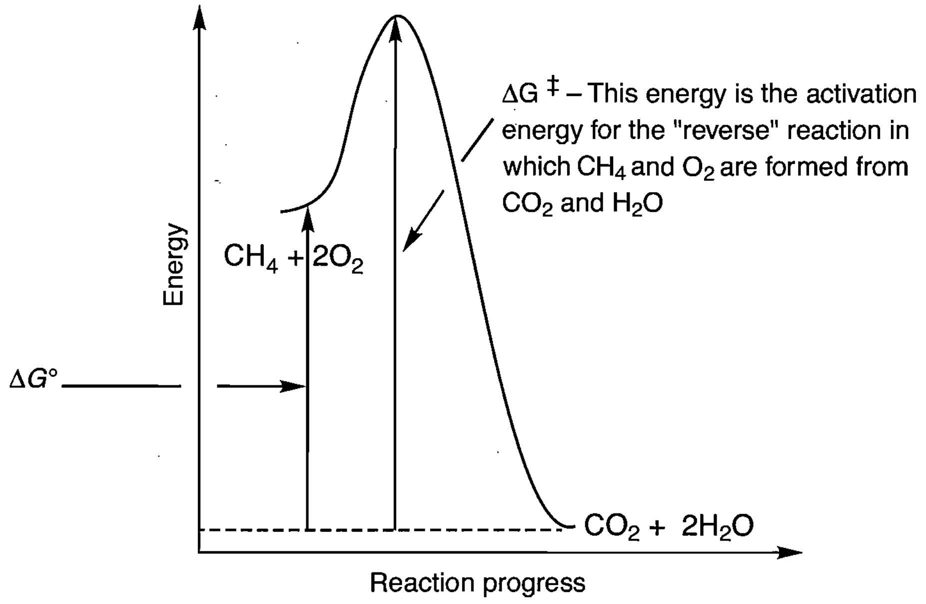
$H—CH_2CH_3 \longrightarrow H\bullet + \bullet CH_2CH_3 \quad \Delta H° = 101.1$ kcal/mol
(primary radical more stable than methyl radical by 3.9 kcal/mol)

$H—CH(CH_3)_2 \longrightarrow H\bullet + \bullet CH(CH_3)_2 \quad \Delta H° = 98.6$ kcal/mol
(secondary radical more stable than primary radical by 2.5 kcal/mol)

$H—C(CH_3)_3 \longrightarrow H\bullet + \bullet C(CH_3)_3 \quad \Delta H° = 96.5$ kcal/mol
(tertiary radical more stable than secondary radical by 2.1 kcal/mol)

Problem 7.9

$\Delta G^{\ddagger}$ reverse reaction) = $\Delta G^{\ddagger}$ (left to right reaction) + $\Delta G°$



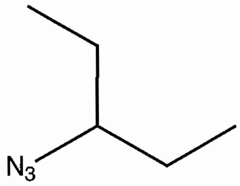
Problem 7.10 Inversion has occurred, but both starting material and product are (*R*) configuration. We can be convinced that inversion has occurred by comparing the starting material to the product. The iodide in the starting material has been replaced by a hydroxide. Notice that the hydroxide has attached to what was the backside of the C—I bond. The chloro and methyl groups have moved to the other side of the carbon. This reaction takes place with inversion. Because the

starting material is the (*R*) configuration, we expect the product of inversion to have the (*S*) configuration. But in this case, the product is also (*R*). There is no guarantee that inversion will result in a change in configuration in a substitution reaction. The (*R*) and (*S*) configurations are determined using the Cahn–Ingold–Prelog system (p. 156), which is based on the atomic numbers of the atoms attached to the stereogenic carbon. The nucleophile may not have the same position in the order of atomic numbers as the leaving group. In this example, the starting material has (I, Cl, C, H) and the product has (Cl, O, C, H).

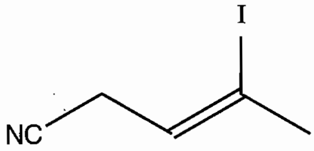
Problem 7.11 An argument has just been made (p. 291) that steric factors are important in determining the rate of the S_N2 reaction. The more substituted the substrate, the slower the reaction. In tertiary substrates, the three R groups guard the rear of the C—L bond so efficiently that the S_N2 reaction completely fails. There should be no surprise that the size of the entering nucleophile is important as well. The larger the nucleophile [$(CH_3)_3C—O^- > CH_3—O^-$], the greater the steric interactions, and the slower the reaction.

Problem 7.12

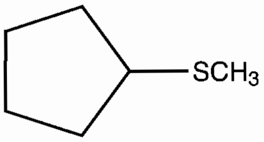
(a) This is an S_N2 reaction. The starting material is a secondary iodide and the azide anion ($^-N_3$) is an excellent nucleophile. The product is 3-azidopentane.



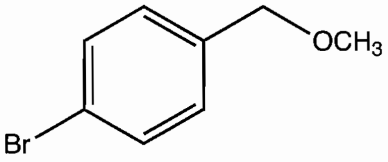
(b) This is an S_N2 reaction. The starting material is a primary bromide. A bromide is a good leaving group and the cyanide anion (^-CN) is an excellent nucleophile. The iodide is a better leaving group than a bromide, but we will only see S_N2 reactions on sp^3-hybridized carbons. See Problem 7.67. So there is no substitution of the vinyl iodide.



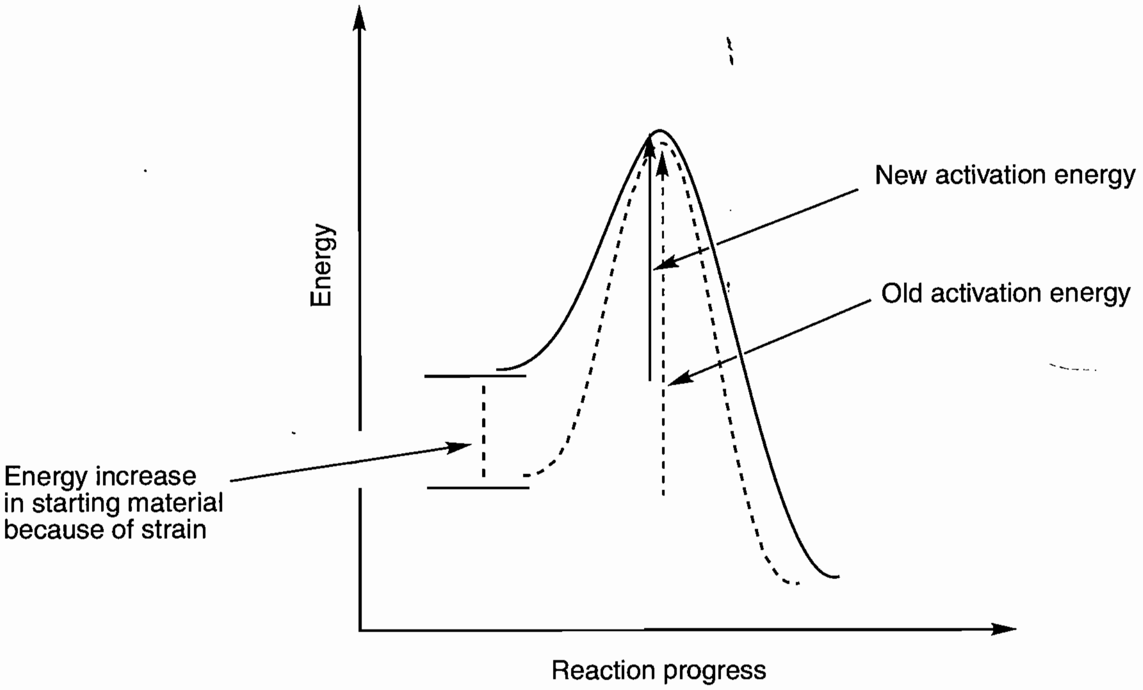
(c) This is an S_N2 reaction. The starting material is a secondary bromide and the thiolate (CH_3S^-) is an excellent nucleophile. The product is a thioether.



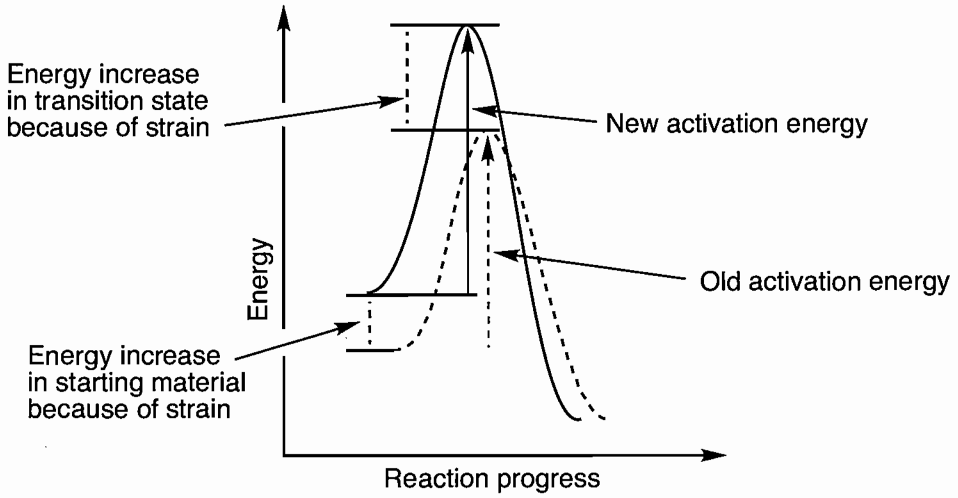
(d) This is an S_N2 reaction. There are two leaving groups in this molecule, but only the primary bromide will react with a nucleophile. The backside of the bromide on the aromatic ring is not accessible by any nucleophile. No inversion can occur at the sp^2-hybridized carbon in a ring. Methoxide (CH_3O^-) is a good nucleophile.



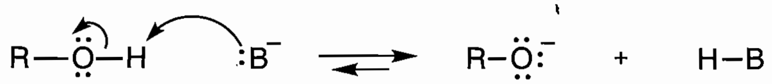
Problem 7.13 Strain in the starting material will raise its energy, and any change of this kind will lower the activation energy for a reaction if there is no change in the energy of the transition state, a most unlikely prospect.



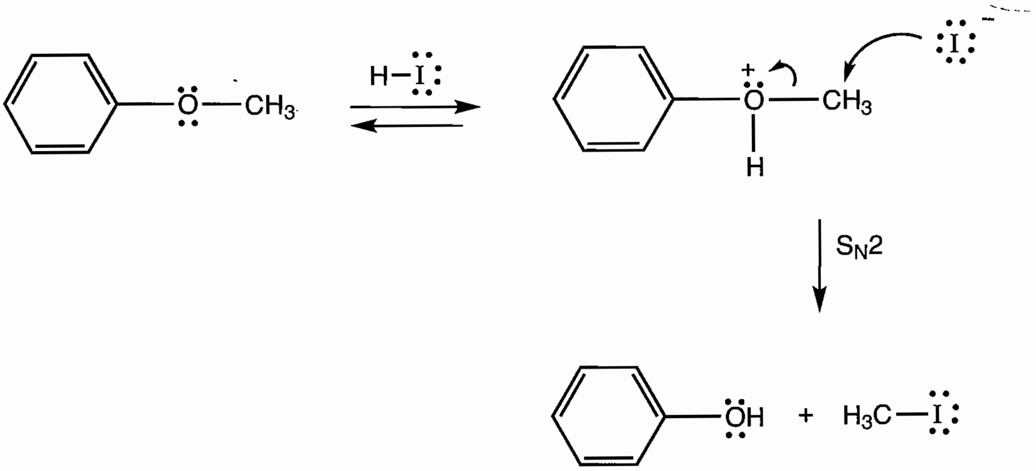
In fact, in this case the energy of the transition state is raised *more* than is the energy of the starting material. The hint tells us to consider the structures of both starting material and transition state. Let's focus on deviations from ideal angles. In the starting material, the cyclopropane "wants" something like 109°, but is restricted to 60°. There are some 49° of angle strain. In the transition state, the sp^2 carbon "wants" 120°, but is restricted to 60° (see Fig. 7.44). There are 60° of angle strain, and the transition state is more destabilized than the starting material by angle strain effects. The result is an increase in activation energy even though the starting material is destabilized by angle strain.



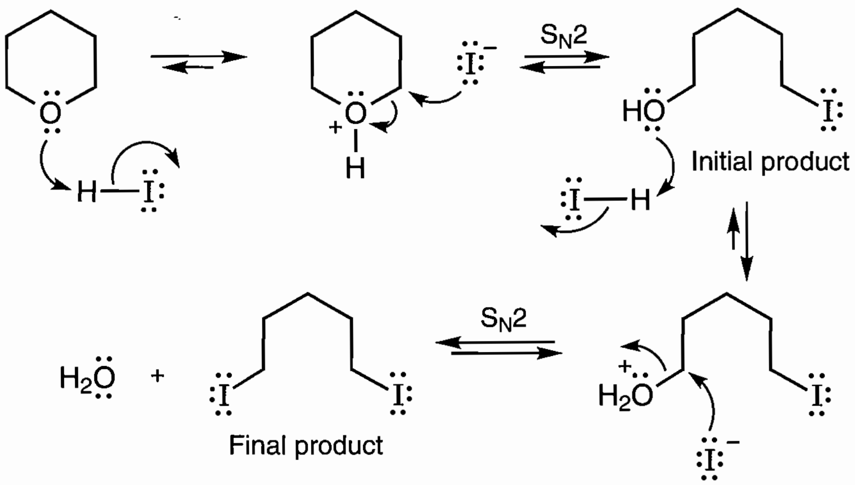
Problem 7.15 It is amazing how hard this question is. Perhaps our focus on displacement reactions makes it difficult to see the good old-fashioned Brønsted acid–base chemistry. The strong base removes the proton from the alcohol to give the alkoxide ion, RO^-. You need to be able to consider more than one reaction at the same time.



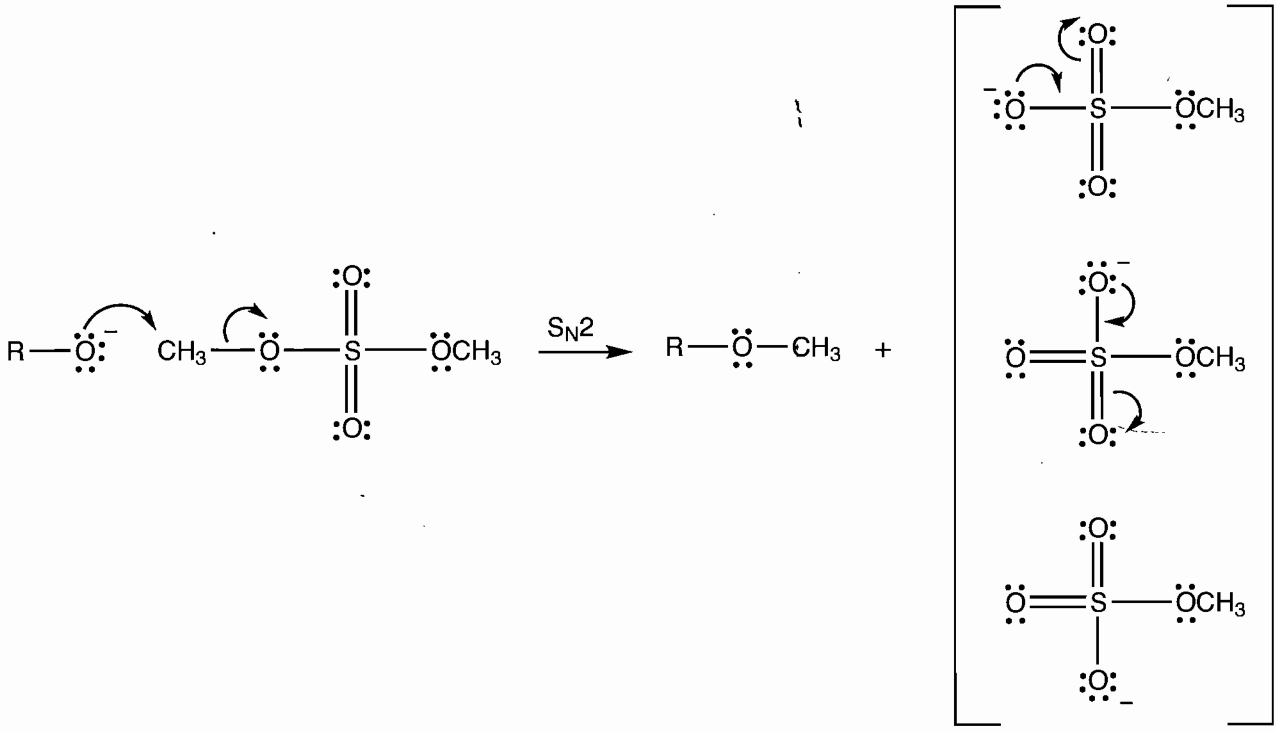
Problem 7.16 Protonation by hydrogen iodide yields an intermediate in which only one S_N2 reaction is possible. There can be no S_N2 reaction at the carbon of the benzene ring—the ring blocks access for the iodide ion.



Problem 7.17 The mechanism is a standard ether cleavage reaction applied in a cyclic system. It is complicated by the transformation of the initial product, an iodo alcohol, into a diiodide.

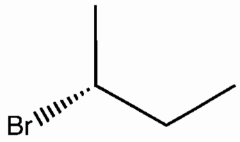


Problem 7.18 This problem is nothing more than a simple S_N2 displacement of a good leaving group by an alkoxide.

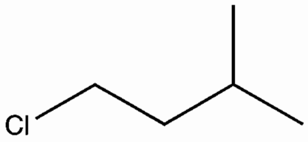


Problem 7.19

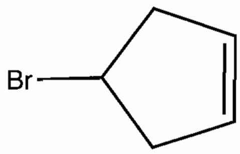
(a)



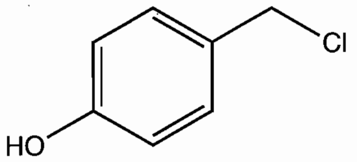
(b)



(c)

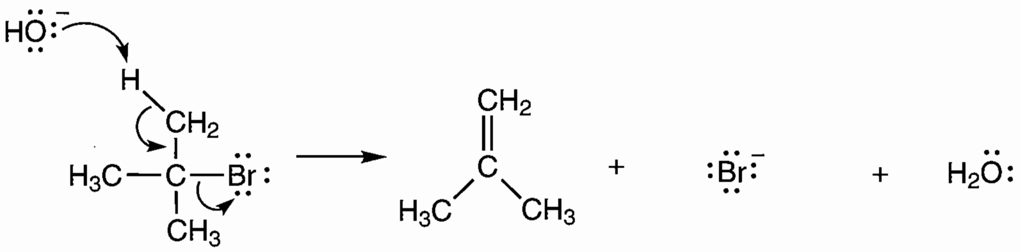


(d)

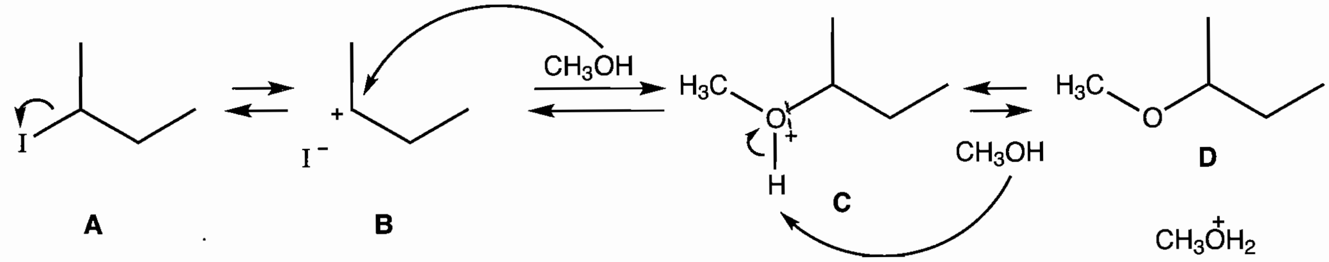


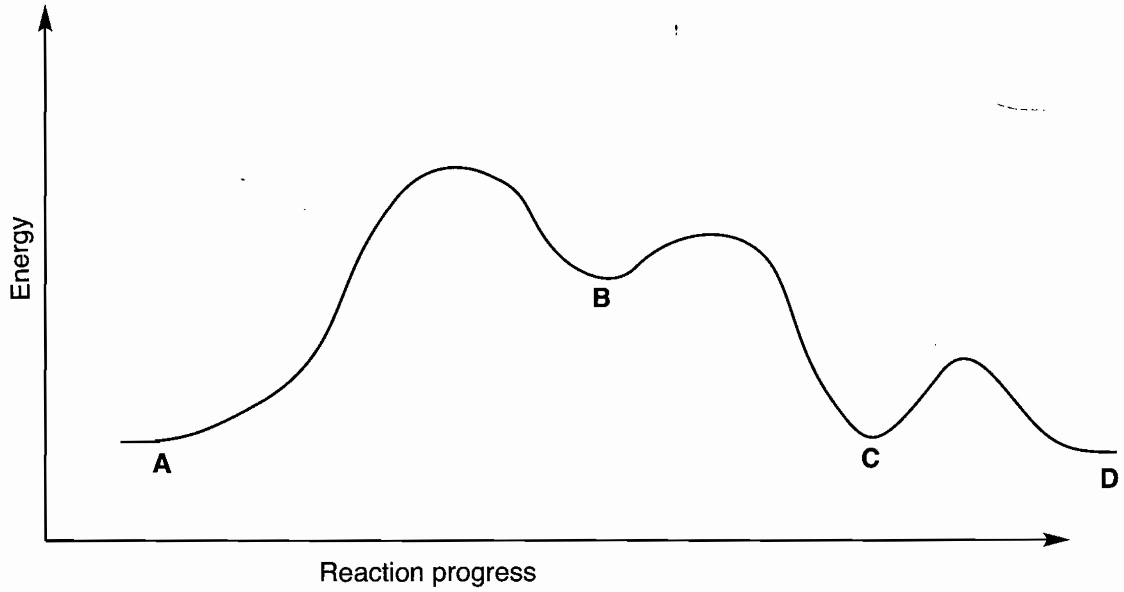
The OH on the aromatic ring will not undergo substitution. The backside of the C—O bond is inaccessible

Problem 7.20 In this problem, you are asked to outline an arrow formalism for a reaction you have not yet seen, although you will certainly see this reaction later in the next chapter. You need to reason backward from the product, visualize what must have happened, and then supply the arrows. The elements of HBr are eliminated to give the alkene 2-methylpropene. The formula C_4H_8 suggests this much. Here is the product along with an arrow formalism for the process.

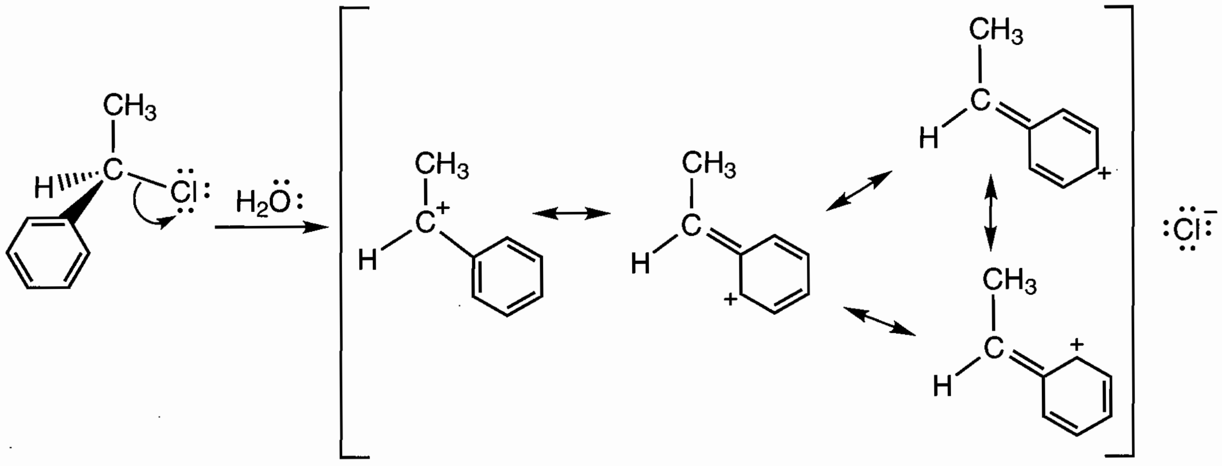


Problem 7.21



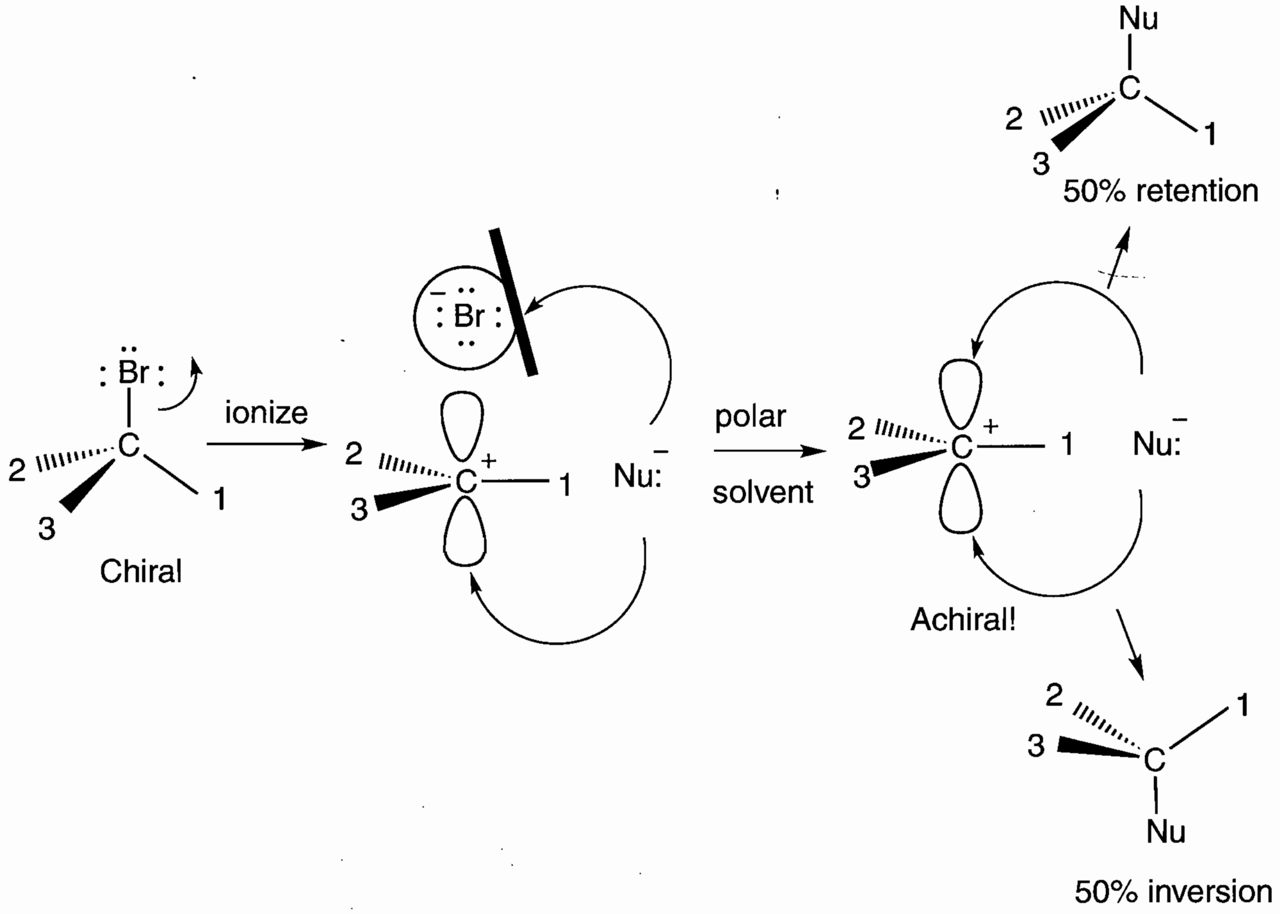


Problem 7.22 The S_N1 reaction is usually more favorable for tertiary halides such as the one shown at the top of Figure 7.76. However, this particular secondary halide leads to an especially stable carbocation. Localized charge is bad, and delocalized charge is better. The phenyl (cyclohexatriene) ring provides a way to delocalize the charge generated on ionization. This delocalization makes this phenyl secondary carbocation relatively stable, and therefore relatively easy to form.



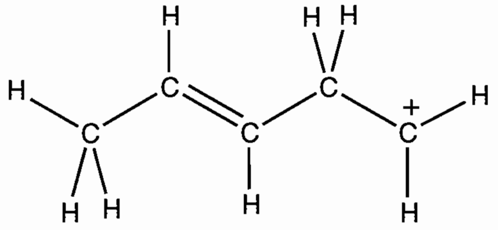
Several resonance forms make for a stable species

Problem 7.23 Polar solvents stabilize ions. The more stable an ion is, the less reactive it is, and the longer it lives. Long life allows for movement of the two ions away from their positions in the original ion pair. So, the more polar the solvent, the more likely it is that the symmetrical ion of Figure 7.75 will be formed from the unsymmetrical ion pair of Figure 7.77. A polar solvent favors racemization, the inevitable result of formation of the symmetrical carbocation of Figure 7.75.



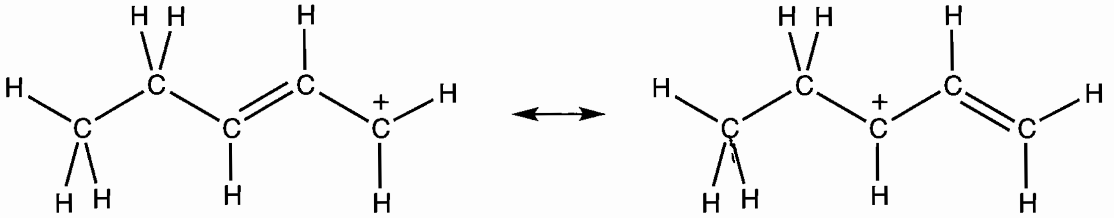
Problem 7.25

$CH_3CH{=}CHCH_2CH_2^+$



Primary cation

$CH_3CH_2CH{=}CHCH_2^+$

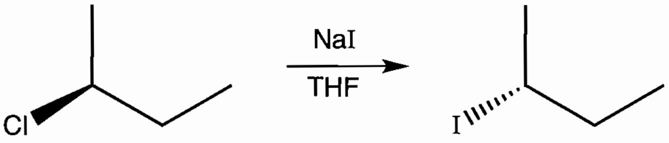


Allylic cation

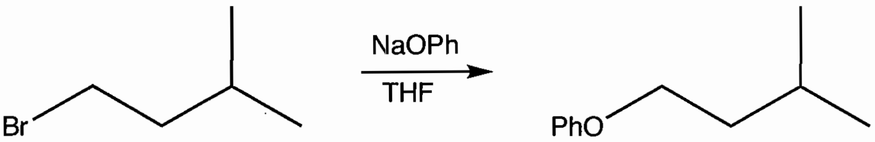
The allylic cation is more stable because resonance allows for sharing of electrons. As a result of resonance, the carbocation is equally shared by two atoms. A primary allylic cation is more stable than a primary cation.

Problem 7.26

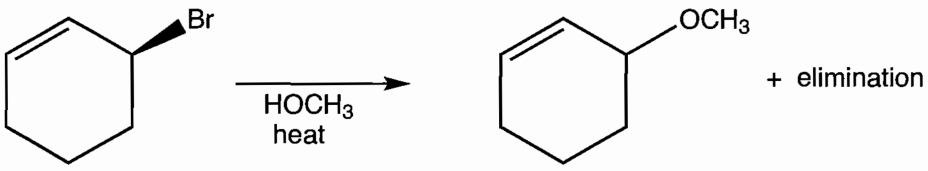
(a) This reaction is an S_N2 displacement. Iodide is an excellent nucleophile, and it will displace the secondary chloride. There are many solvents that will work. THF is a commonly used solvent. Acetone would also work well. Water could be used, but it would slow down the rate by solvating the iodide.



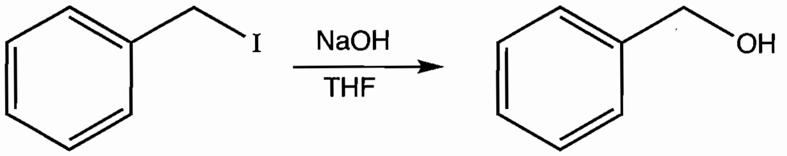
(b) This reaction is an S_N2 displacement. The phenoxide anion (PhO^-) is a good nucleophile. THF is the best solvent for this reaction.



(c) This is an S_N1 solvolysis. We can tell that by noting the loss of stereochemistry. We will see in Chapter 8 that this reaction will also give elimination products. Methanol (CH_3OH) is a good solvent and nucleophile for this reaction. But we would not want to use water. Water would compete in the substitution reaction, giving 2-cyclohexenol rather than the desired ether.

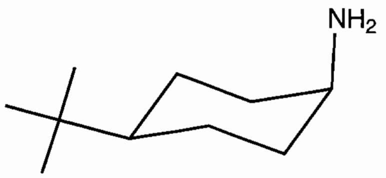


(d) This is an S_N2 reaction. Hydroxide is a good nucleophile. Hydroxide is also a base, but there are no elimination products possible for this primary iodide. THF is a fine choice for solvent in this reaction. Water would also work. We would not want to use methanol because the hydroxide could deprotonate the methanol to give methoxide, which would compete with the hydroxide for the substitution.

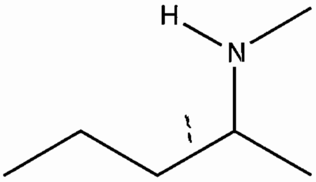


Problem 7.28

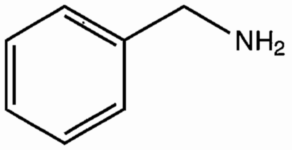
(a)



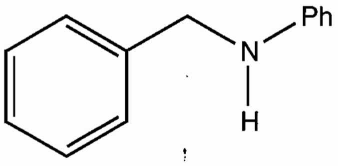
(b)



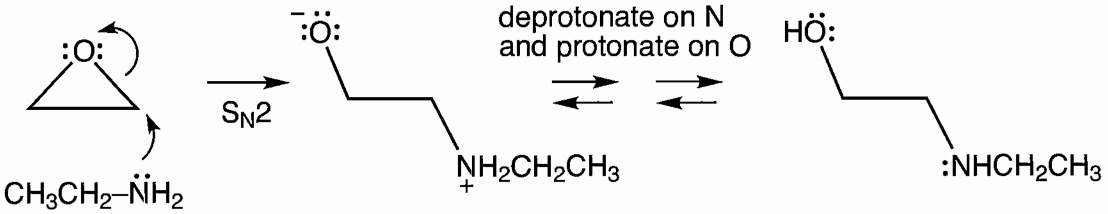
(c)



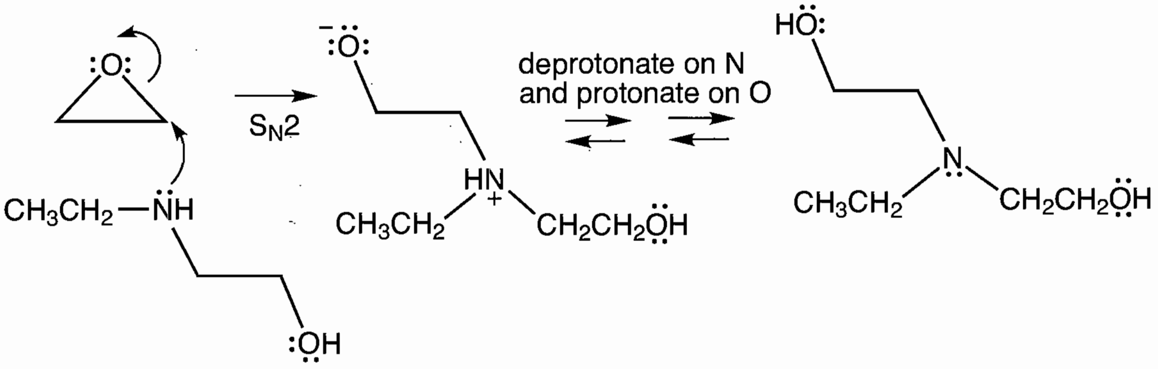
(d)



Problem 7.29 Epoxides react with nucleophiles to open the three-membered ring. Here ethylamine acts as nucleophile in the S_N2 reaction. Protonation gives the first product.



The first-formed product is still a strong enough nucleophile to react with the epoxide, and so a second step takes place.



Although this product is still a nucleophile, it is apparently too sterically hindered to react further with another epoxide.

Problem 7.30

(a) $HO^- + CH_3Br \longrightarrow CH_3OH$ This will be an S_N2 reaction

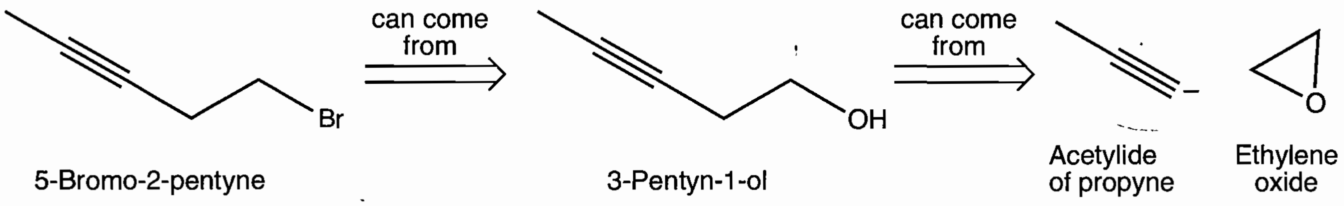
(b) $HO^- + CH_3(CH_2)_3CH_2Br \longrightarrow CH_3(CH_2)_3CH_2OH$ This will be an S_N2 reaction – hydroxide is also a good base so elimination (Chapter 8) will compete

(c) $H_2O + (CH_3)_3CBr \longrightarrow (CH_3)_3COH$ This will be an S_N1 reaction – elimination (Chapter 8) will compete

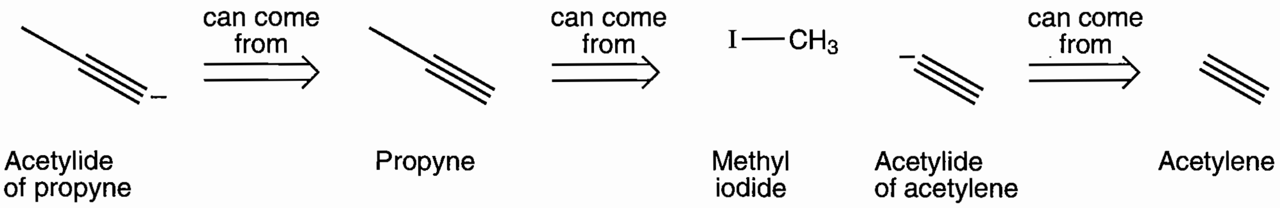
(d)

$H_2O + CH_3(CH_2)_3CH_2Br \longrightarrow$ No reaction in this case – this primary bromide can only do S_N2 chemistry, but water is not nucleophilic enough to be useful for S_N2 reactions

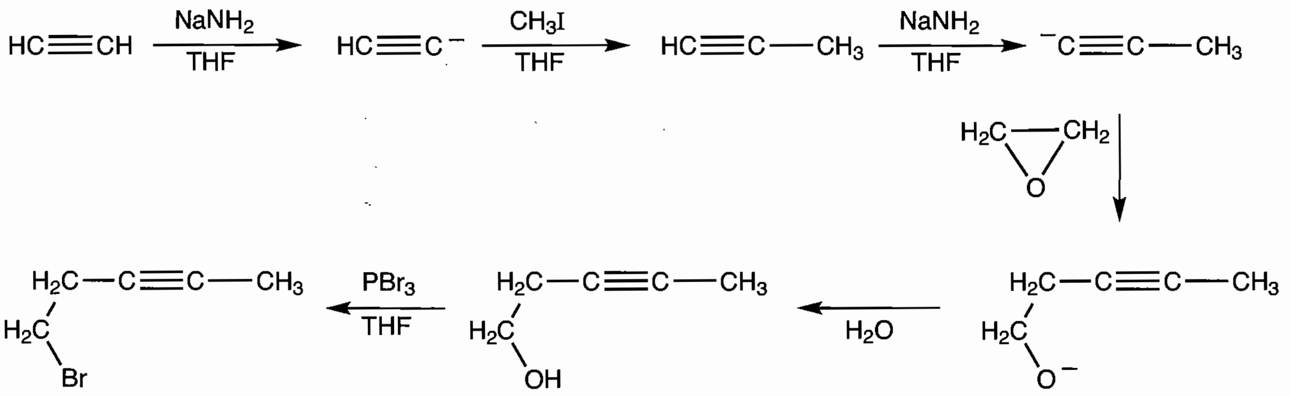
Problem 7.31 There are many correct solutions to this problem. Here is one way to do it. We can use ethylene oxide as an electrophile, as we saw in Problem 7.29, where we opened the epoxide ring with an amine. We know how to make an acetylide (p. 316), and that can be used to attack the epoxide. The best way to solve a synthesis problem like this is to think backward. The 5-bromo-2-pentyne can be made from the corresponding alcohol (3-pentyn-1-ol). That alcohol can be made from the addition of an acetylide of propyne to ethylene oxide.



The acetylide of propyne can come from acetylene and methyl iodide.



Here is the solution going forward using this approach.



Problem 7.32

(a) 2-Bromobutane will be faster in the S_N1 reaction (secondary carbocation more stable than a primary carbocation) and 1-bromobutane faster in the S_N2 reaction (primary bromide less sterically hindered than the secondary bromide).

(b) Cyclopentyl chloride will be faster in the S_N1 reaction and 1-chloropentane faster in the S_N2 reaction for the same reasons as in (a).

(c) 1-Iodopropane will be faster in the S_N2 reaction because iodide is a better leaving group than is chloride. Neither molecule will undergo the S_N1 reaction because a primary carbocation must be formed.

(continued)

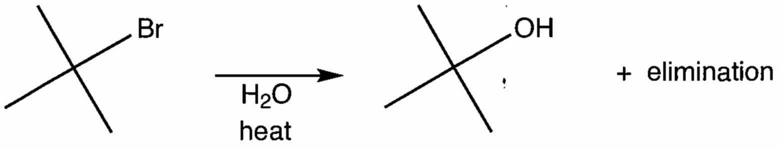
Problem 7.32 *(continued)*

(d) *tert*-Butyl iodide will be faster in the S_N1 reaction because the tertiary carbocation is more stable than a secondary carbocation and therefore formed more easily. Isopropyl iodide will be faster in the S_N2 reaction because it is less sterically hindered. Approach to the rear of the carbon–iodine bond is less hindered in the secondary system than in the tertiary system.

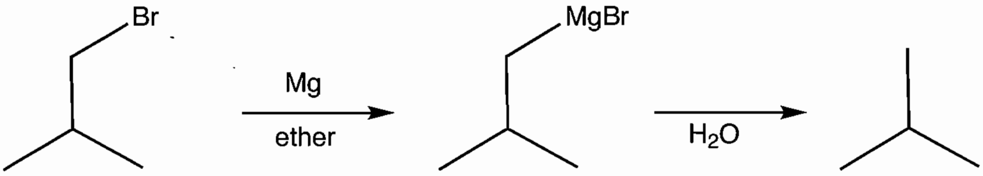
(e) Neither *tert*-butyl iodide nor *tert*-butyl chloride will react at all in the S_N2 reaction. *tert*-Butyl iodide will be more reactive in the S_N1 reaction because iodide is a better leaving group than is chloride.

Problem 7.33

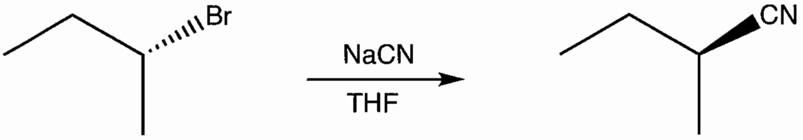
(a)



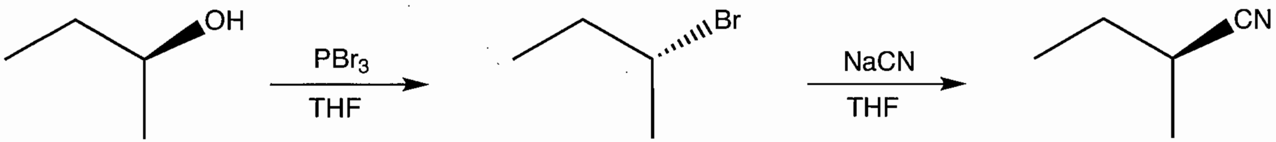
(b)



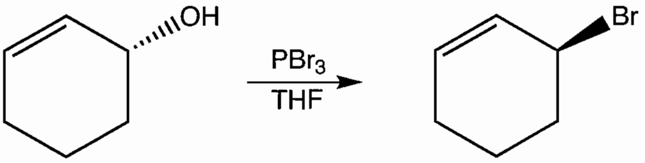
(c)



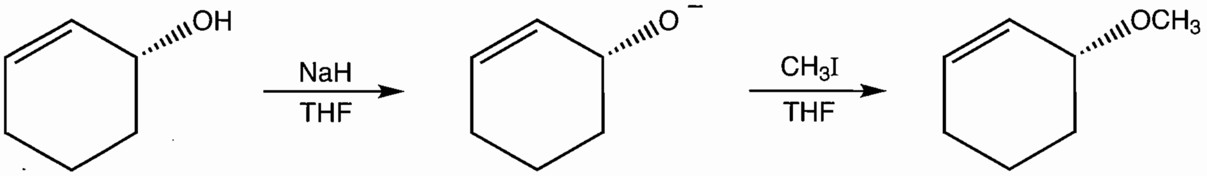
(d) A double inversion is needed here. We don't have a way of doing a substitution with retention. So we can't go directly from the alcohol to the cyano (CN) substituted product retaining the (*S*) stereochemistry.



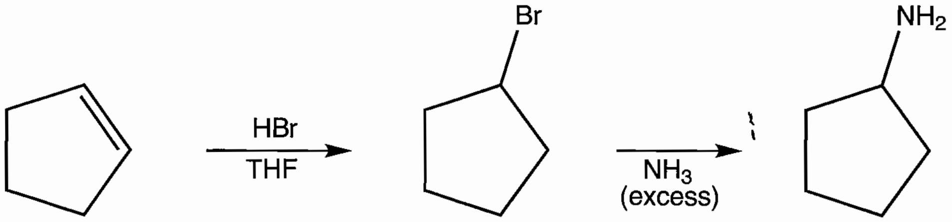
(e)



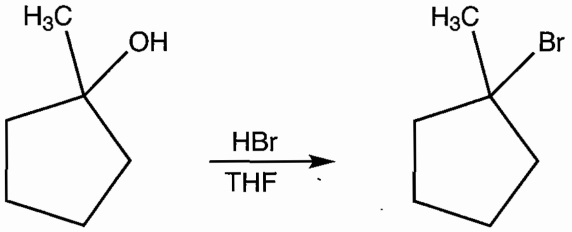
(f)



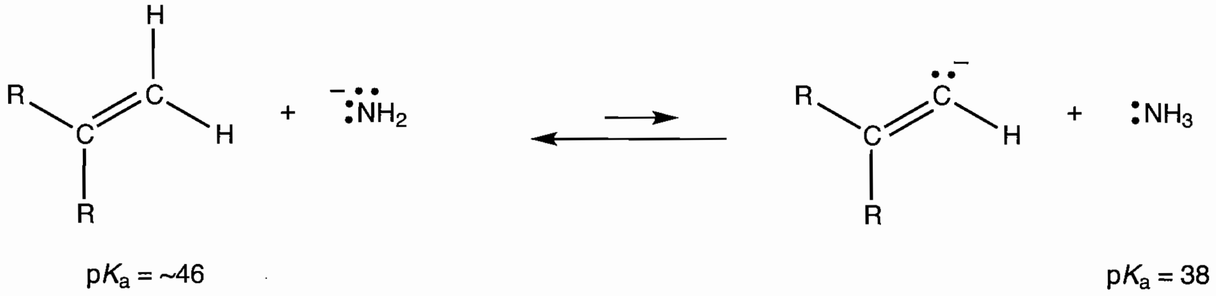
(g) Using excess amine in the S_N2 reaction gives the neutral cyclopentanamine product.



(h)



Problem 7.34



Ammonia is the stronger acid by a factor of 10^8! The amide ion will not effectively deprotonate a vinyl hydrogen.

Additional Problem Answers

Problem 7.35

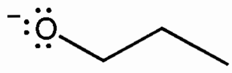
(a) The phosphine is the stronger nucleophile. Third-row atoms are more polarizable than second-row atoms, and hence better nucleophiles (see Figure 7.50, p. 295).

(b) The amide ion is a far better nucleophile than the neutral amine (see Figure 7.50, p. 295).

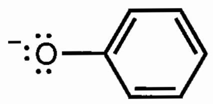
(c) Same answer as part (a). The thiolate is the better nucleophile.

Problem 7.36 Just ask yourself, what replaces the I in the starting material? The nucleophile must be that atom or group of atoms. You also have to be careful to adjust for the proper charge. In (a), the nucleophile must be neutral because the entering group winds up positive. In all the other cases, the nucleophile must be negative.

(a) $:NH_3$ (b) $^-N_3$ (c) $^-:\ddot{S}H$ (d) $^-:CN:$ (e)

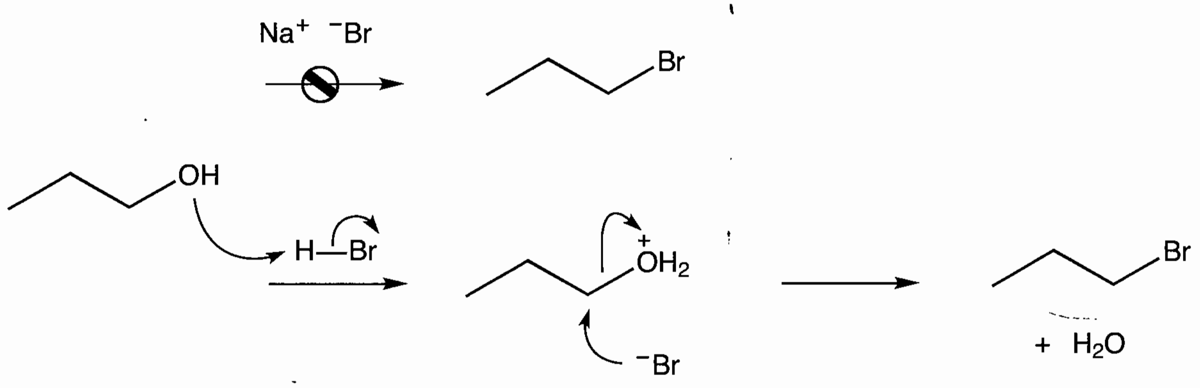


(f)



Problem 7.37 Bromide is by no means a strong enough nucleophile to displace the poor leaving group hydroxide. Indeed, the only possible reaction is a very, very slight deprotonation of the OH, but even this reaction will be poor as HBr is a much stronger acid (p$K_a = -9$) than a simple alcohol (pK_a ~17).

However, when the alcohol is treated with HBr, the first step converts the OH into a far better leaving group, $^+OH_2$, and now the bromide can do the displacement.



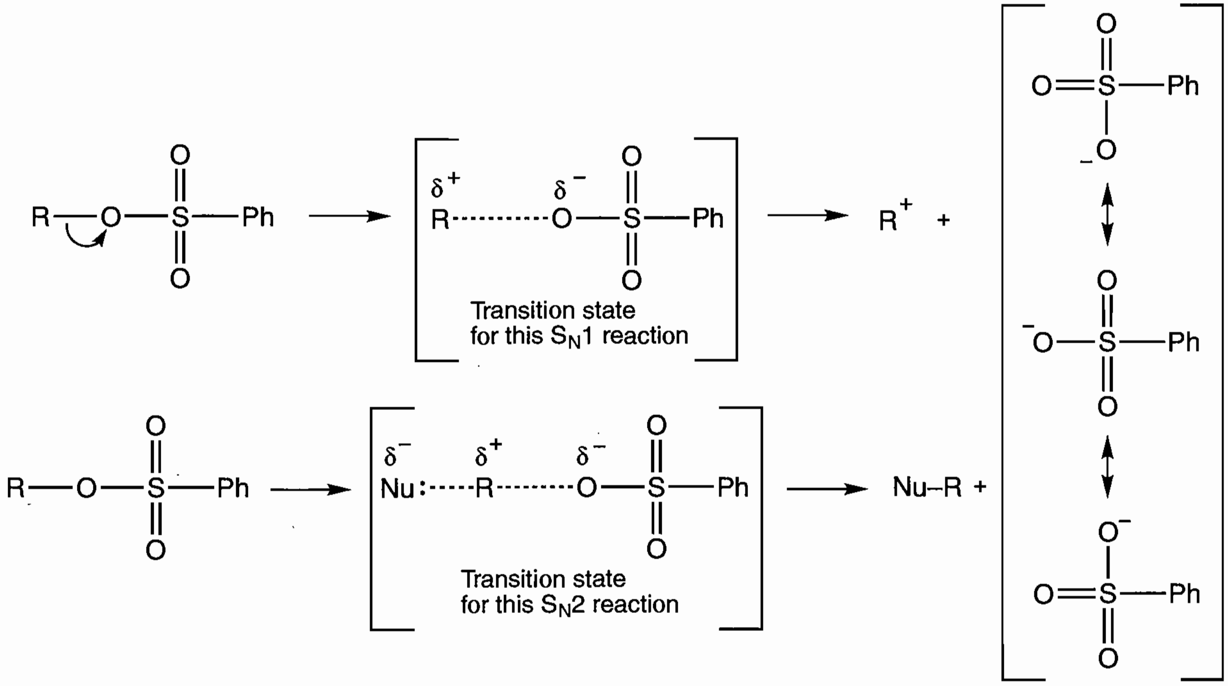
Problem 7.38

(a) HCl
(b) 1. H_3O^+/H_2O 2. NaH 3. CH_3I
(c) 1. HI 2. excess NH_3
(d) 1. HCl 2. Li 3. H_2O

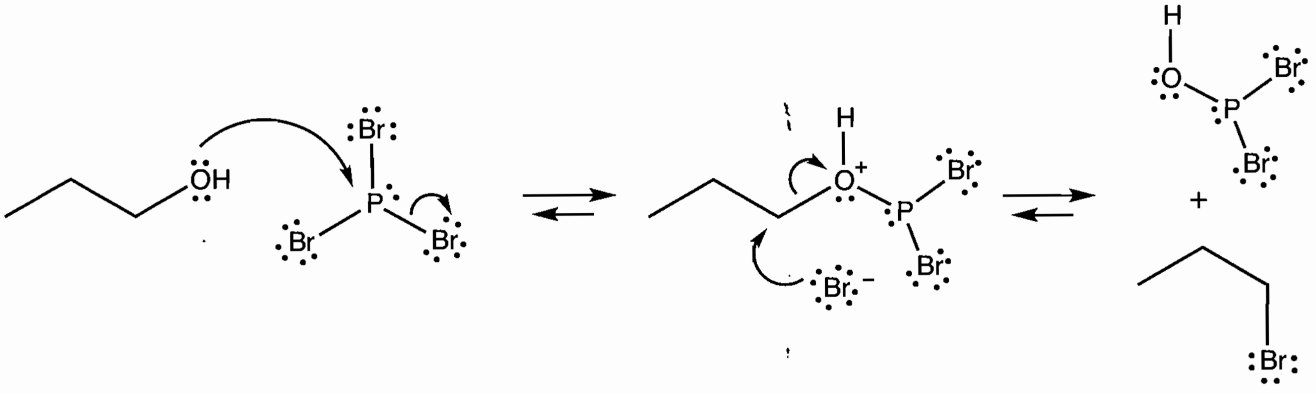
Problem 7.39

(a) HCl
(b) 1. NaH 2. CH_3I
(c) 1. HI 2. excess NH_3
(d) 1. PBr_3 2. NaSH

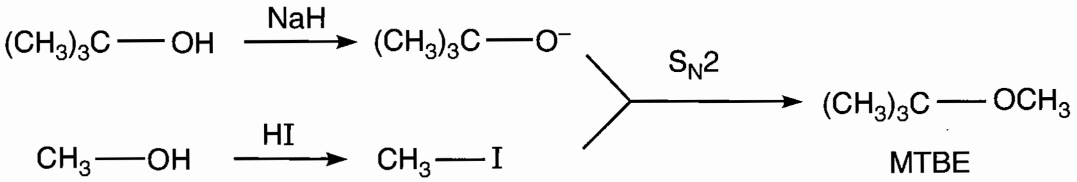
Problem 7.40 The sulfonate anions are well stabilized by resonance, as the negative charge is shared by three oxygen atoms. The transition state for S_N1 ionization or S_N2 displacement will have a partial negative charge (δ^-) developed on the sulfonate oxygen, and the transition state will be stabilized by delocalization.



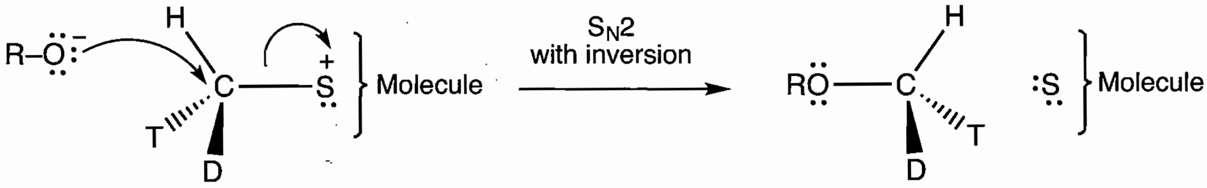
Problem 7.41



Problem 7.42 (See also Problem 7.51.)

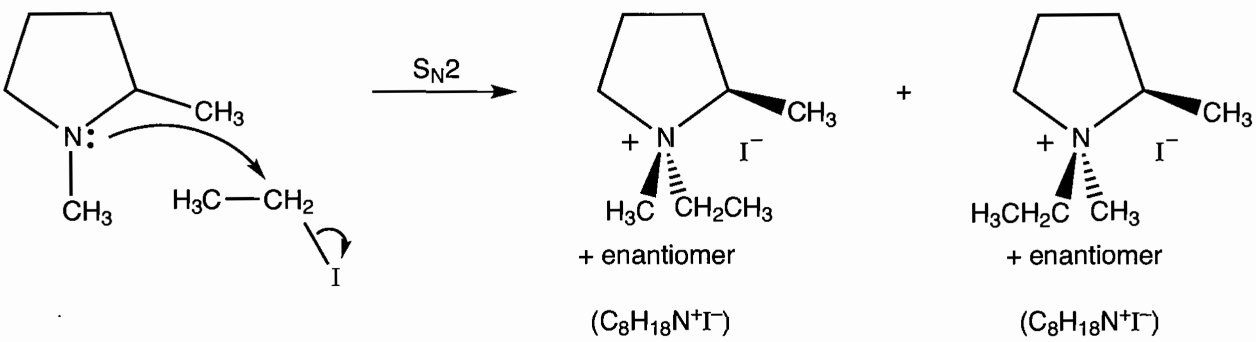


Problem 7.43 There is nothing difficult or profound here, despite the apparent complexity of the molecule. This substitution pattern allows an experimenter to determine the stereochemical course of the reaction. If this methyl transfer is an S_N2 reaction, inversion must take place. The rest of the molecule is really no more than a complicated R group.



Problem 7.44

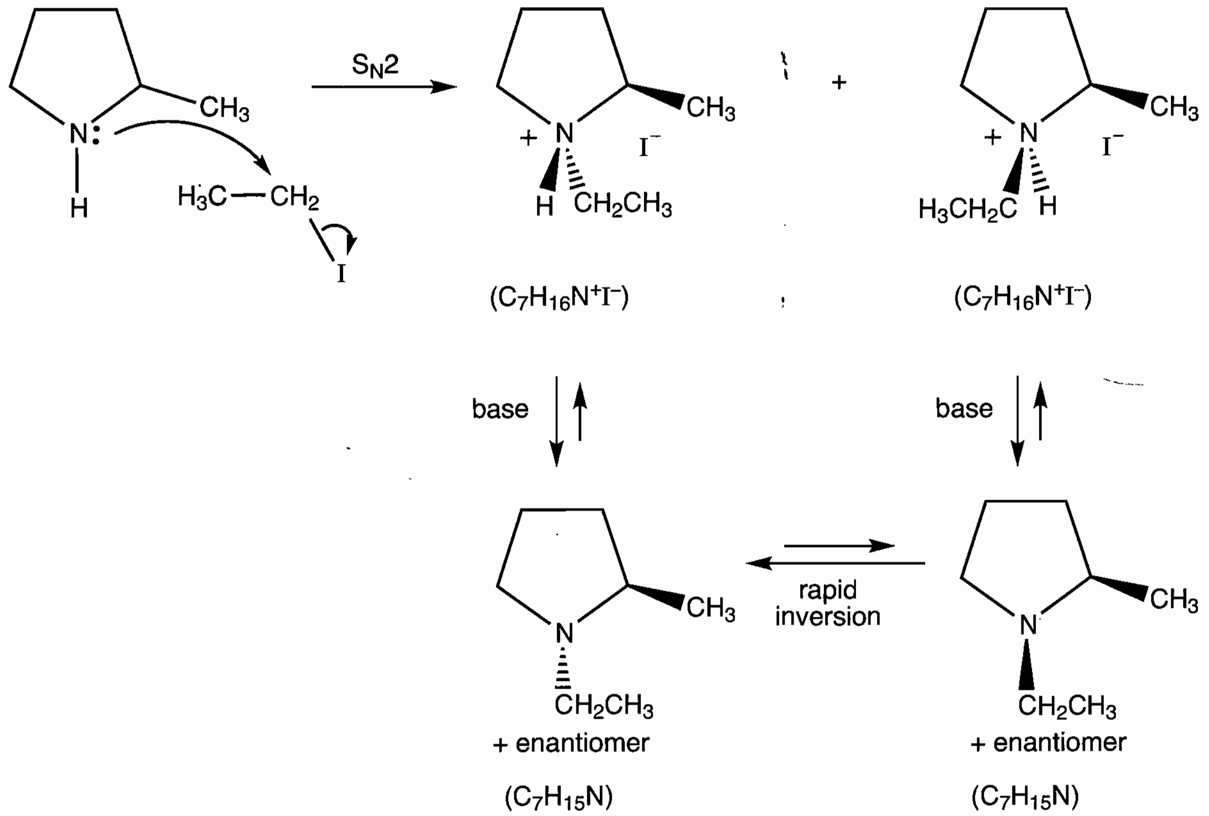
(a) Amine **1** can react with ethyl iodide in S_N2 fashion to give a pair of diastereomeric ammonium ions.



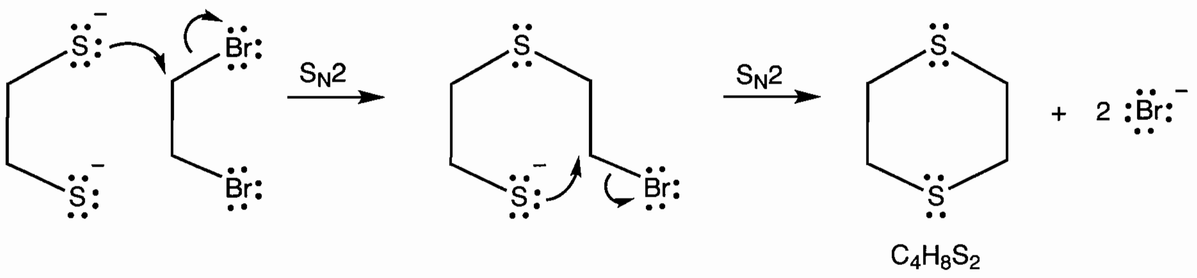
(continued)

Problem 7.44 *(continued)*

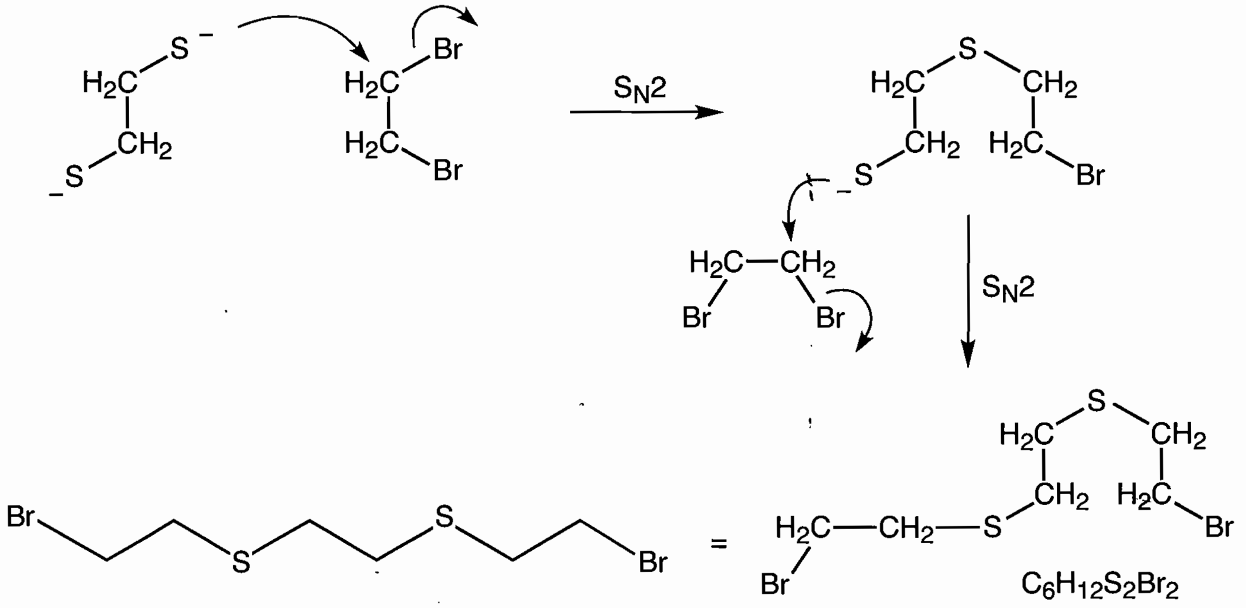
(b) When amine **2** undergoes the same kind of S_N2 reaction, a proton can be removed from the initially formed ammonium ion to give an amine. Amine inversion will interconvert the two possible isomers, and only one set of signals will be observed in the NMR spectrum.



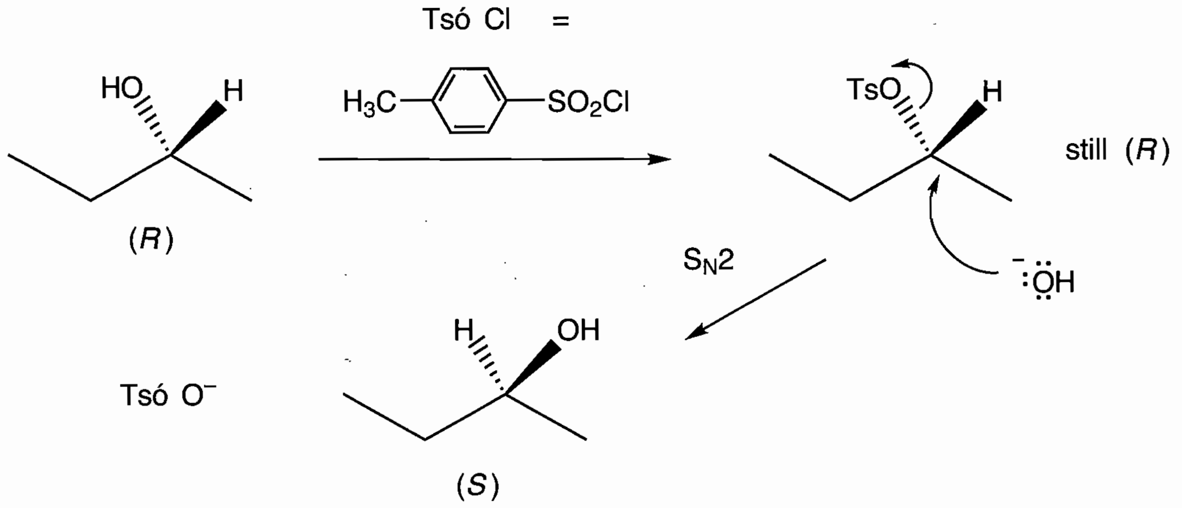
Problem 7.45 Here we have a strong nucleophile, or, really, two of them, in the same molecule, the dithiolate. Surely a double S_N2 displacement of the pair of bromides must lead to one product. The two displacements go one at a time.



The other compound still contains two sulfurs and two bromines, so the double displacement shown above must have been shortcut somehow. Perhaps after one displacement, the second loss of bromide takes place with another molecule of dibromide—the presence of six carbons shows that such an idea is quite reasonable.

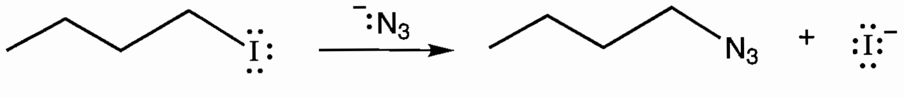


Problem 7.46 Here we need to do an inversion in order to convert the (*R*) enantiomer into the (*S*) enantiomer, but OH is surely not a good leaving group. Before we can displace it, we need to transform the leaving group. Page 299 gives one technique—formation of the tosylate from the alcohol. Now displacement by hydroxide is easy, and the S_N2 reaction provides the necessary inversion. Hydroxide will cause an elimination, as we will see in Chapter 8.

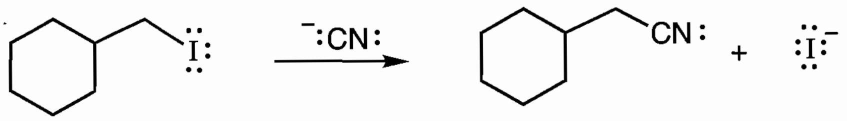


Problem 7.47 This problem should be fairly easy, except for (d) and (e), which ask you to devise intramolecular S_N2 reactions. Nothing is fundamentally changed from the early parts of this problem, but it always seems difficult in the beginning to think "intramolecularly." In parts (a) and (b), there is nothing more than a straightforward displacement of a good leaving group (here chosen as iodide, but many others would do as well) by the appropriate nucleophile.

(a)



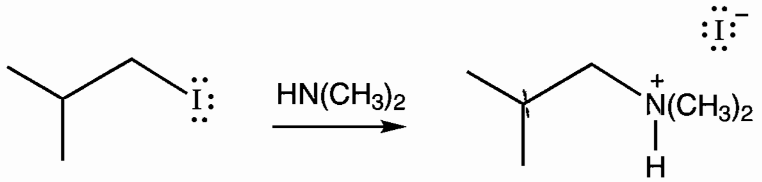
(b)



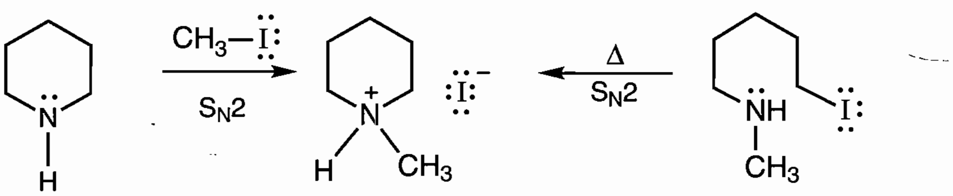
(continued)

Problem 7.47 *(continued)*

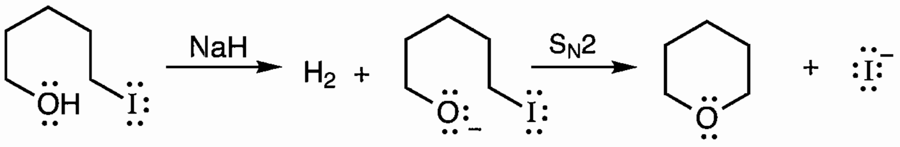
Part (c) is similar, except that a charged species, an ammonium ion, is formed.



Part (d) can be answered reasonably in two ways. In one, we use a cyclic amine to do an intermolecular S_N2 reaction. In the other, we design an intramolecular version of the S_N2 reaction closely resembling (c).

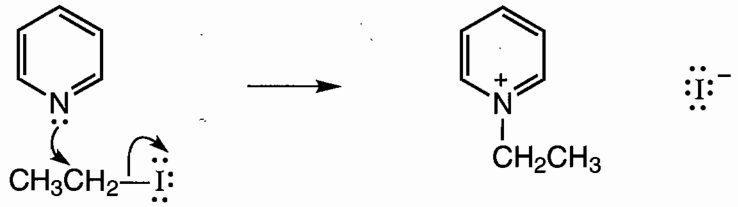


In part (e), we must design another intramolecular S_N2 reaction. The nucleophile required must be formed first from an alcohol by treatment with a base such as sodium hydride.

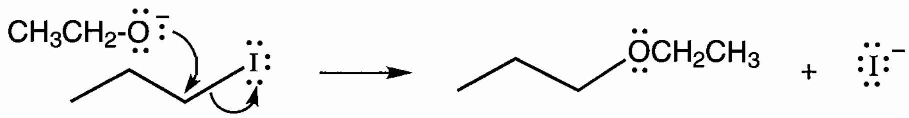


Problem 7.48 Parts (a–c) are straightforward displacements of a leaving group by a nucleophile. Part (a) leads to a pyridinium ion.

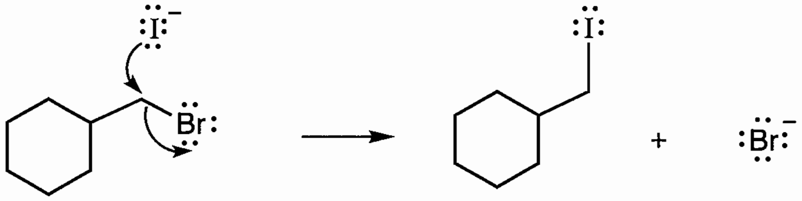
(a)



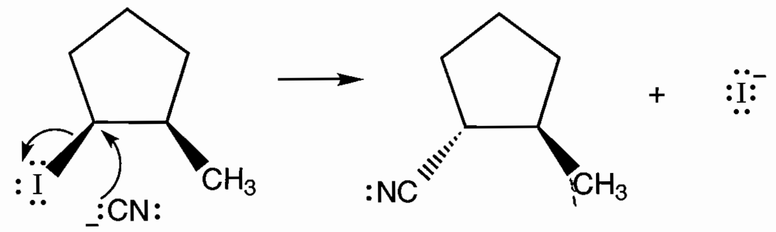
(b)



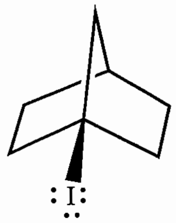
(c)



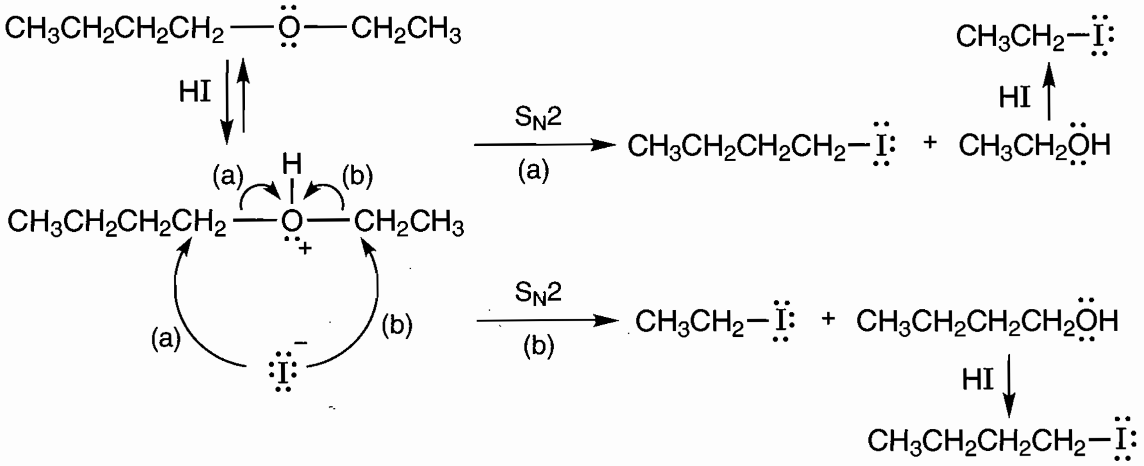
Part (d) requires you to be careful about stereochemistry. The S_N2 reaction always occurs with inversion, so the cis starting material becomes a trans product as iodide is displaced by cyanide.



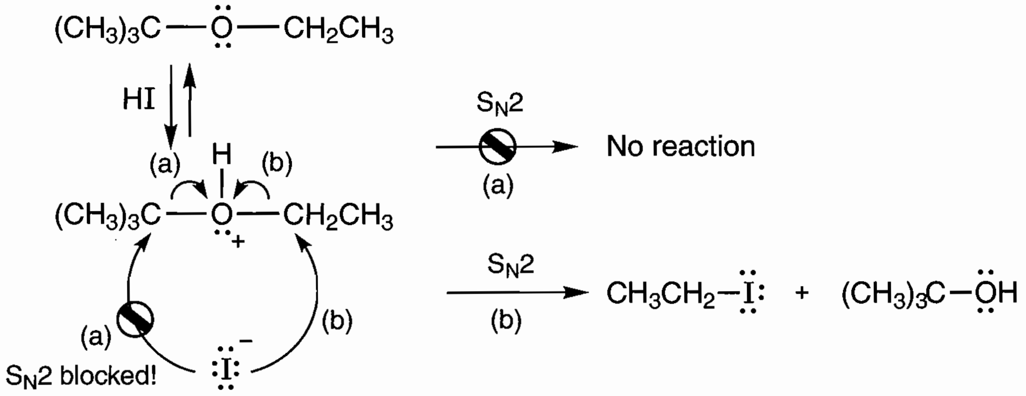
In part (e), there can be no reaction, as the substrate is tertiary and can undergo no S_N2 reaction.


A tertiary iodide—no reaction in the S_N2 process!
The backside of the C—I bond is completely blocked

Problem 7.49 The ether cleavage reaction proceeds through protonation of the ether oxygen and displacement by halide ion. In the first example, this can happen in two ways. In the prescence of excess HI, the alcohol products will also be converted into alkyl iodides.

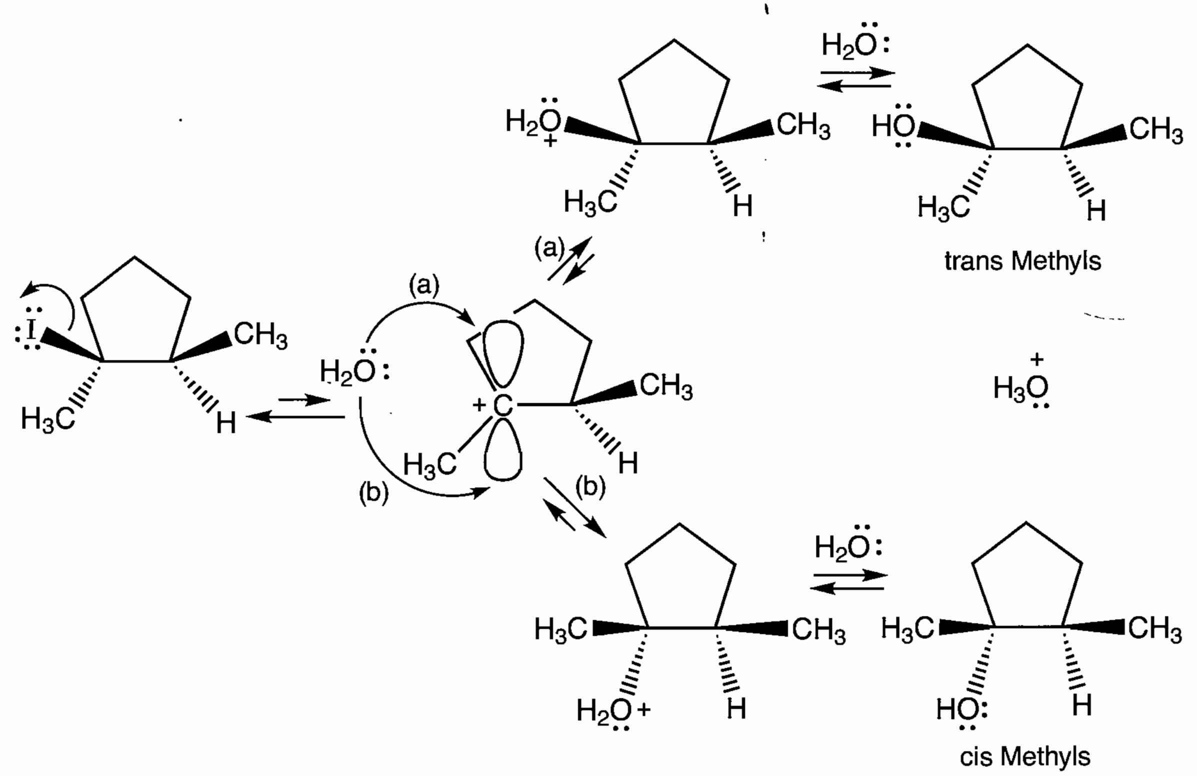


In the second reaction, there is only one possible S_N2 cleavage—one of the two possible displacements involves a tertiary carbon, and the S_N2 reaction never succeeds under such circumstances.

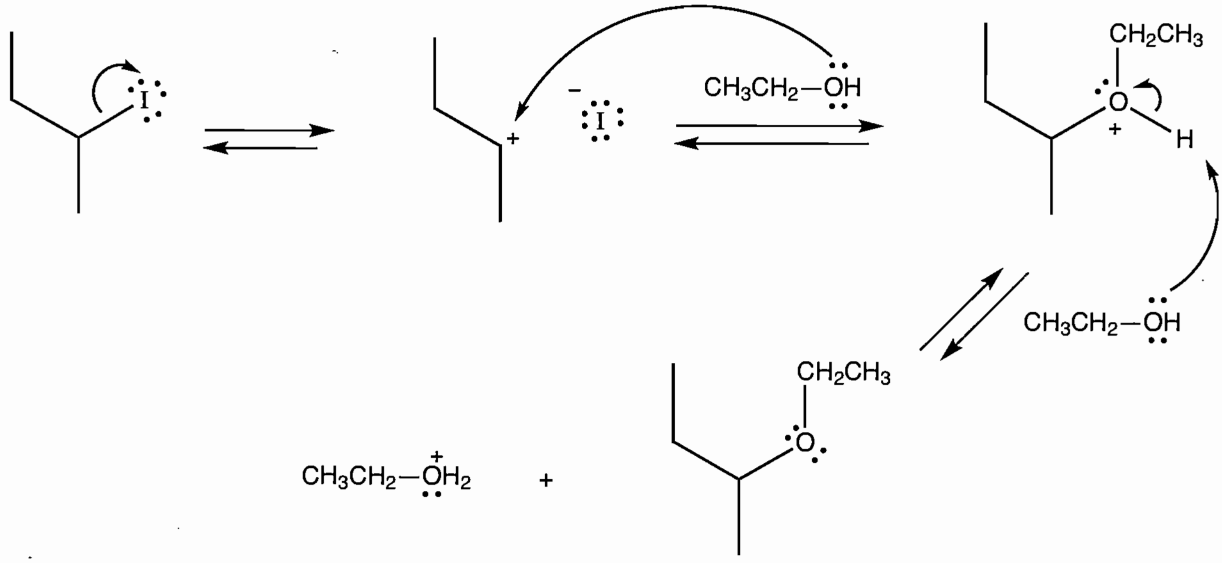


Problem 7.50

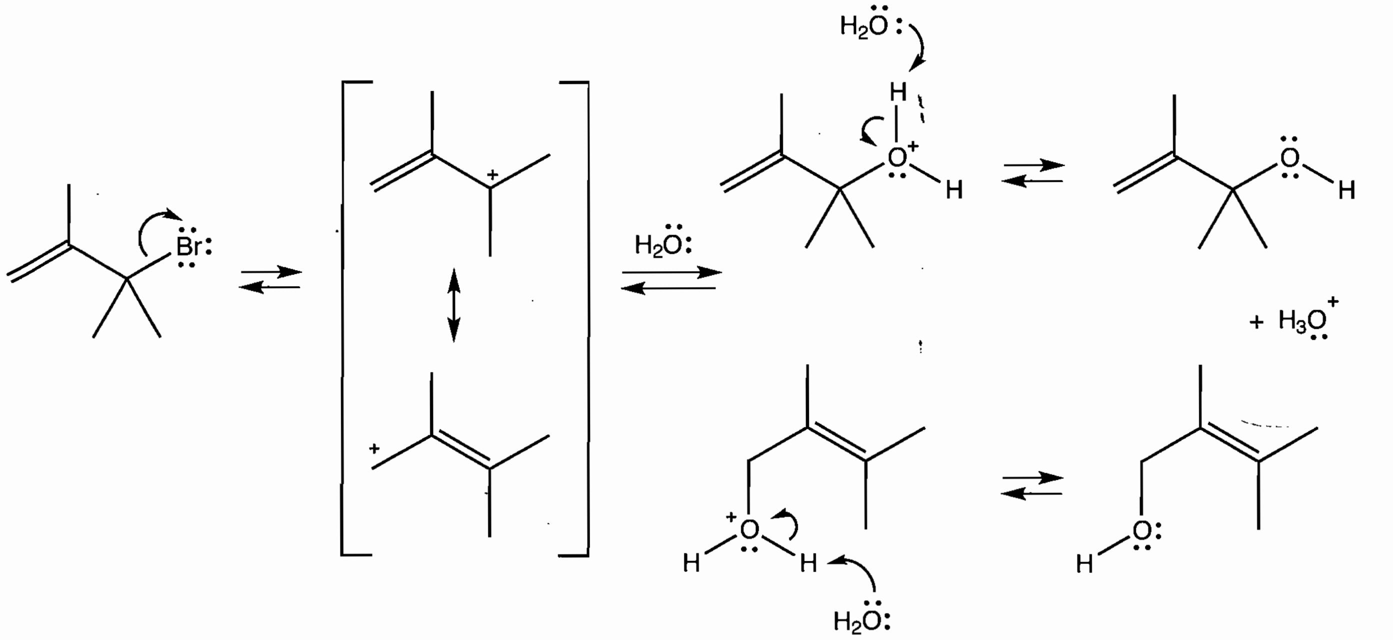
In part (a), a pair of diastereomeric alcohols will be produced as ionization produces a carbocation to which water can add at either the "top" or "bottom" lobe of the $2p$ orbital. The intermediate oxonium ions are deprotonated by water to give the alcohol products.



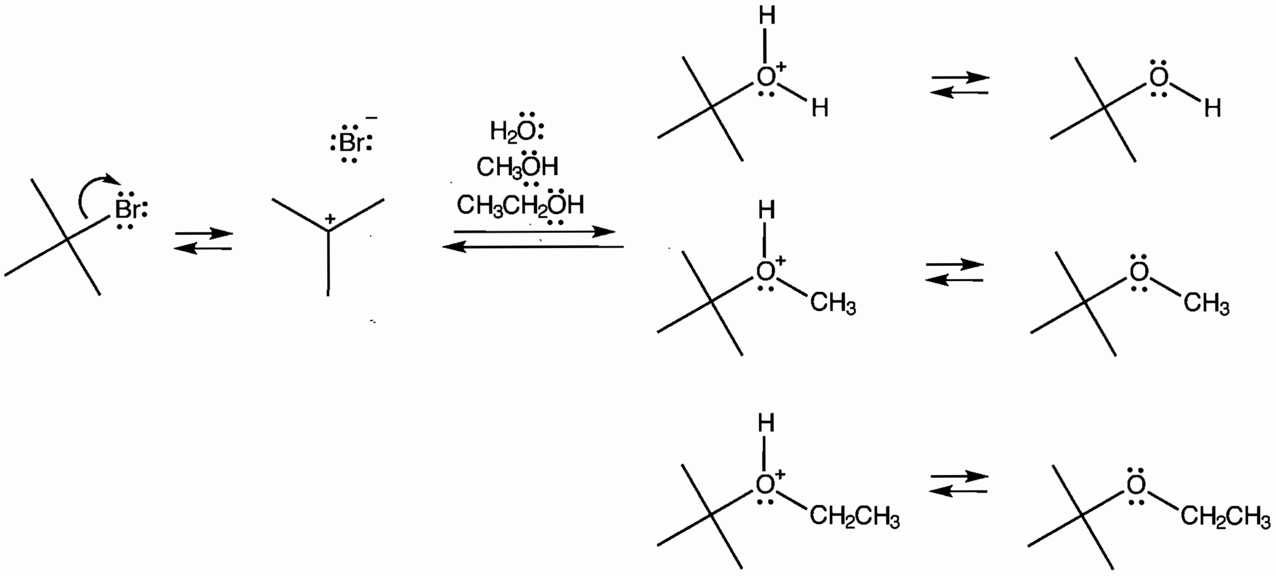
In part (b), ionization to a secondary carbocation leads to capture by the ethyl alcohol (solvolysis) to give an oxonium ion that will be deprotonated to give the ether product, 2-ethoxybutane.



In part (c), a resonance-stabilized carbocation is formed on ionization. This cation can be captured at the two carbons sharing the positive charge to give two products after deprotonation.



In part (d), ionization will give the *tert*-butyl cation. This intermediate can be captured by any available nucleophile. As there are three nucleophiles present, there will be three products.



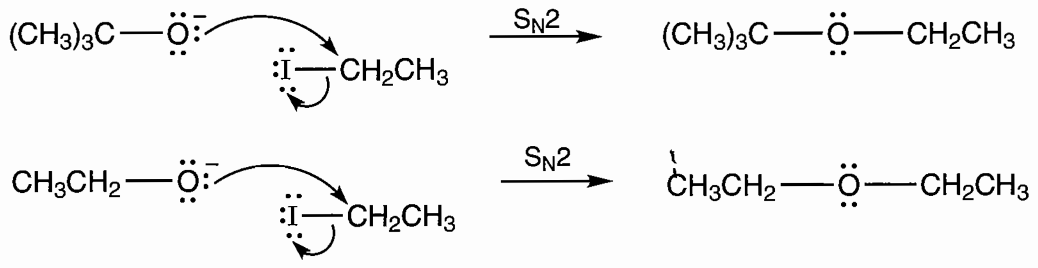
Problem 7.51 In principle, three ethers are possible; *tert*-butyl ethyl ether, di-*tert*-butyl ether, and diethyl ether.

$$CH_3CH_2{-}\underset{\cdot\cdot}{\ddot{O}}{-}C(CH_3)_3 \quad (CH_3)_3C{-}\underset{\cdot\cdot}{\ddot{O}}{-}C(CH_3)_3 \quad CH_3CH_2{-}\underset{\cdot\cdot}{\ddot{O}}{-}CH_2CH_3$$

In practice, only two of these can be made from the starting materials given. *tert*-Butyl iodide cannot be used as a substrate in the S_N2 reaction because it is a tertiary halide and the S_N2 reaction will not proceed with tertiary halides (an elimination will occur instead, as we will see in Chapter 8). We are restricted to using ethyl iodide as the halide, and this leads to only two of the three possible ethers.

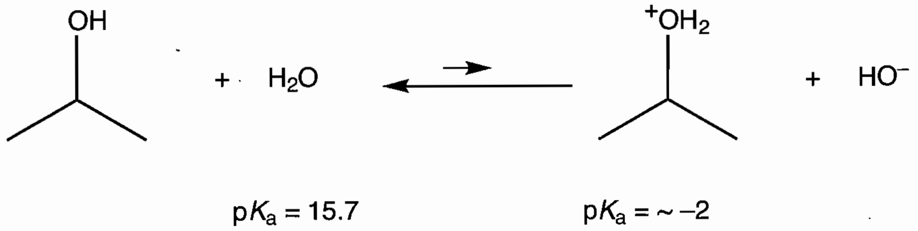
(continued)

Problem 7.51 *(continued)*

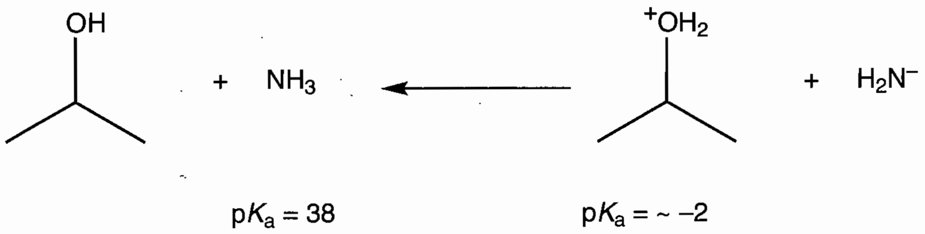


Problem 7.52

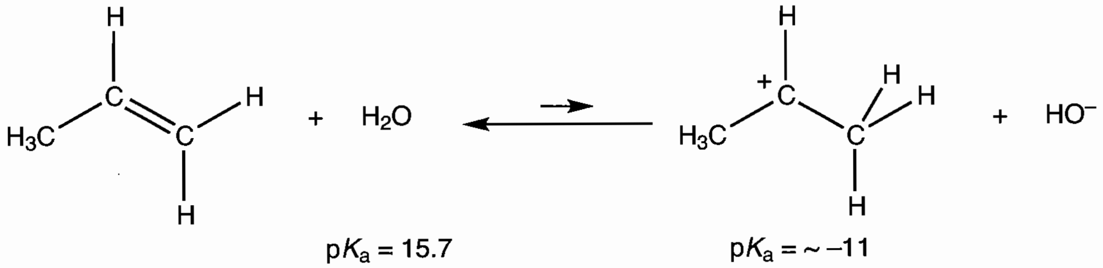
(a) The equilibrium for this reaction favors the left by an enormous factor of 10^{18}! It is *not* practical to protonate an alcohol with water.



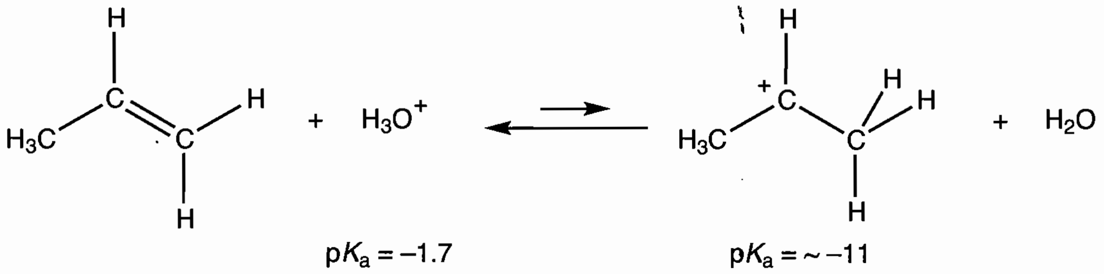
(b) This equilibrium is even less likely. The difference in pK_a is a factor of 10^{40}. This is so unlikely that we wouldn't draw the forward arrow in the equilibrium. We don't think of an alcohol as a base in comparison to ammonia (or an amine).



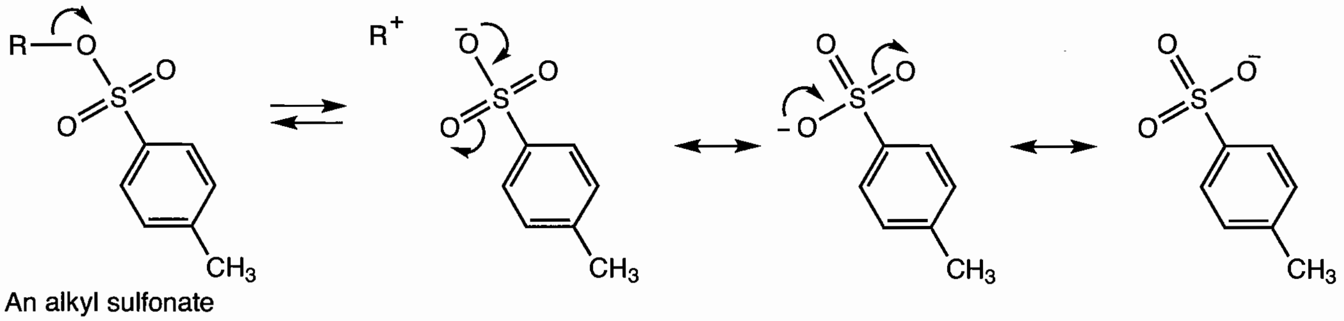
(c) This is another case of an equilibrium that is not very reversible. The estimated pK_a for this cation is –11, which means that the alkene is favored by a factor of 10^{27}. It is not practical to protonate an alkene with water.

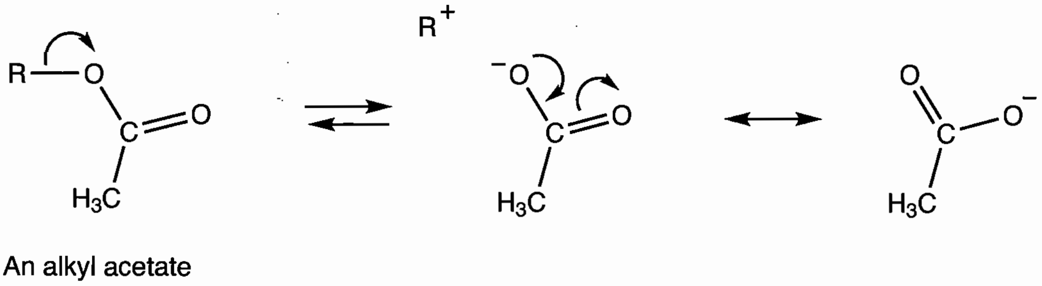


(d) The equilibrium favors the alkene and protonated water, but by a factor of about 10^9, which means that there will be some carbocation formed (one part in about a billion). Notice that this reaction becomes more favorable with a stronger acid, such as HCl (pK_a of –8) or HBr (pK_a of –9).



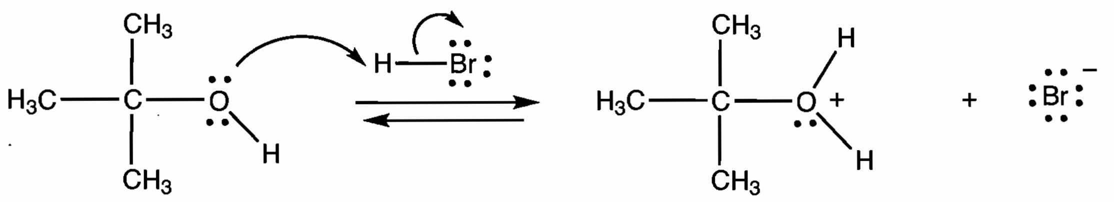
Problem 7.53 A sulfonate is a better leaving group than an acetate because it is a more stabilized conjugate base. There are three resonance structures for the oxygen anion of the sulfonate compared to the two resonance structures for the oxygen anion of the acetate leaving group.





Problem 7.54

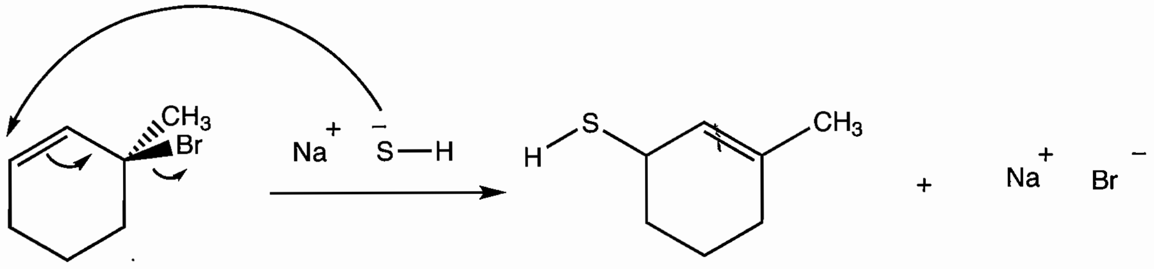
(a)



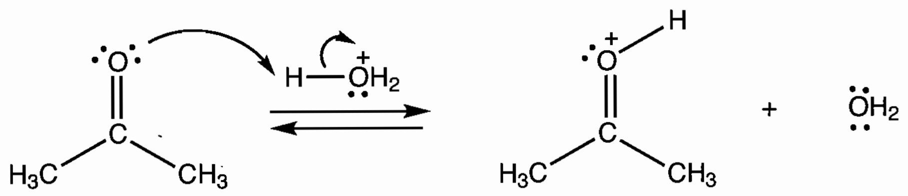
(continued)

Problem 7.54 *(continued)*

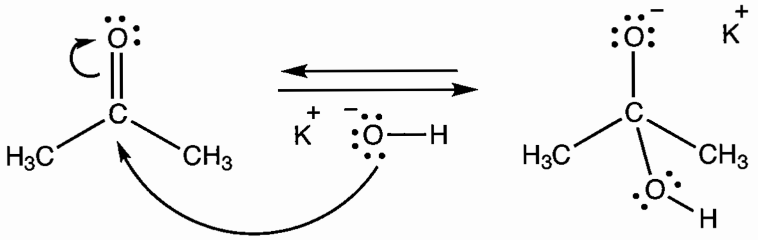
(b)



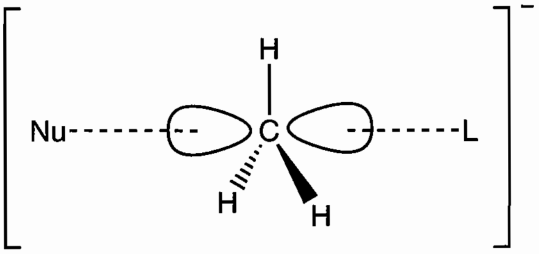
(c)



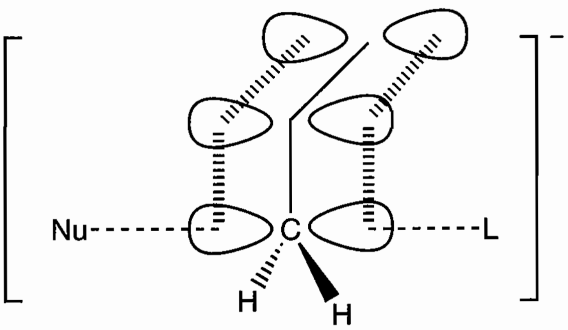
(d)



Problem 7.55 Recall that in the transition state for the S_N2 reaction, the carbon at which displacement occurs is approximately sp^2 hybridized. The transition state for S_N2 displacement in allyl systems benefits from delocalization through overlap of the alkene π orbitals with the 2*p* orbital at the "central" carbon.



Transition state for typical S_N2 displacement reaction of CH_3—L



Transition state for S_N2 displacement reaction in an allyl system; note the overlap with the π orbitals of the double bond

Problem 7.56

(a) The primary bromide of 1-bromobutane will react faster than the secondary bromide in 2-bromobutane in an S_N2 reaction because the backside of the C—Br bond in the secondary position is more sterically hindered. It is more difficult for the nucleophile to approach the empty C—Br antibonding orbital on the secondary carbon.

(b) A protonated alcohol is a very good leaving group. An alcohol is not a leaving group. Therefore, it is the protonated alcohol that will react more rapidly in an S_N2 reaction.

(c) A chloride is a better leaving group than a fluoride. Therefore, 1-chlorobutane will react faster than 1-fluorobutane in an S_N2 reaction.

(d) The 3-bromocyclopentene will react faster than bromocyclopentane in an S_N2 reaction because the 3-bromocyclopentene has the bromo group in an allylic position (p. 291). Leaving groups in the allylic position are especially easily displaced in S_N2 reactions because the transition state for displacement is delocalized (see Problem 7.55).

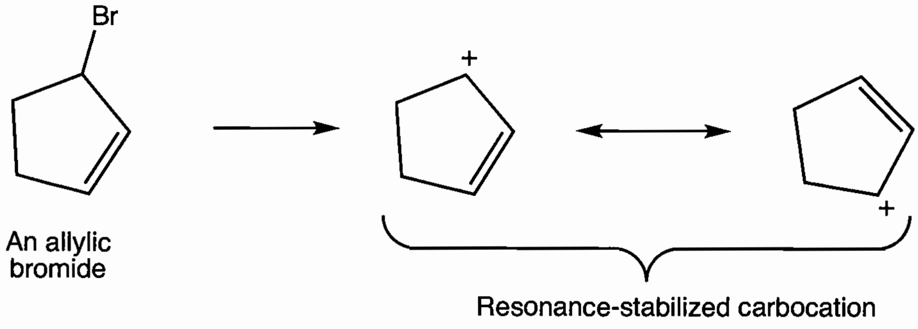
Problem 7.57

(a) The secondary bromide (2-bromobutane) will react much faster than the primary bromide (1-bromobutane) in an S_N1 reaction. Remember that it is very difficult to make a primary carbocation. That intermediate is too high in energy, too unstable, for a typical organic reaction.

(b) The secondary bromide (3-bromopentane) will react faster than the secondary chloride (3-chloropentane) in an S_N1 reaction because the bromide is a better leaving group. The C—Br bond is weaker than the C—Cl bond.

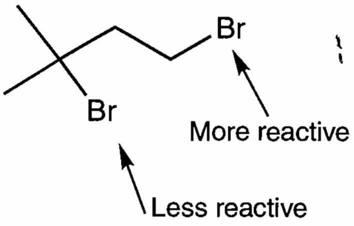
(c) A tosylate is a better leaving group than a chloride. Therefore, the structure on the right will react faster in an S_N1 reaction. The tosylate is a better leaving group because it can accommodate the negative charge so well. There are three resonance structures of the tosylate anion (see Problem 7.53).

(d) The allylic bromide of 3-bromocyclopentene is more reactive than the secondary bromide of bromocyclopentane in an S_N1 reaction because the carbocation intermediate that is allylic is more stable. Formation of the more stable carbocation has a lower energy transition state than formation of the higher energy, less stable carbocation.

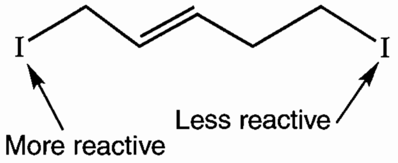


Problem 7.58

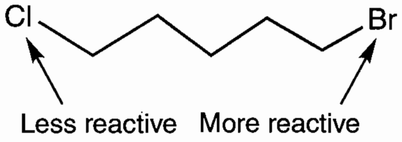
(a) The primary bromide will surely be more reactive than the tertiary bromide in the S_N2 reaction.



(b) It will be the allylic iodide that is the more reactive, as the transition state for S_N2 displacement will benefit from delocalization (Table 7.3, p. 291, Problem 7.55, p. 328).

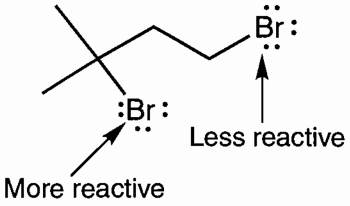


(c) Bromide is a better leaving group than chloride and will be more reactive in the S_N2 reaction.

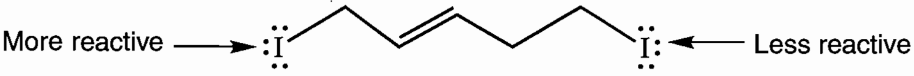


Problem 7.59

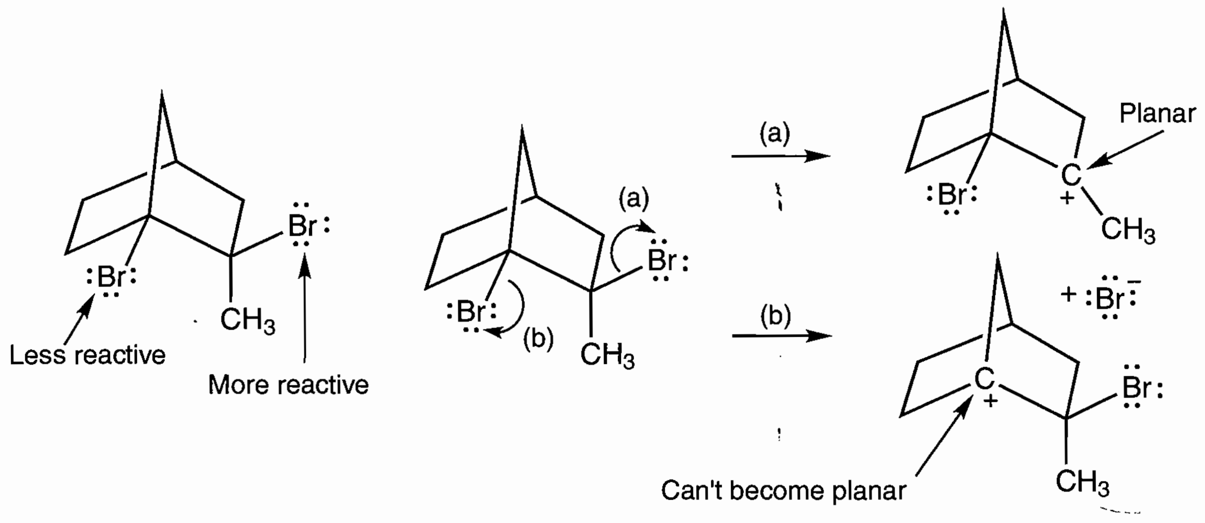
(a) The tertiary bromide will ionize to a relatively stable tertiary carbocation. It will be much more reactive in the S_N1 reaction than the primary bromide.



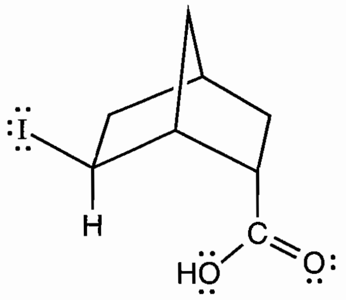
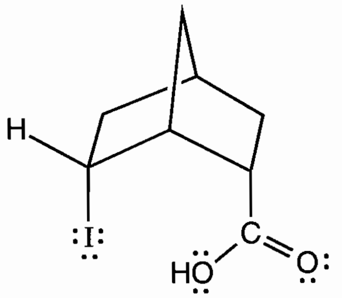
(b) Ionization of the allylic iodide would give a resonance-stabilized carbocation. This reaction will be preferred to ionization of the primary iodide.



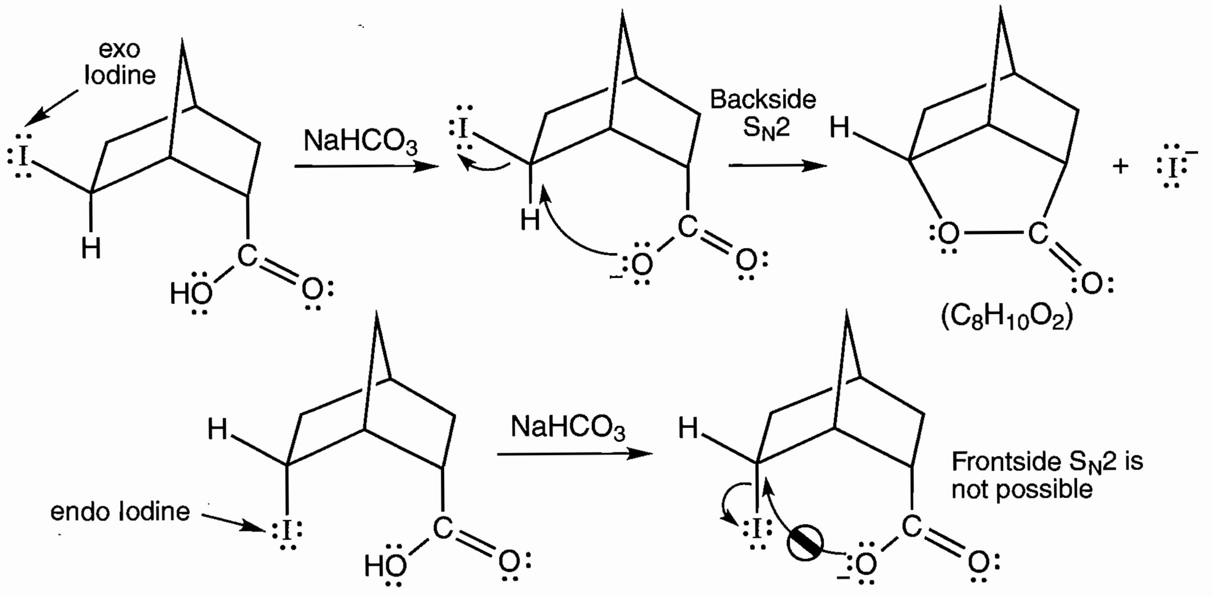
(c) Ionization of either bromide would lead to a tertiary carbocation. However, only one of the carbocations can become planar. As carbocations are most stable when planar, it will be that bromide that is lost more easily.



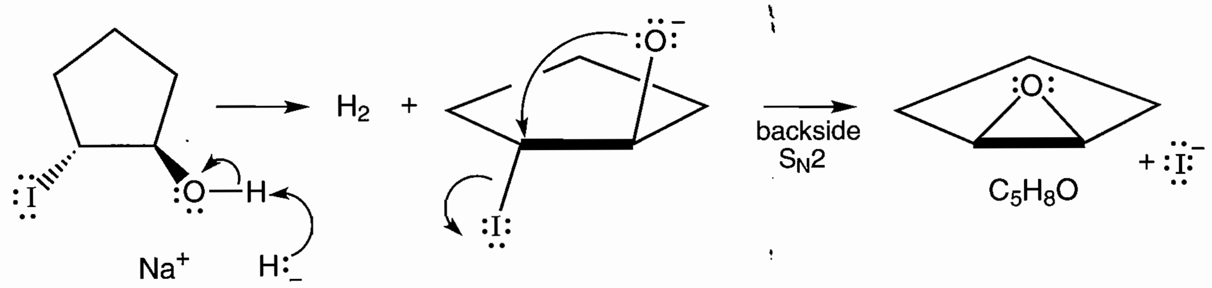
Problem 7.60 The first thing to do is to draw the two possible iodides. What does that squiggly bond really mean? The two possibilities are

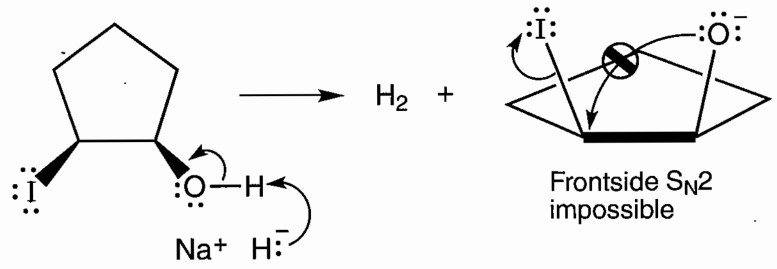



Notice that only one of the salts has a carboxylate in position to do a backside S_N2 displacement of iodide. This displacement leads to the compound $C_8H_{10}O_2$. The other alkoxide would have to do a frontside S_N2 reaction, and, as we know, this never happens. So, the molecule that undergoes the intramolecular S_N2 reaction has the iodine in the "exo" position, and the molecule that cannot do the S_N2 reaction must have the iodine "endo."



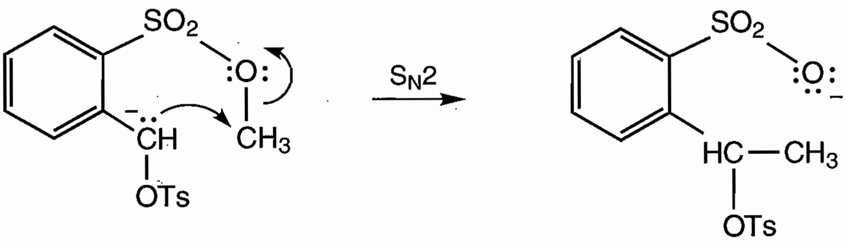
Problem 7.61 The same point is made in this problem as in the last one. The impossibility of a frontside S_N2 reaction renders one stereoisomer unreactive. The isomer that can undergo a backside S_N2 reaction does so to produce the new compound. The compound that reacts is the trans isomer and the one that does not is the cis isomer.



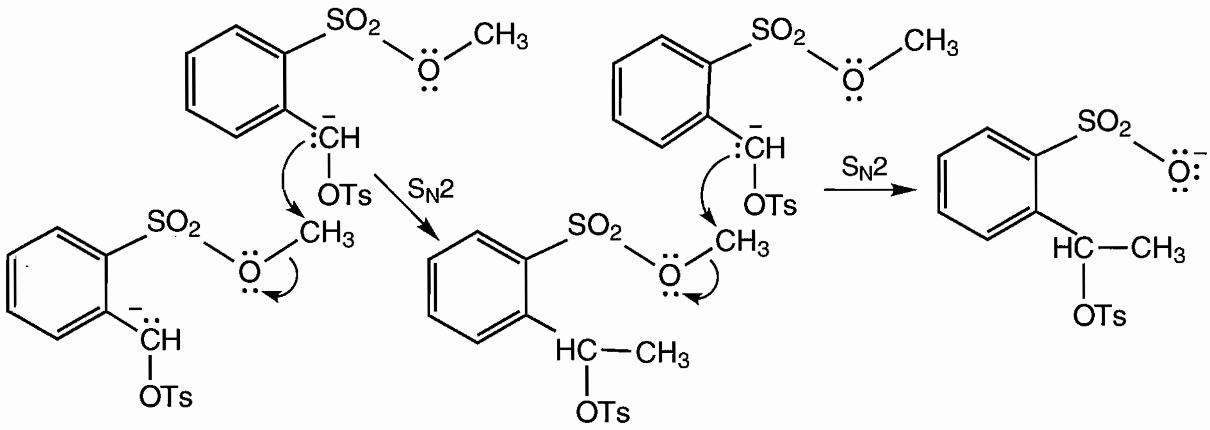


Problem 7.62

(a) The "obvious" mechanism is an intramolecular S_N2 reaction to transfer the methyl group from oxygen to carbon.

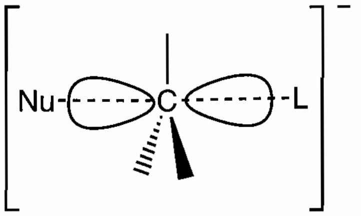


(b) If the reaction is bimolecular, two molecules must be involved in the transition state for the reaction. The mechanism cannot be the simple unimolecular *intramolecular* displacement we wrote in (a). Perhaps the methyl group is transferred in a normal *intermolecular* S_N2 reaction.

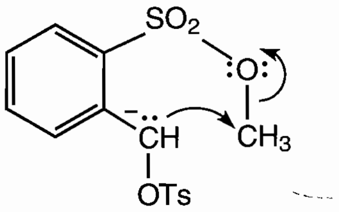


(c) Why is this intermolecular process more favorable energetically than the intramolecular reaction? There is a good nucleophile and an excellent leaving group. However, the transition state for the S_N2 reaction is ideally linear, and a linear arrangement of nucleophile, substrate carbon, and leaving group cannot be attained in the cyclic process. Apparently, this poor alignment is enough to make the bimolecular reaction more favorable.

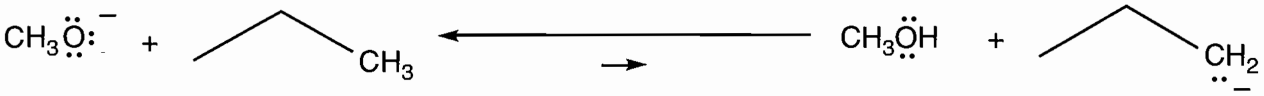
Note the linear relationship in the transition state for the S_N2 reaction



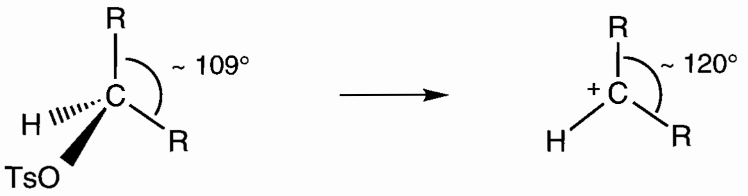
A linear relationship cannot be attained here



Problem 7.63 No! The methoxide ion is not strong enough to deprotonate propane. Methanol is a much, much stronger acid than propane.



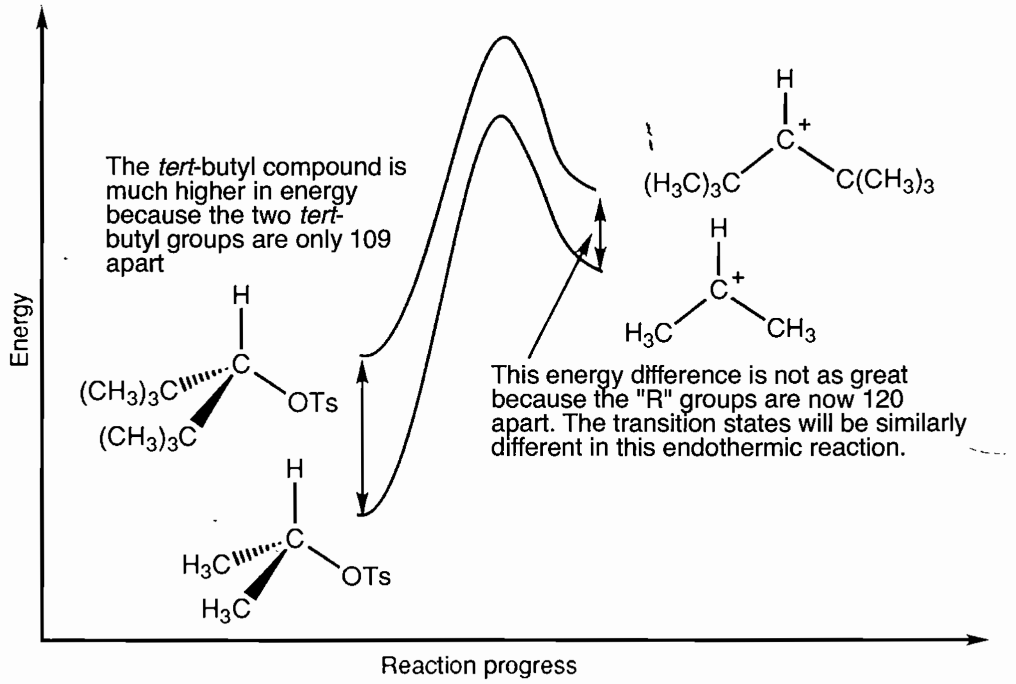
Problem 7.64 In the ionization, the angles around the central carbon expand from approximately 109° (sp^3) to approximately 120° (sp^2). The large *tert*-butyl groups are further apart in the planar, sp^2 carbocation than they are in the starting material. The larger the R group, the more strain relief there will be on ionization, and the faster the reaction.



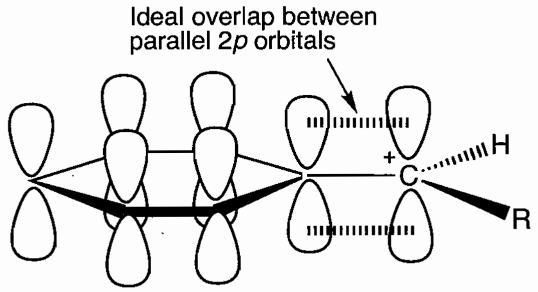
(continued)

Problem 7.64 *(continued)*

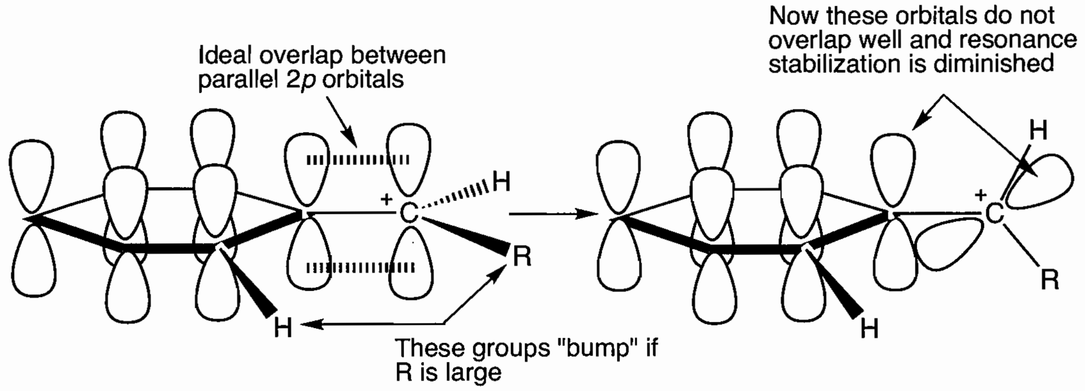
Here is an energy versus reaction progress diagram for the two reactions:



Problem 7.65 The stabilization by resonance of the cation formed from ionization of the starting halides depends on overlap between an exo-ring $2p$ orbital and the π orbitals of the ring.



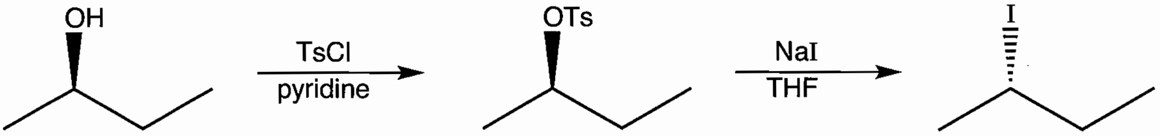
However, when "R" is large, it "bumps" with the nearby hydrogens. This destabilizing interaction can be relieved by rotation about a carbon–carbon bond, but this rotation decreases resonance stabilization in the carbocation and makes the intermediate more difficult to form.



Accordingly, the bigger the "R" group, the more difficult it is to form the carbocation in this example.

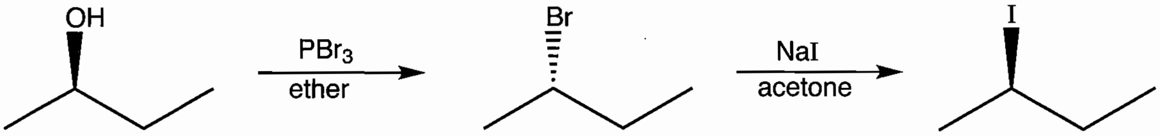
Problem 7.66 We want to make (*S*)-2-iodobutane from (*R*)-2-butanol. This looks rather easy, if we can use phosphorus triiodide. But you may have noticed that we haven't used this reagent in the text. That's because it is violently reactive with water. It's fine to use it as your answer to this problem, but in the lab, you might want to consider an alternative route. The reaction we hoped you would consider is the conversion of the alcohol to the tosylate, which occurs with no change of stereochemistry, and then an S_N2 reaction using the iodide anion as the nucleophile.

Answer:



Making the (*R*)-2-iodobutane from the (*R*)-2-butanol is more difficult. One way to perform a substitution with retention is to do two substitutions that are both with inversion. That is the way to go in this case.

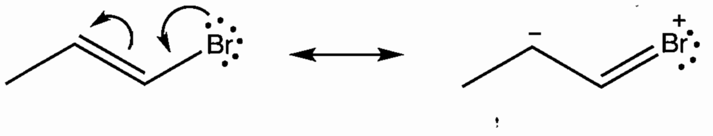
Answer:



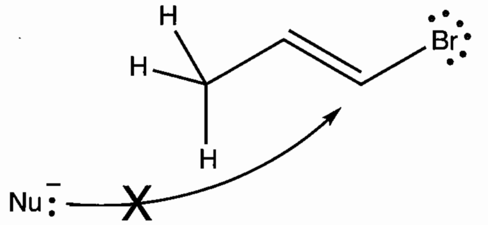
Problem 7.67 Vinyl halides don't undergo S_N2 reactions. Here are a few logical explanations.

(1) The carbon–halide bond of an *sp*^{2} carbon is stronger than the *sp*^{3} carbon–halogen bond we have been breaking in a typical S_N2 reaction. The bond is stronger partly because it is shorter.

(2) Resonance! Perhaps the S_N2 reaction doesn't occur because there is resonance between the halide and the alkene. It's not a carbon–halogen single bond; it has appreciable double bond character.



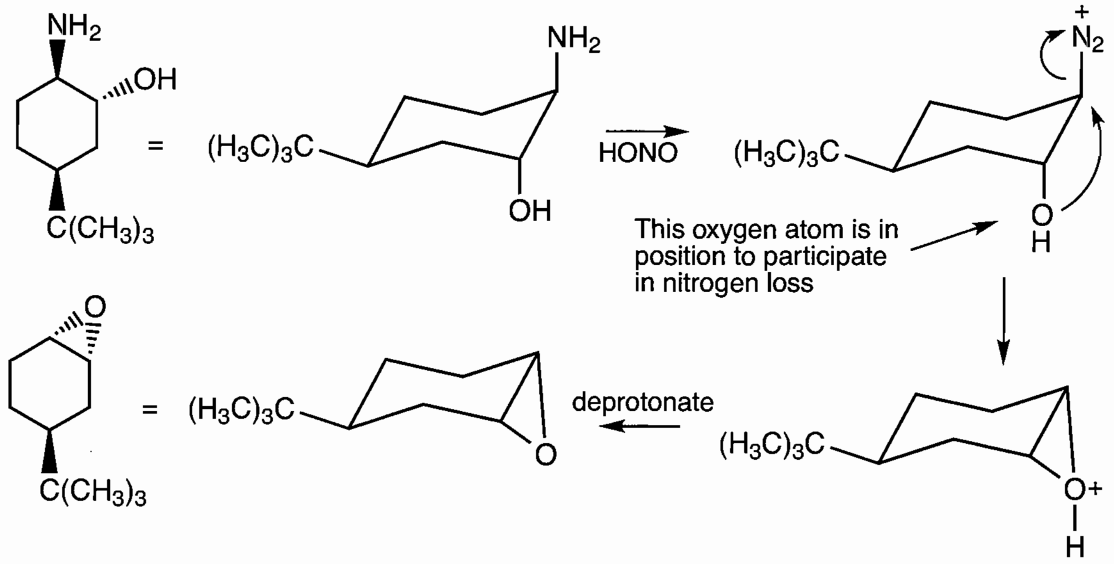
(3) The vinyl carbon–halogen antibonding orbital is more hindered than a typical *sp*^{3}- hybridized carbon. The methyl group in this example blocks access to the backside of the C—Br.



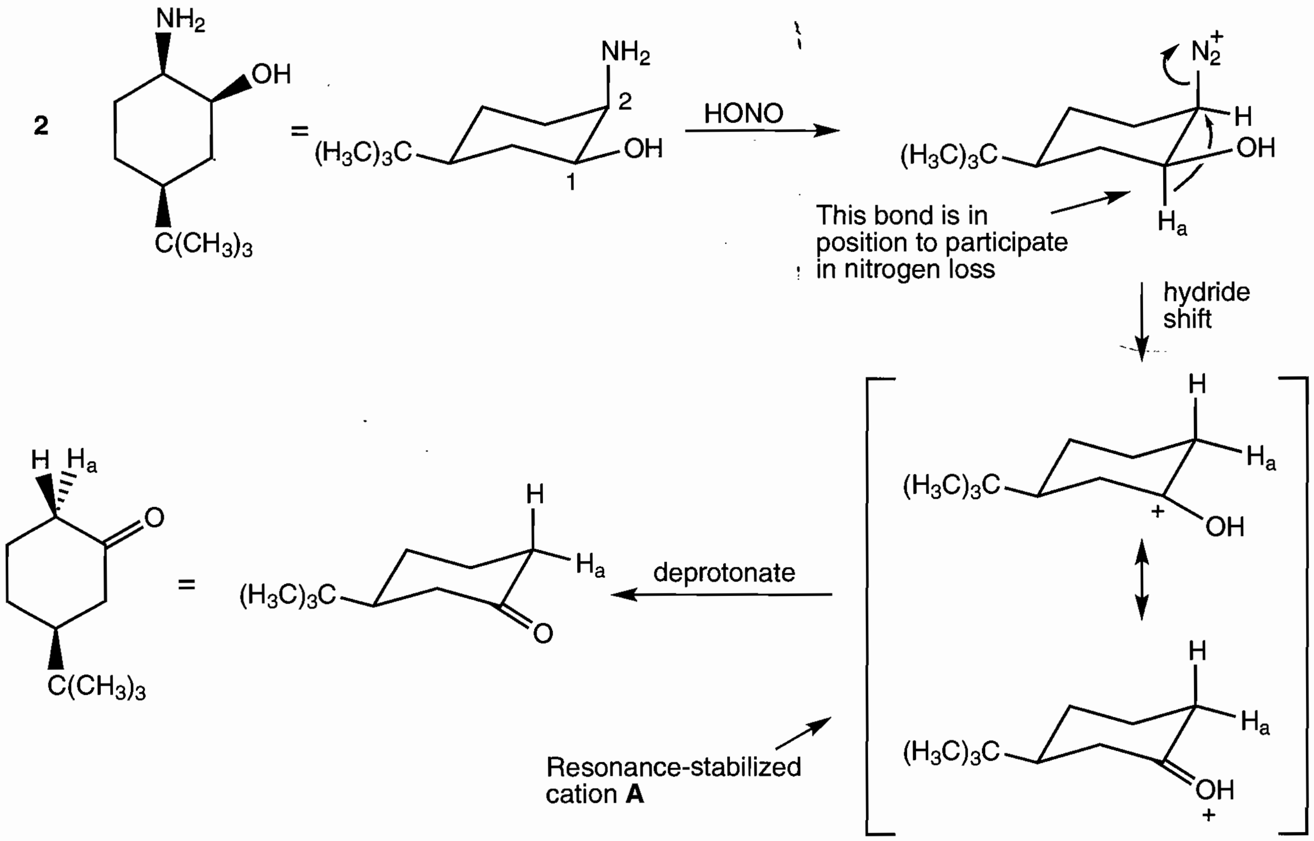
(4) The antibond of a stronger bond is higher in energy and more unlikely to mix with the typical nucleophile. Remember that the orbital mixing works best if the HOMO and the LUMO are similar in energy (p. 36).

Problem 7.68 The amine group in each molecule is first converted into a diazonium ion. In order to see what happens next, we need better three-dimensional drawings of these diazonium ions. So, first draw out the chair conformations of these molecules, and be careful to keep the large *tert*-butyl group in the lower energy equatorial position. In each case, nitrogen will be displaced by a group or bond in the proper position (180°, antiperiplanar) to assist departure by displacement from the rear.

1



In the second case, the hydroxyl oxygen is no longer in a position to displace nitrogen. Instead, the axial carbon–hydrogen bond is in position. A hydride shift, which we will learn more about in Chapter 8, takes place to give the resonance-stabilized cation **A**. Deprotonation gives the ketone.



This bond is in position to participate in nitrogen loss

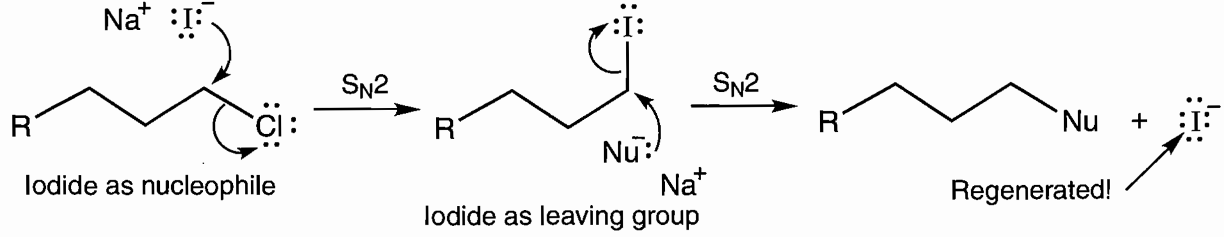
hydride shift

deprotonate

Resonance-stabilized cation **A**

It is H_a that is able to shift from C(1) to C(2). Because H_a shifts with its electrons, we call it a hydride shift. It is this hydrogen that shifts because the electrons in the C(1)—H bond are aligned perfectly to feed into the antibond of the C(2)—N bond. Remember that N_2^+ is the world's best leaving group. When H_a moves to C(2), there is inversion at C(2). The hydrogen that was originally on C(2) moves from the equatorial position to the axial position as the carbon goes through inversion.

Problem 7.69 This procedure takes advantage of iodide being both an excellent nucleophile and an excellent leaving group (Tables 7.5 and 7.6). Initially, the small amount of iodide displaces chloride (S_N2) to give an intermediate iodide that is more reactive in the S_N2 reaction than the original chloride. The nucleophile now displaces iodide (S_N2 again) to generate a molecule of product and *regenerate* iodide ion. The iodide now can recycle, displacing another chloride, etc.

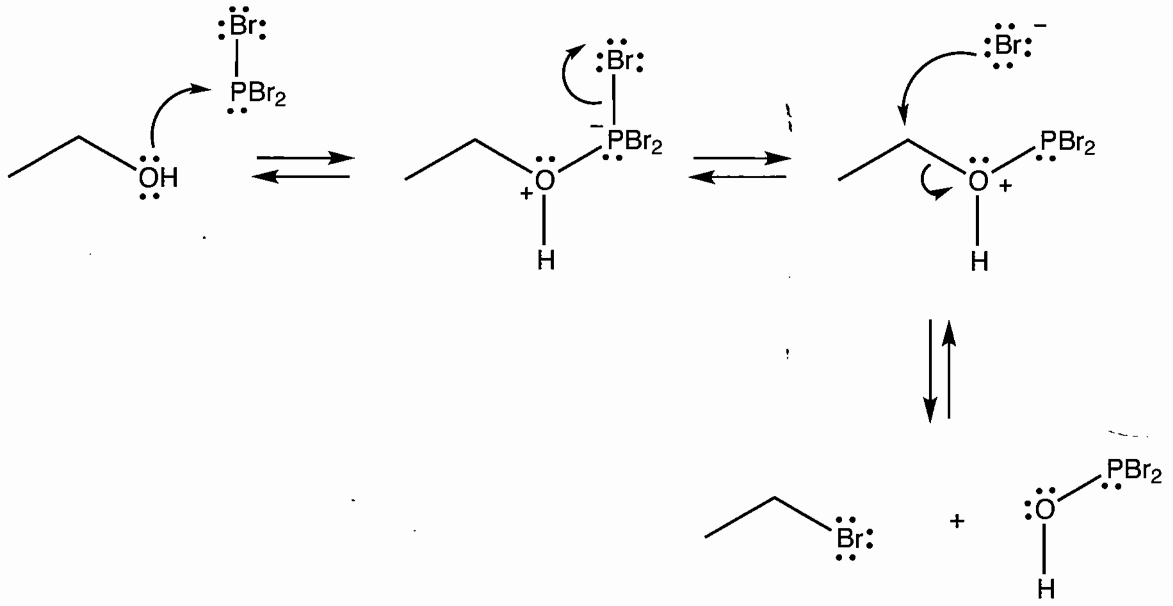


Iodide as nucleophile

Iodide as leaving group

Regenerated!

Problem 7.70 Here is the reaction:



The animation shows two intermediates. The first intermediate has a phosphorus atom with an expanded sphere (10 electrons in the outer shell). It is entirely possible that the alcohol does an S_N2 reaction on the phosphorus, thus bypassing the first intermediate. In that case, there would be only one intermediate.

The fastest step is probably the last one—the bromide attacking the carbon and displacing the $HOPBr_2$.

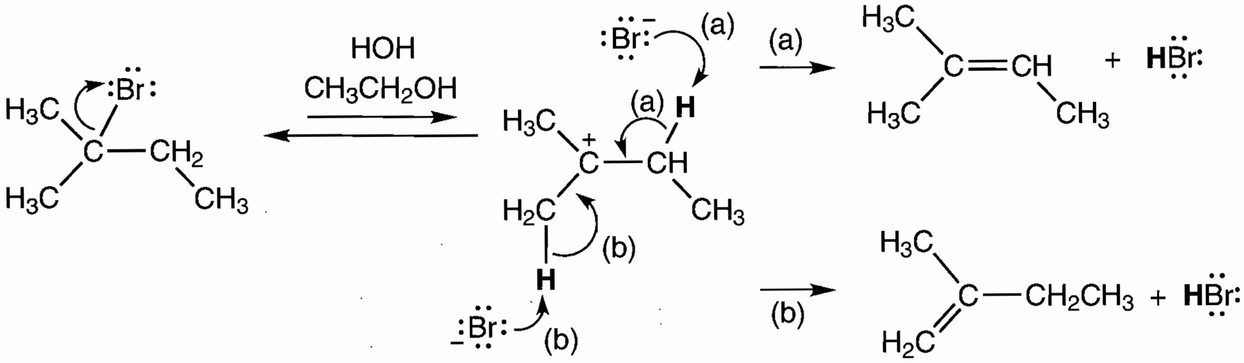
Problem 7.71 Other intermediates that are likely to be present in this reaction are $ROPBr_2$, $(RO)_2PBr$, $(RO)_3P$, $ROP(OH)_2$, $(RO)_2POH$, and the protonated versions of each of these.

Problem 7.72 The animation suggests that the last step is an S_N2 reaction. The bromide attacks from the backside of the carbon–oxygen bond. This pathway is not possible for a tertiary alcohol. The tertiary alcohol does react with PBr_3 to give the tertiary bromide, but it is undoubtedly through an S_N1 pathway.

8

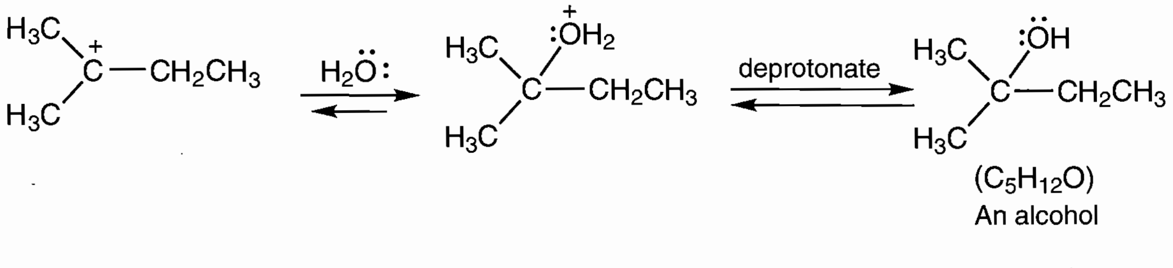
Elimination Reactions: The E1 and E2 Reactions

Problem 8.1



A key point here is the assistance in loss of H^+ by a base, here shown as bromide ion.

Problem 8.2 The S_N1 reaction involves ionization followed by product formation through addition of a nucleophile. The carbocation can be captured by any of the nucleophiles present. If bromide ion captures the carbocation, starting material is regenerated. The other nucleophiles present are ethyl alcohol (CH_3CH_2OH) and water. Reaction of these molecules with the carbocation leads ultimately to an alcohol and an ethyl ether:



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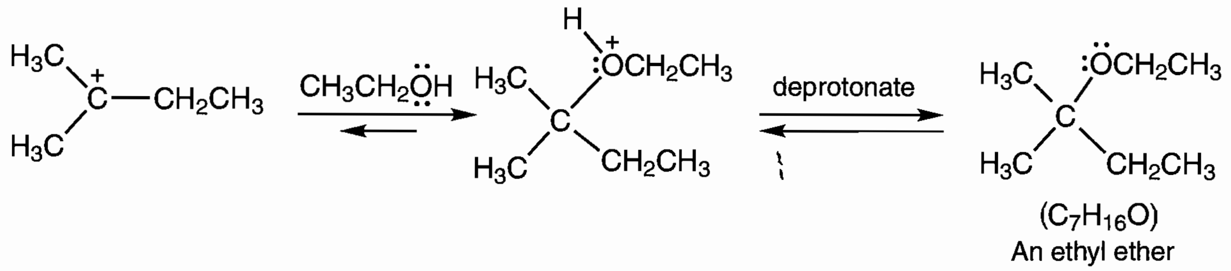
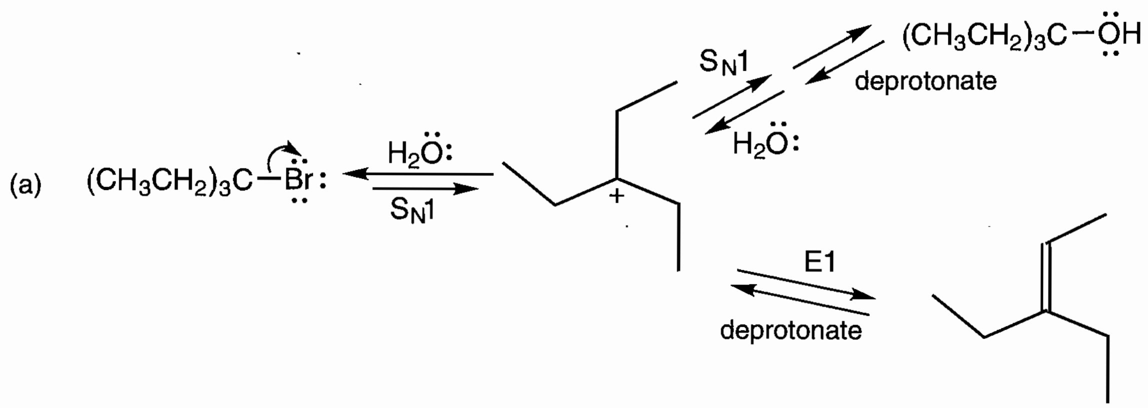
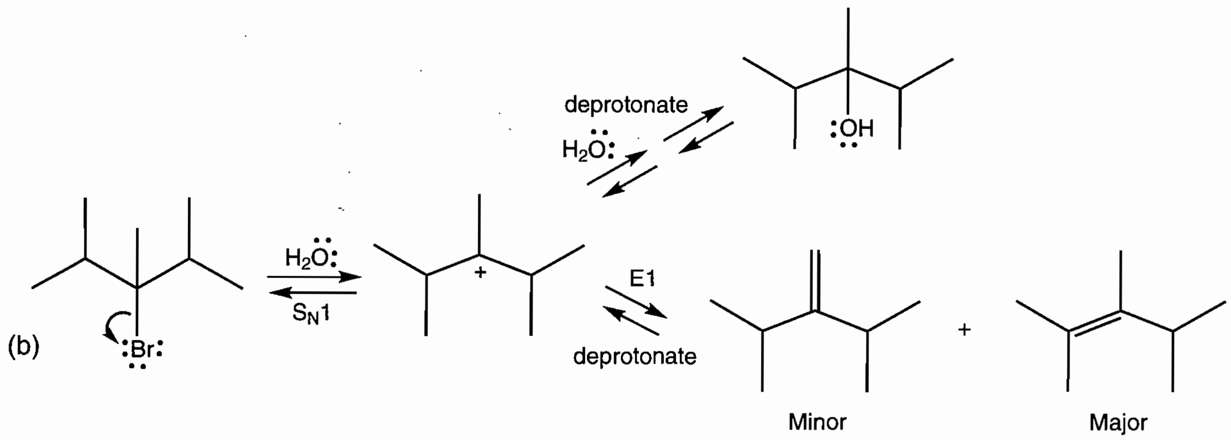
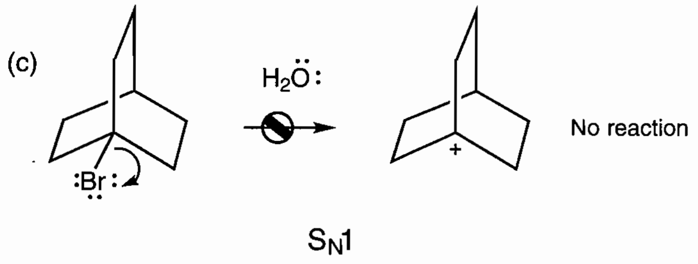
Problem 8.2 *(continued)*



Problem 8.3 The interesting case here is the last, bicyclic molecule. Ionization to the bridgehead cation cannot take place, even though the ion is tertiary. The bicyclic system ensures that the intermediate cation cannot become planar, and that destabilization is enough to stop the reaction. The lesson here is that you can never suspend thought. You have to look critically at each reaction intermediate in every reaction.

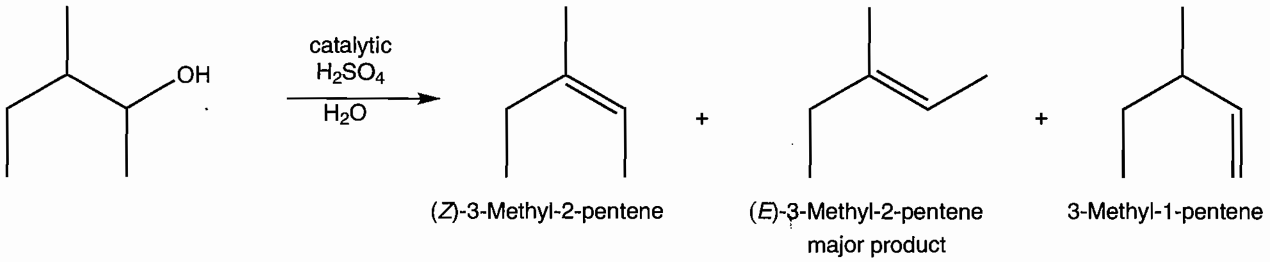




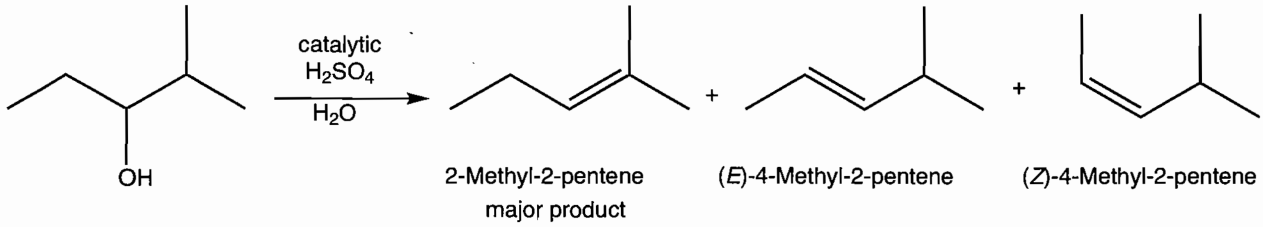


Problem 8.4 These are E1 reactions. The major product in each case will be the thermodynamically most stable product (Saytzeff product). We will expect minor amounts of the less stable alkenes. There are also minor products in (a), (b), and (c) that we can only predict after we have learned about carbocation rearrangements (Section 8.5).

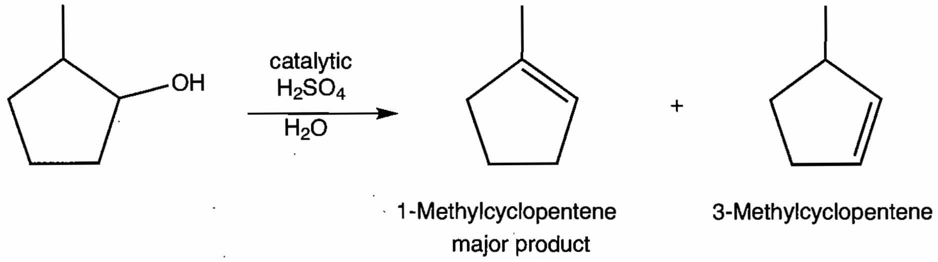
(a) The (*E*)-3-methyl-2-pentene is slightly more stable than the (*Z*)-3-methyl-2-pentene.



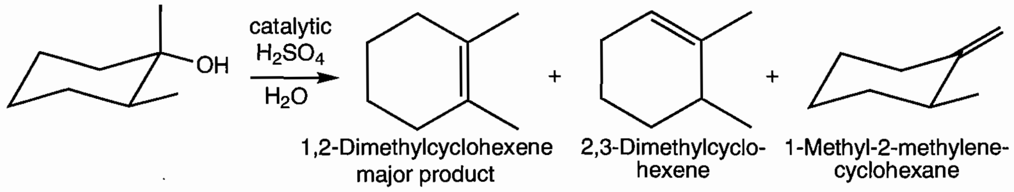
(b) For this reaction we expect one major product and two minor products.



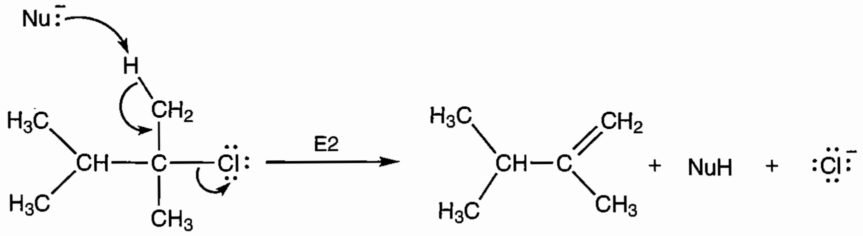
(c) You should be able to predict the major product for this reaction. We also expect 3-methylcyclopentene.



(d)

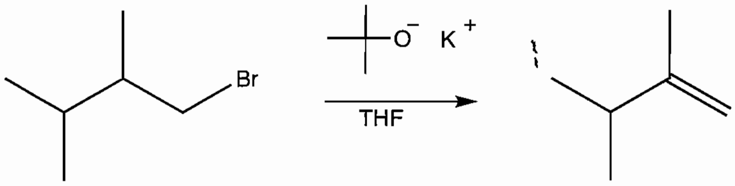


Problem 8.5 There is a second E2 elimination possible in which one of the six equivalent methyl hydrogens is lost.



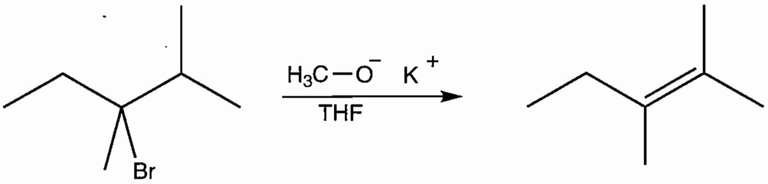
Problem 8.7 These are E2 reactions.

(a) This molecule is a primary bromide, but the strong base is bulky. We only expect an E2 reaction. S_N2 will not compete.



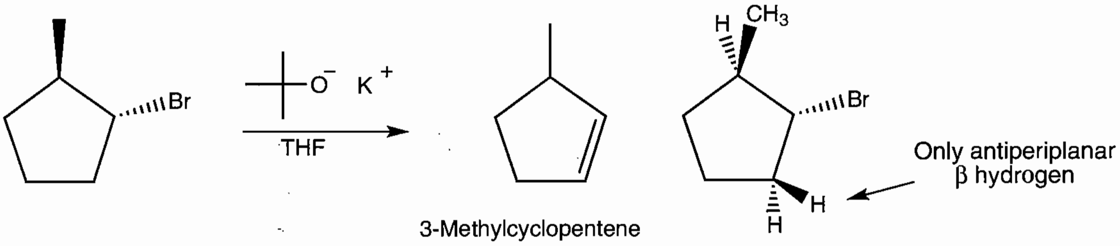
2,3-Dimethyl-1-butene

(b) This molecule is a tertiary bromide reacting with a strong base. S_N2 will not compete. The major product will be the Saytzeff product. There will likely be some minor products that result from attack at the other β hydrogens. The minor products would be (*E*)- and (*Z*)-3,4-dimethyl-2-pentene and 2-ethyl-3-methyl-1-butene.



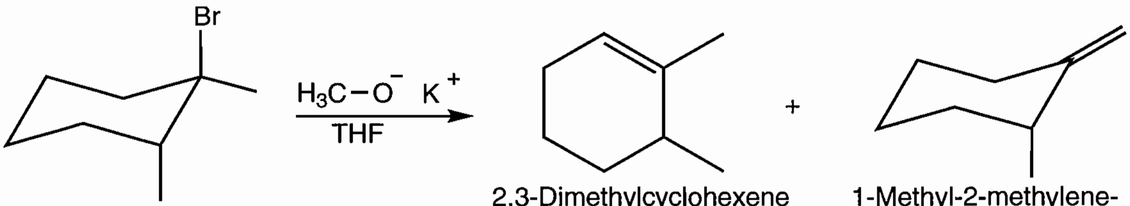
2,3-Dimethyl-2-pentene
major product

(c) This E2 reaction involves a secondary bromide and a strong, bulky base. There is only one product expected in this elimination. That is because there is only one β hydrogen that can be anti to the leaving group.



3-Methylcyclopentene
major product

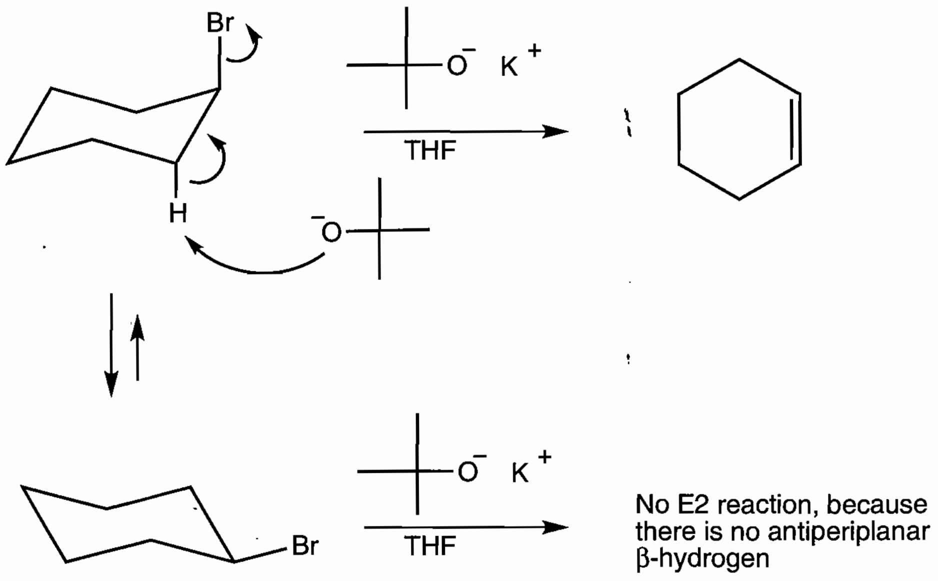
(d) This reaction involves a tertiary bromide and a strong base, therefore it will be an E2 reaction. There are two antiperiplanar β hydrogens available for this dehydrohalogenation. The major product is pre-dicted to be the more substituted alkene (the Saytzeff product).



2,3-Dimethylcyclohexene
major product

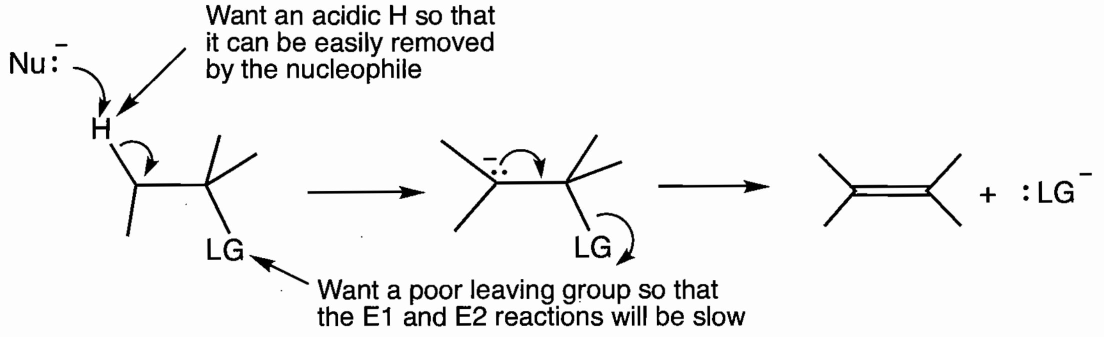
1-Methyl-2-methylene-cyclohexane

Problem 8.8



No E2 reaction, because there is no antiperiplanar β-hydrogen

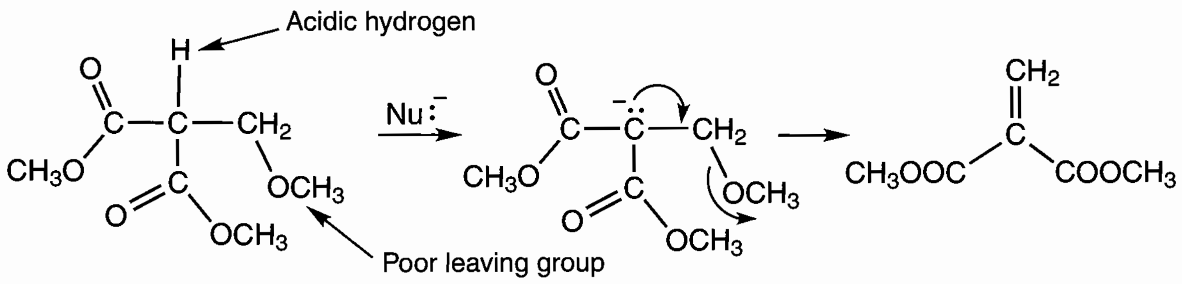
Problem 8.9 For a good E1cB reaction, a poor leaving group and a highly acidic hydrogen are needed.



Want an acidic H so that it can be easily removed by the nucleophile

Want a poor leaving group so that the E1 and E2 reactions will be slow

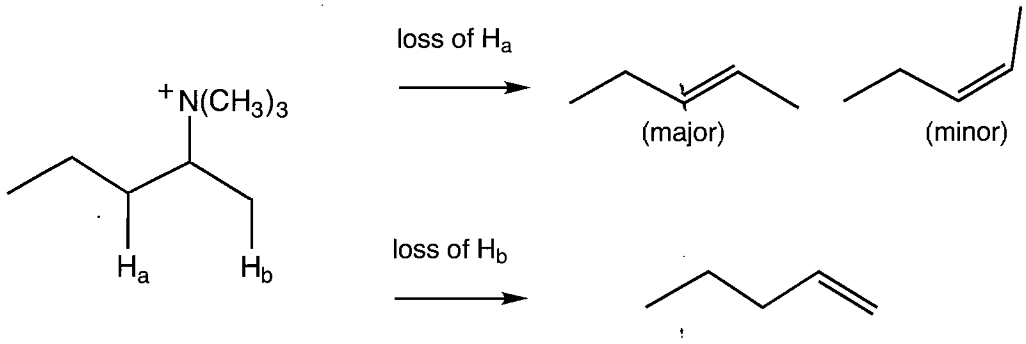
The following molecule fills the bill. Methoxide is a poor leaving group, and the two $COOCH_3$ (methyl ester) groups will stabilize the negative charge on an adjacent carbon by resonance, thus making the loss of a proton easier. There are many other possible answers, of course.



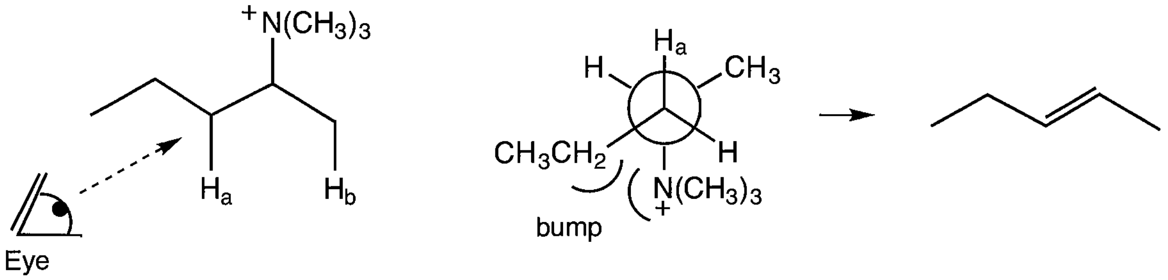
Acidic hydrogen

Poor leaving group

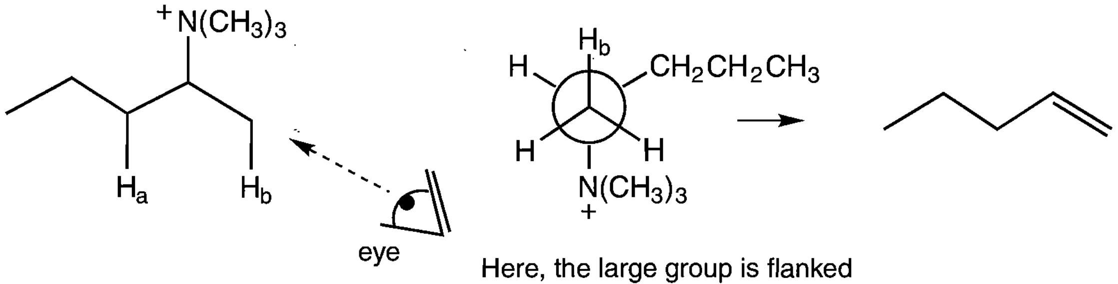
Problem 8.10 The possible products are



Here are the Newman projections for loss of H_a and H_b:



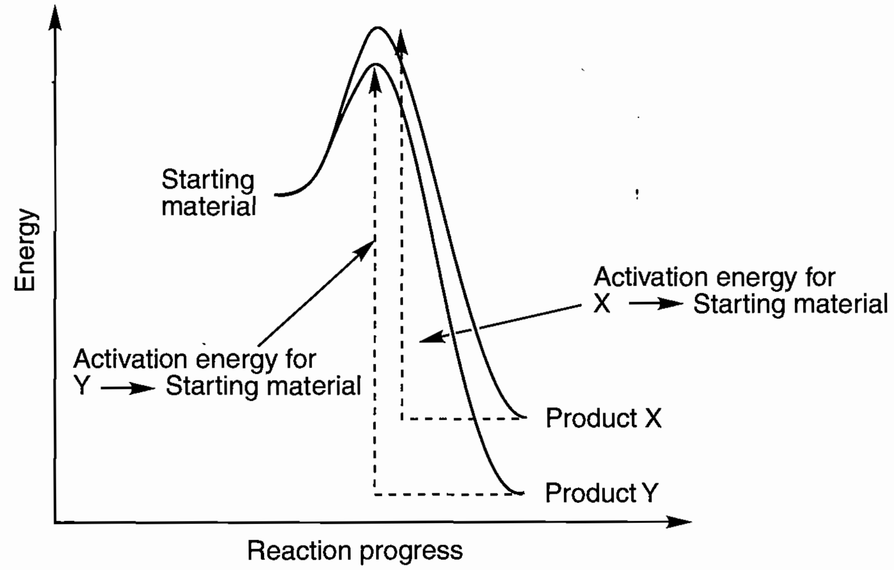
In the 180° arrangement for E2 elimination, there is a bad gauche interaction between ethyl and the large trialkylammonium ion



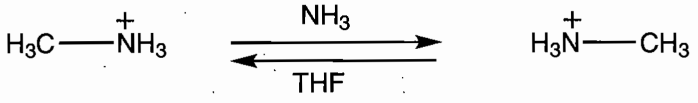
Here, the large group is flanked by two small hydrogens—a more stable arrangement

The larger the leaving group, the worse will be the steric interaction with the ethyl group in the 180° arrangement giving the more stable, more substituted product. By contrast, the arrangement leading to the less stable, less substituted product is relatively unhindered.

Problem 8.12 The activation energy for product Y going to starting material is higher than the activation energy for product X going to starting material. That is because product Y is *more* stable than product X *and* the transition states differ in energy *less* than do the products. If the transition state from product X were higher in energy than the transition state from product Y by an amount larger than the $\Delta G°$, then the activation energy for X going back to starting material would be higher than the activation energy for product Y going back to starting material.

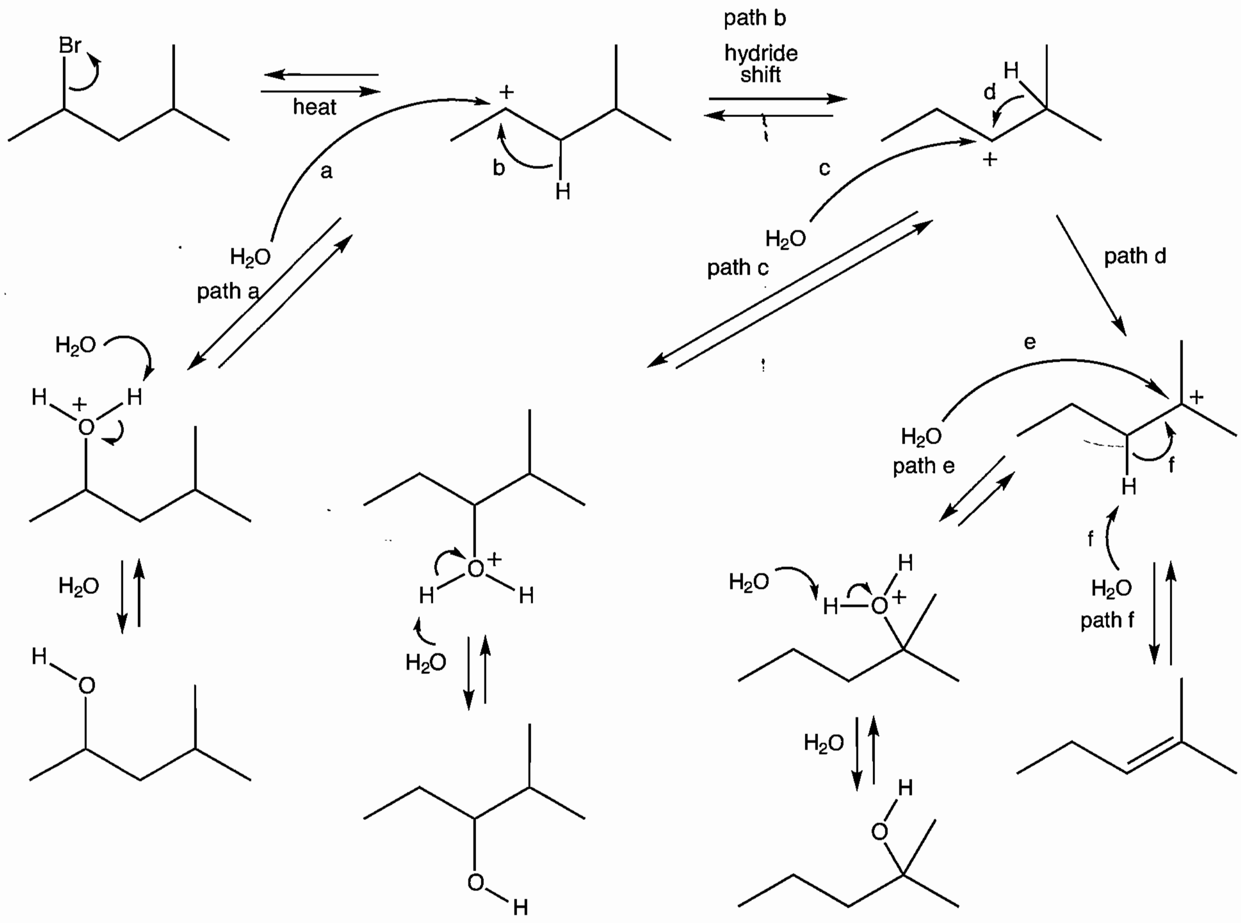


Problem 8.14 On page 286 of the text, we saw the essentially degenerate S_N2 reaction between methyl iodide and radioactive iodide (*I⁻). Here's a completely degenerate S_N2 reaction. One would not be able to monitor this reaction, as the product is exactly the same as the starting material.

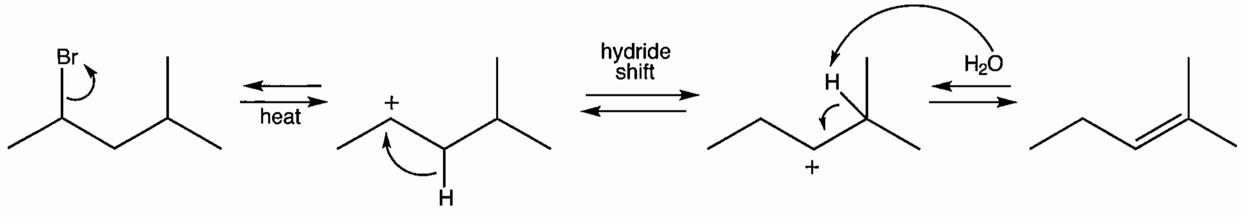


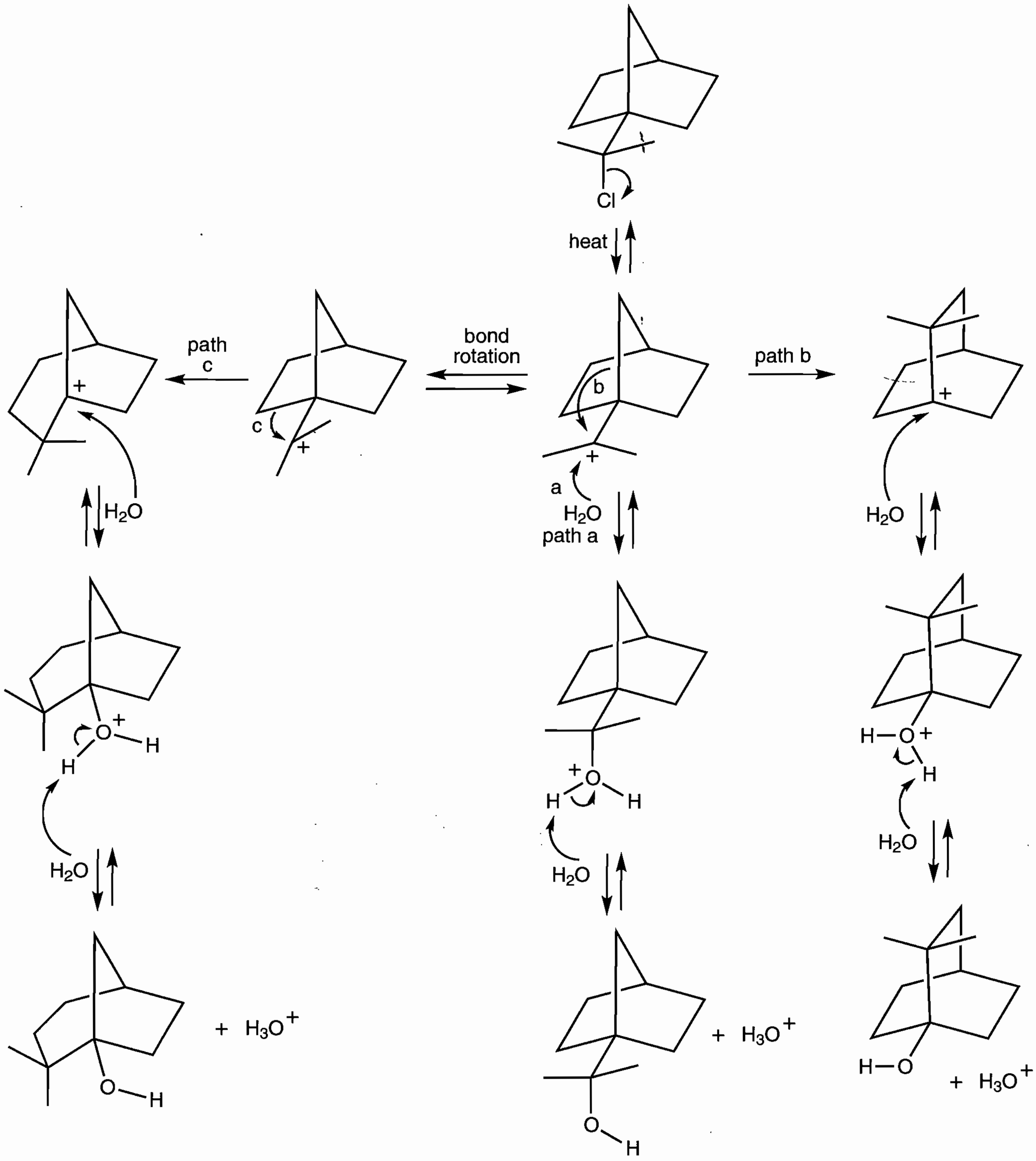
$$H_3C{-}\overset{+}{N}H_3 \underset{THF}{\overset{NH_3}{\rightleftharpoons}} H_3\overset{+}{N}{-}CH_3$$

Problem 8.15

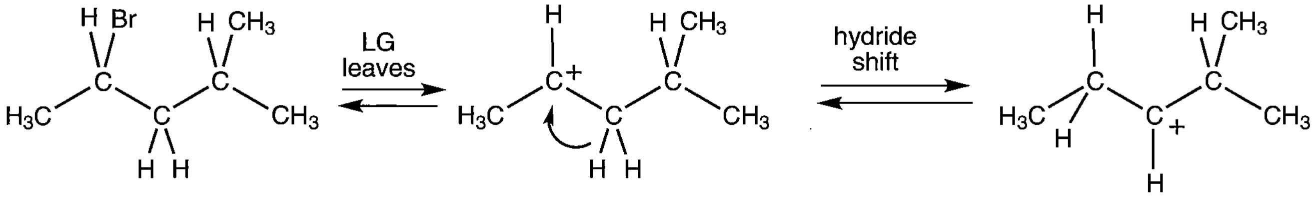


The alkene product can be formed from the tertiary carbocation in path f, as shown in the preceding scheme. It is also possible to form the same alkene from the second carbocation, as shown in the following scheme. Each reaction pathway regenerates H_3O^+.

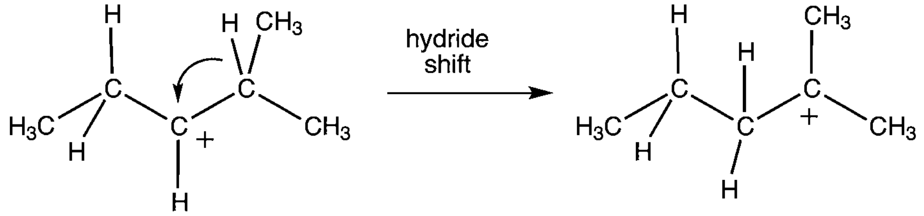



Cl
heat
bond
rotation
path
c
c
+
b
path b
+
+
a
H_2O
path a
H_2O
H_2O
+
H
H
+
H
H
+
H
H
+
H
H_2O
H_2O
H_2O
O
H
+ H_3O^+
O
H
+ H_3O^+
H
O
+ H_3O^+

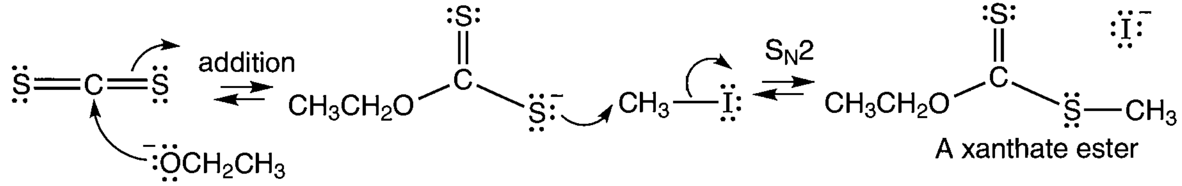
Problem 8.16 There are two hydride shifts that occur in the first part of Problem 8.15. These are shown in more detail here. In the first hydride shift, one of the hydrogens on carbon 3 moves to the carbocation carbon (path b). The hydrogen moves with its pair of electrons from the C—H bond (the nucleophile) to the empty orbital of the carbocation (the electrophile). In this case, two secondary carbocations interconvert. Therefore, the rearrangement is reversible.



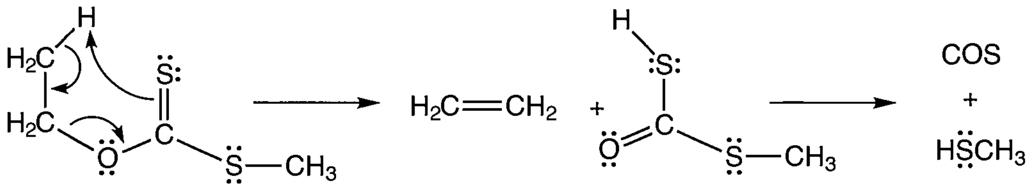
The second hydride shift for this reaction is shown next. In this case, a secondary carbocation becomes a tertiary carbocation as a result of the hydride shift. The tertiary carbocation is much more stable, so we don't consider this a reversible reaction. Once again the migrating hydrogen and its electrons from the C—H bond move to the empty *p* orbital of the adjacent carbocation. We see that the shifting hydride (with its pair of electrons) is the nucleophile. The carbocation (with the empty orbital) is the electrophile.



Problem 8.17 There is nothing tricky here. The only problem is to make the connection between carbon disulfide (CS_2), which you have not encountered before, and carbon dioxide (CO_2), which you have. Addition to carbon disulfide is followed by an S_N2 reaction to make the xanthate.

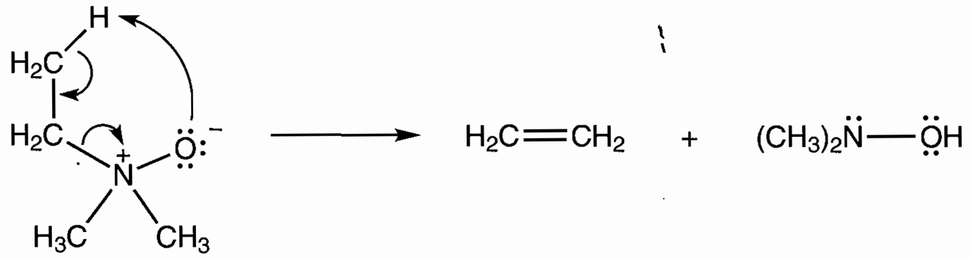


Now a reaction very much like that of Figure 8.43 occurs.

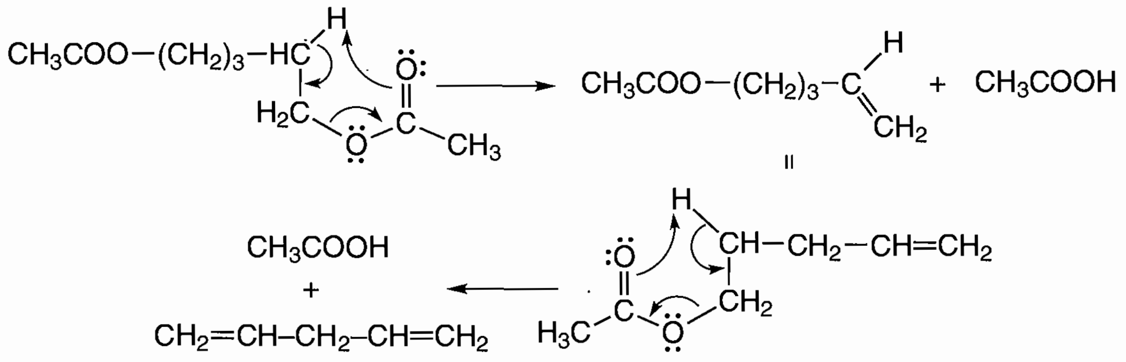


Problem 8.18

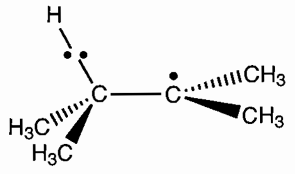
(a) These are both examples of thermal elimination reactions. In part (a), it is the negative oxygen atom that acts as base and removes a proton.

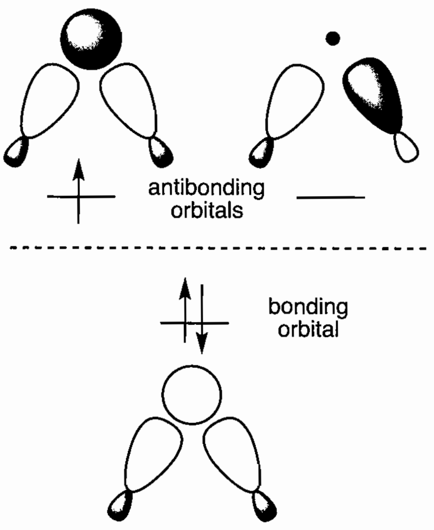


Reaction (b) is just a double ester elimination.



Problem 8.19 The mixing of the three orbitals involved in the migration of a hydrogen from one carbon to an adjacent carbon gives the molecular orbitals shown in Figure 8.50. The three orbitals for the cation contain two electrons, and both of those electrons are in the bonding orbital. The radical would have three electrons involved in the migration. The electron in the antibonding orbital destabilizes the transition state sufficiently to make this rearrangement relatively uncommon in radical intermediates.

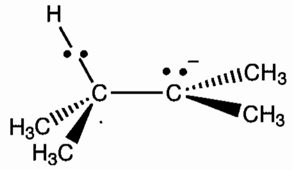


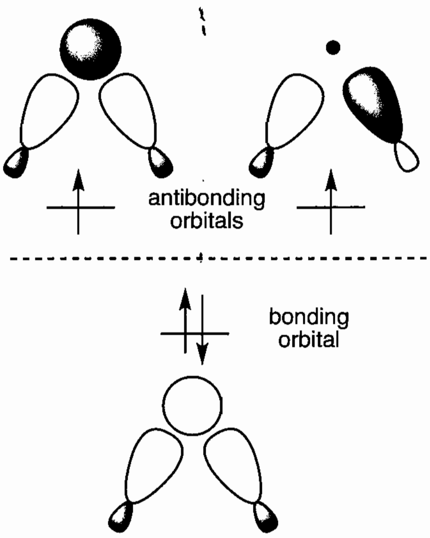


(continued)

Problem 8.19 *(continued)*

The anion would have four electrons involved in the migration. This scenario is even worse than the radical case. With two electrons in the antibonding orbitals, there is no net favorable mixing of the orbitals for this transition state. We will learn that there is an even more unfavorable interaction of this molecular orbital picture when we get to the aromatic ring chapter (Chapter 14).



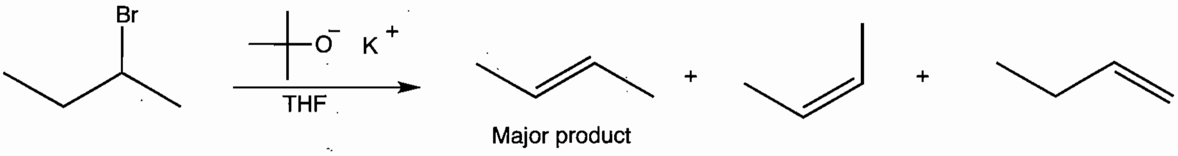


Migration of an alkyl group involves a similar set of orbital interactions. However, it is an sp^3 orbital rather than an *s* orbital that is involved in mixing.

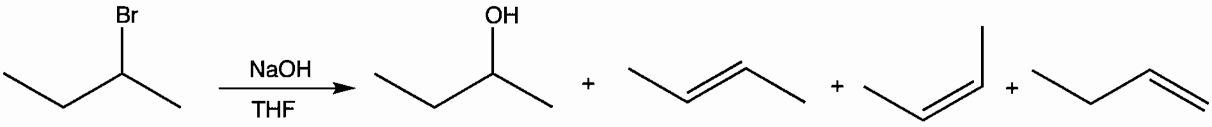
Additional Problem Answers

Problem 8.20

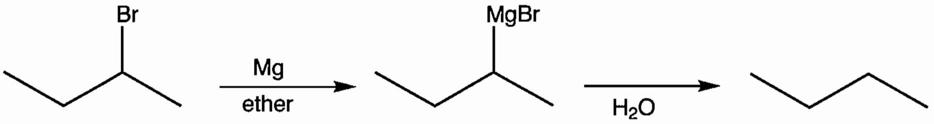
(a)



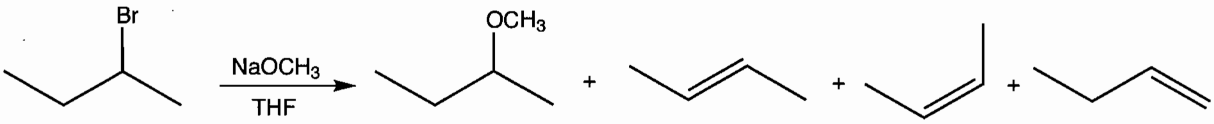
(b)



(c)

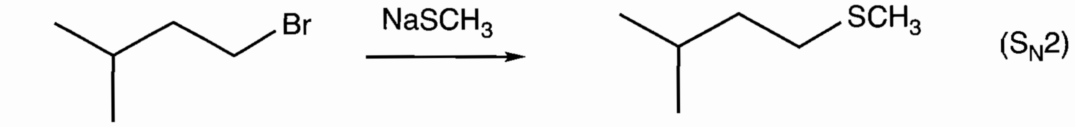


(d)

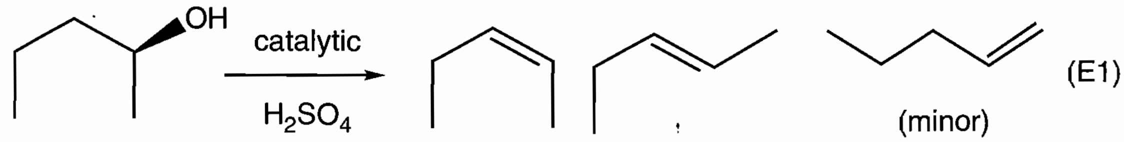


Problem 8.21

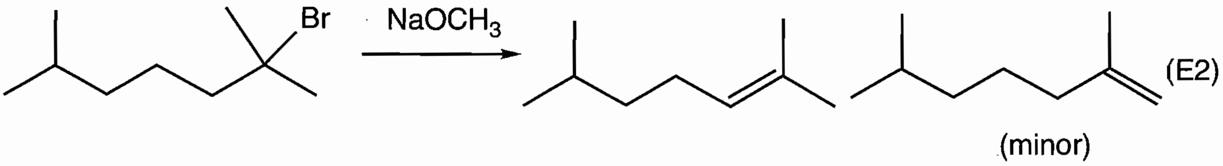
(a)



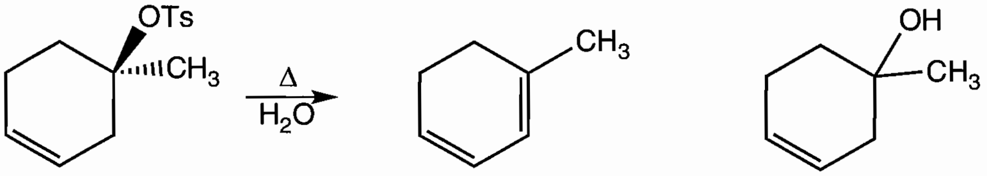
(b)



(c)



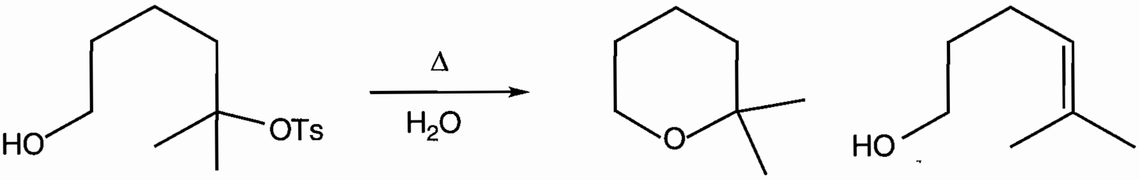
(d)



(E1 to give the more stable conjugated product—double bonds separated by a single bond are "conjugated" as we will see in Chapter 9)

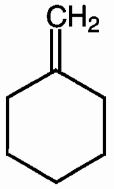
(S$_N$1 with a loss of stereochemisty)

(e)

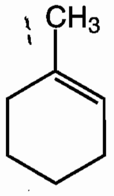


(E1/S$_N$1—ionization followed by capture by OH group and deprotonation or elimination)

Problem 8.22 These reactions all seem to be elimination reactions, and the presence of the strong base *tert*-butoxide must lead us to think of the E2 process. So, the two possible alkenes are methylenecyclohexane and 1-methylcyclohexene. Which we get will depend on the position and structure (Saytzeff or Hofmann) of the leaving group.



Methylenecyclohexane has only five ^{13}C NMR signals

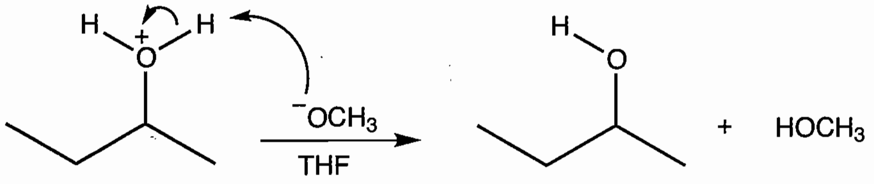


1-Methylcyclohexene has seven different carbons and seven ^{13}C NMR signals

Compound (a) has a Hofmann leaving group, F, and must give mostly the less-substituted alkene, methylenecyclohexane. Compound (b) can only give methylenecyclohexane because of the position of the leaving group—no other product is possible. So (a) and (b) are the two compounds that give the alkene with only five ^{13}C NMR signals.

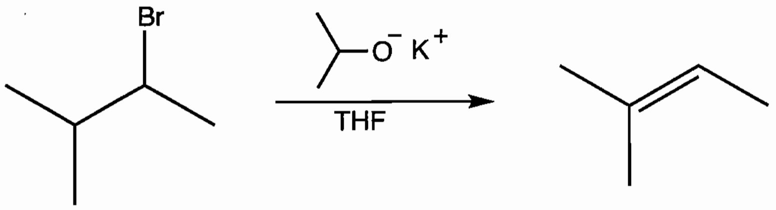
Compounds (c) and (d) have Saytzeff leaving groups and must give mostly the most highly substituted alkene possible, in this case, 1-methylcyclohexene, which shows seven ^{13}C signals in its NMR spectrum.

Problem 8.23 An E2 reaction requires a strong base. We typically use hydroxide (LiOH, NaOH, or KOH) or alkoxide (NaOR). A protonated alcohol is a strong acid. The pK_a of a protonated alcohol is about –2. If we try to use a strong base in the presence of a strong acid, we will only have proton transfer. An example is shown here. The base deprotonates the acidic hydrogen rather than initiating the E2 reaction.

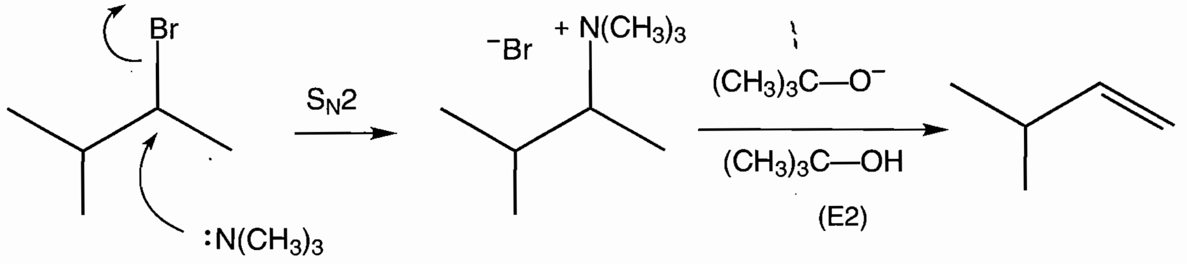


Problem 8.24

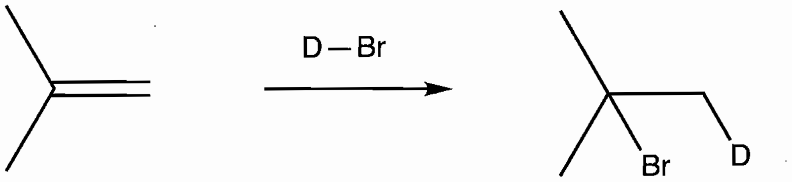
Part (a) is a straightforward E2 elimination with a Saytzeff leaving group. Any strong base will do, and isopropoxide will work well.



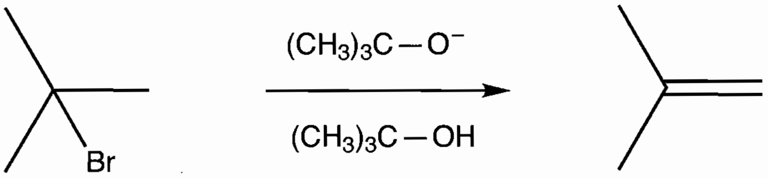
Part (b) is trickier, as we need to do a Hofmann elimination and the molecule contains a Saytzeff leaving group. Clearly, we need to switch leaving groups somehow. Why not displace the bromide with trimethylamine, giving us the ammonium ion, a Hofmann leaving group? Now we can do our E2 reaction and the major product will be the desired less-substituted alkene.



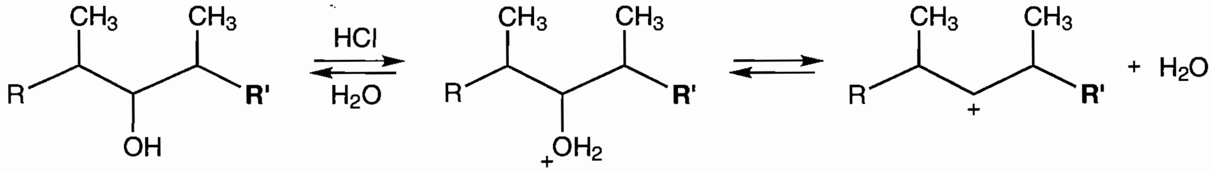
Part (c) is hard, as again you need to do two reactions in sequence. The simplest way to produce the final product is to add DBr to isobutene, so this part of the problem quickly resolves into a search for a way to make isobutene from *tert*-butyl bromide.



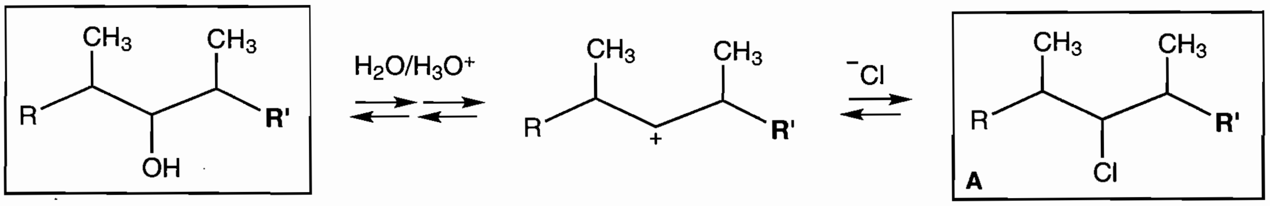
An E2 elimination will produce the required alkene.



Problem 8.25 There is quite a number of products possible! First of all, what's likely? Protonation of the alcohol, followed by loss of water, to give the carbocation starts us off on an S_N1/E1 process.



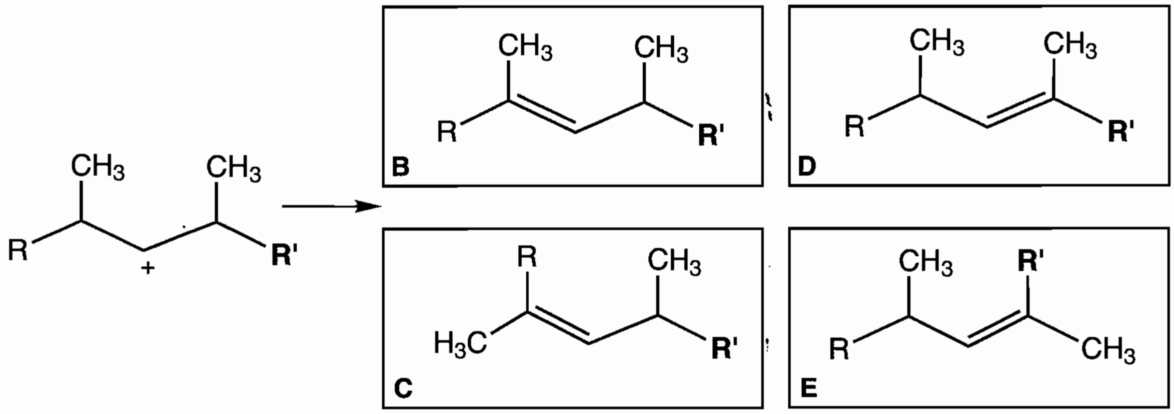
There are two nucleophiles present, chloride ion and water. So, two possible products are the starting alcohol and the corresponding chloride, **A**. This is the S_N1 part of this reaction.



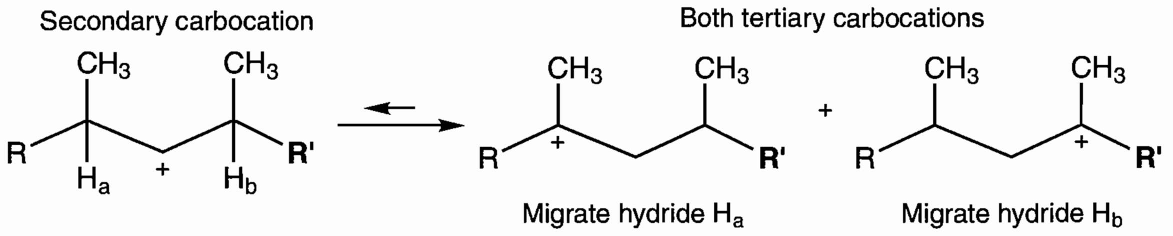
(continued)

Problem 8.25 *(continued)*

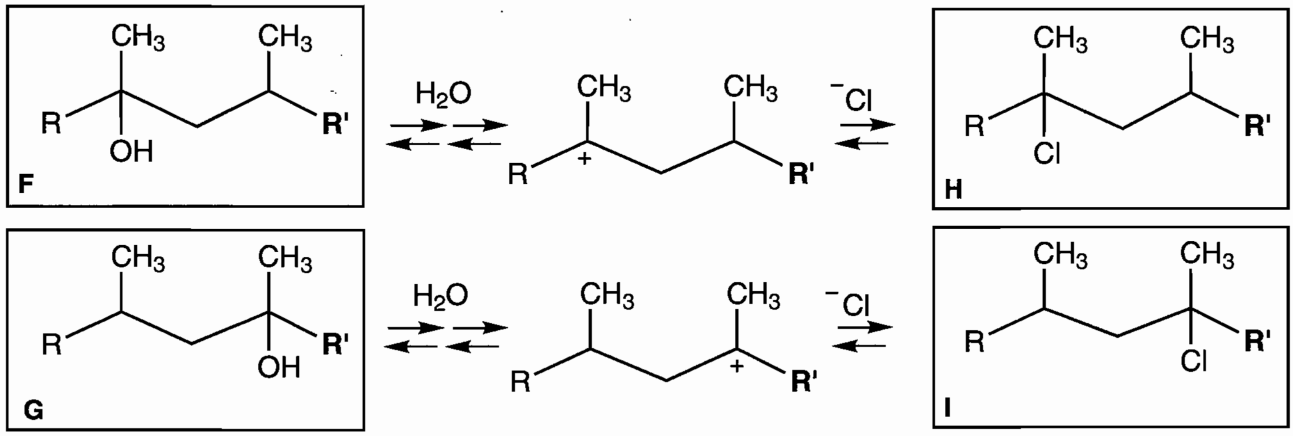
The E1 part involves deprotonation of the carbocation to give an alkene. Deprotonation can occur in two directions, and there are two stereoisomers of each alkene. Now we have products **B–E**.



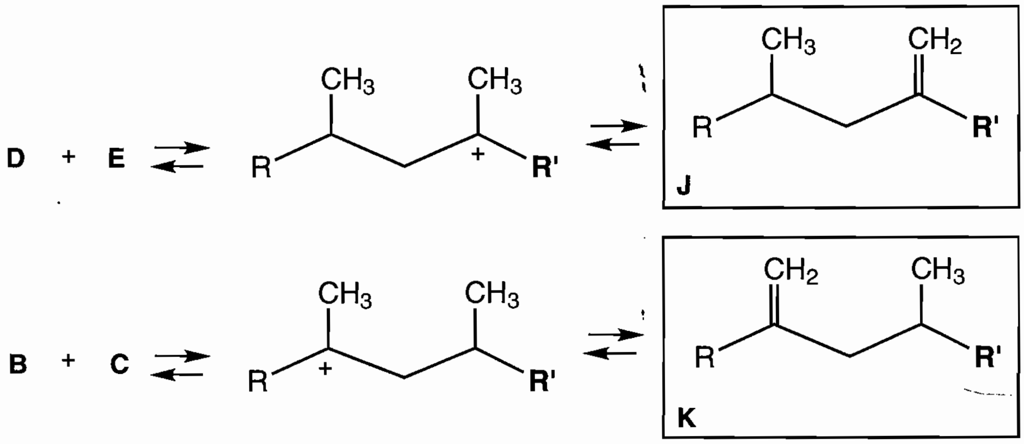
But remember—if a hydride shift to give a more stable carbocation can occur, it will. In this case, there are two such reactions, each of which generates a tertiary carbocation from a secondary carbocation.



Each new carbocation can react with the two nucleophiles present, water and chloride ion. Four new products, **F–I**, are formed.

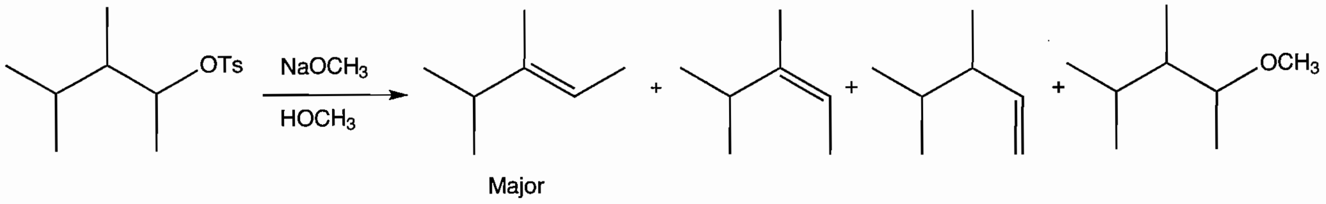


Finally, each of the tertiary carbocations can lose a proton in an E1 reaction to give two more new products, **J** and **K**, as well as alkenes **B**, **C**, **D**, and **E**.

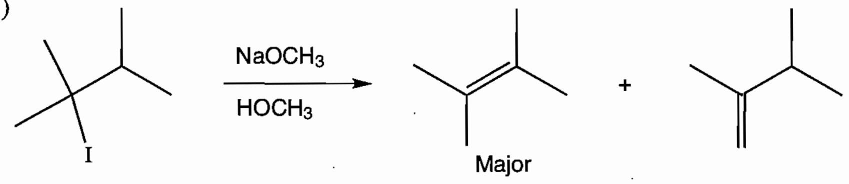


Problem 8.26

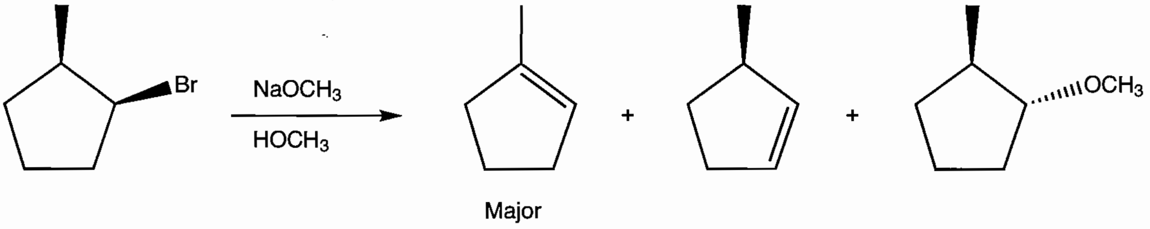
(a)



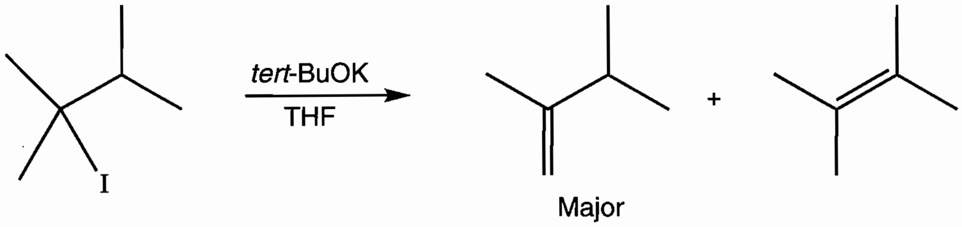
(b)



(c)

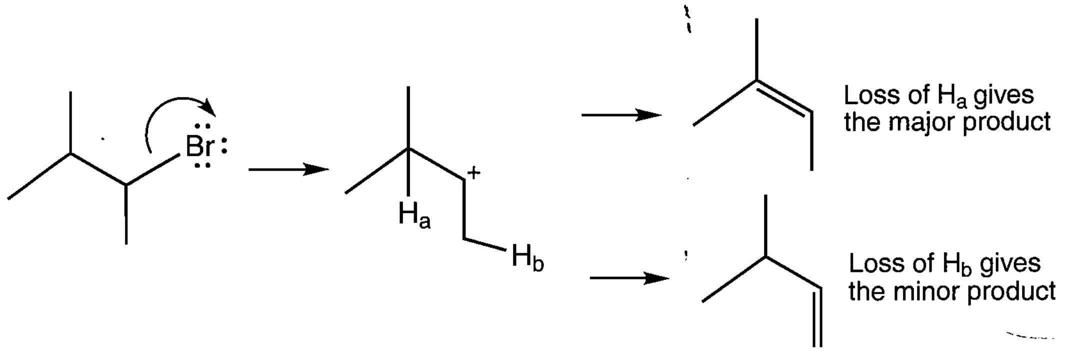


(d) Because the *tert*-butoxide base is bulky, we expect that the less-substituted alkene will be the major product. It is a sterically congested hydrogen that would have to be removed in order to give the more-substituted alkene.

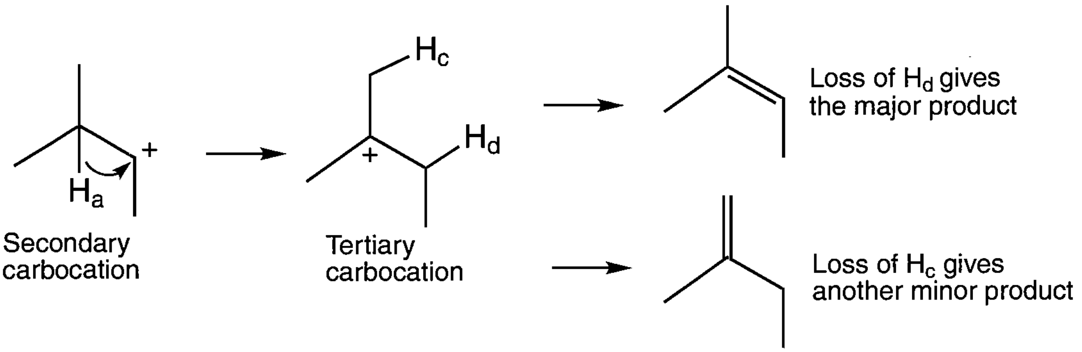


Problem 8.27

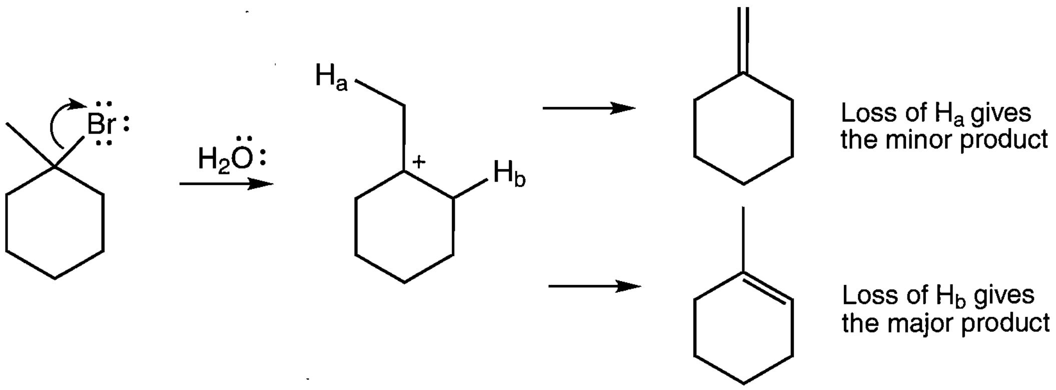
(a) This reaction should lead to three products. Two are straightforward. Ionization will give initially the secondary carbocation, and there are two possible losses of hydrogen to give an alkene. It will be the more stable alkene (the trisubstituted one in this case) that dominates (Saytzeff elimination).



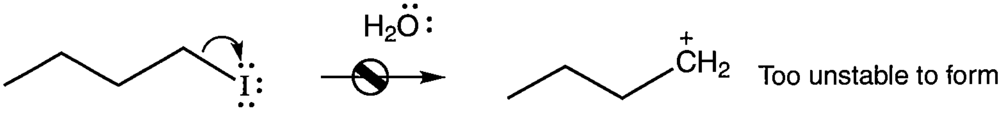
However, we can also expect rearrangement through hydride shift to give a more stable tertiary carbocation, and there are also two different hydrogens (H_c and H_d) that can be lost to give an alkene. One of the product alkenes is the same as the major one formed from the secondary carbocation, but the other one is new. All three will be produced.



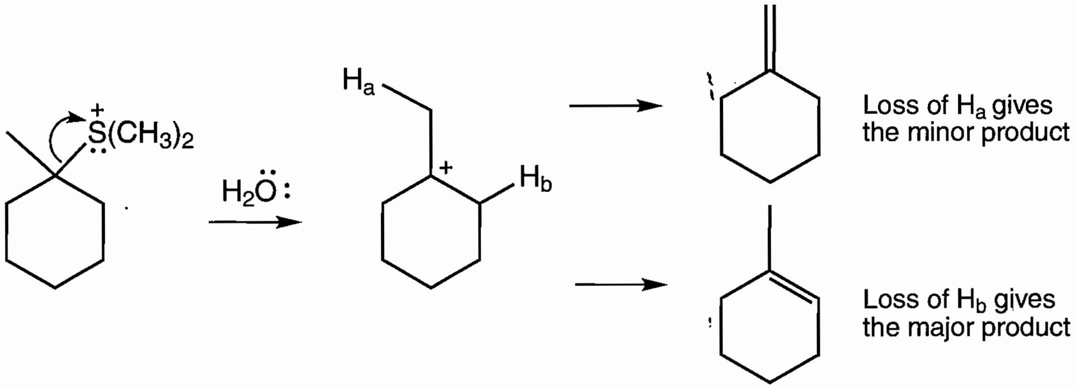
(b) This reaction is a straightforward Saytzeff elimination. The tertiary carbocation will be formed on ionization, and two protons can be removed to give different alkenes. The more substituted, more stable alkene will be the major product.



(c) There can be no E1 reaction, as a primary carbocation must be formed.

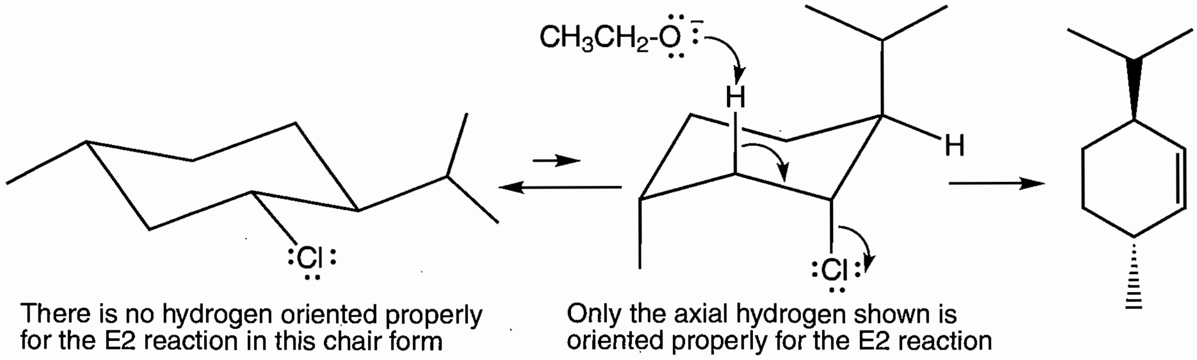


(d) Even though the leaving group is a "Hofmann" leaving group, this E1 reaction will give the more substituted alkene (Saytzeff elimination) as the major product. The intermediate is the same as in (b), and there can be no substantial change in product distribution.

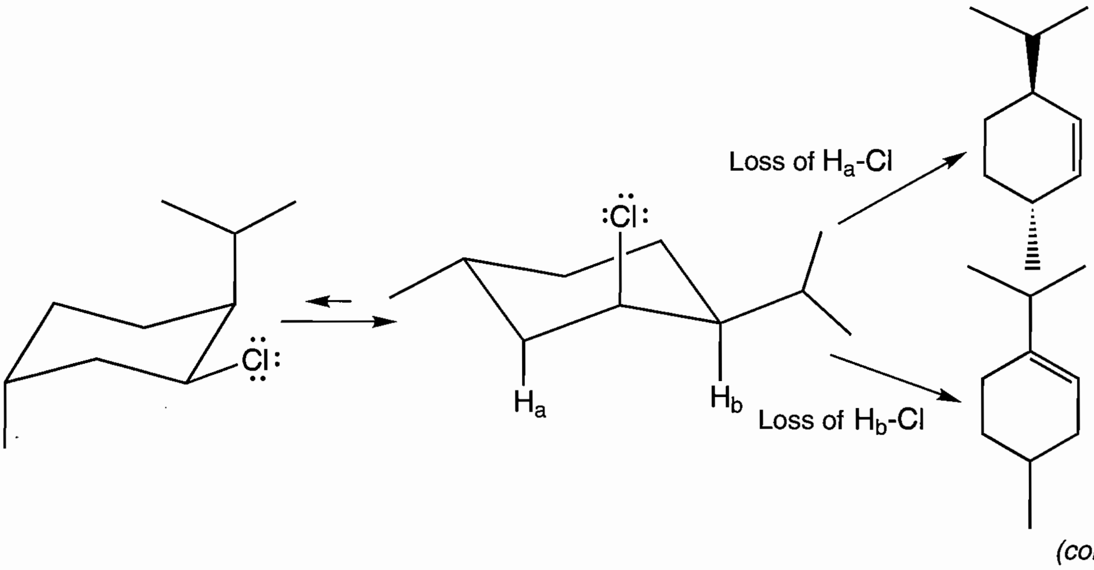


Problem 8.28

(a) Start with a good three-dimensional drawing of menthyl chloride. In the more stable chair form, there is no hydrogen oriented at the optimal 180° angle for E2 elimination. In the less stable chair form, there is only one hydrogen in the proper 180° orientation to the chloride for an E2 elimination. Thus, there is only one product.



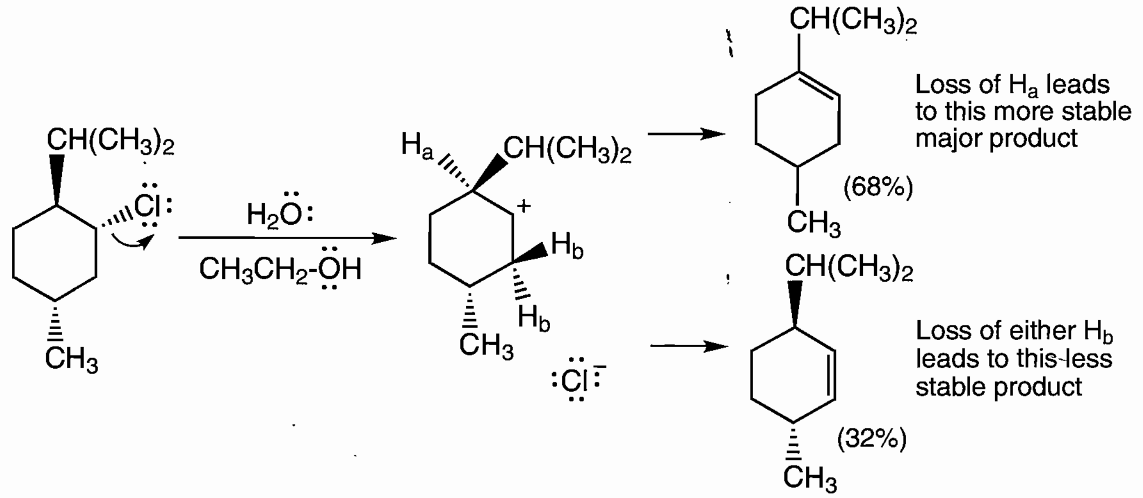
The more stable chair conformation for neomenthyl chloride has the chlorine axial. In this molecule, there are *two* axial hydrogens that can be lost in a "perfect" 180° E2 reaction. As usual, the more stable product is the major one formed (Saytzeff elimination).



(continued)

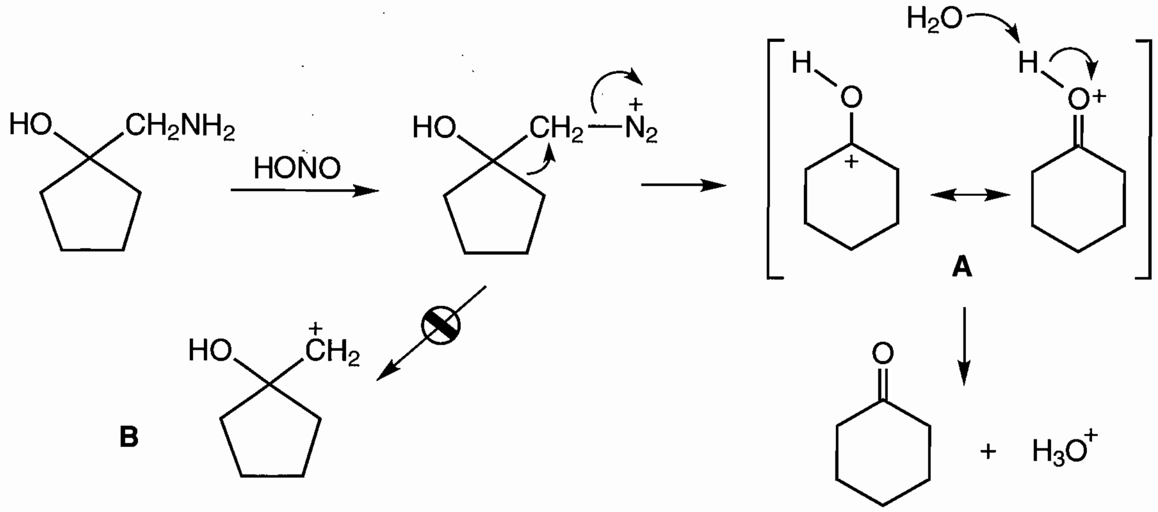
Problem 8.28 *(continued)*

(b) This reaction is E1, and ionization will generate a planar carbocation that can lose either of two protons to give the two products shown in the problem. The more stable, trisubstituted alkene will be favored (Saytzeff elimination).

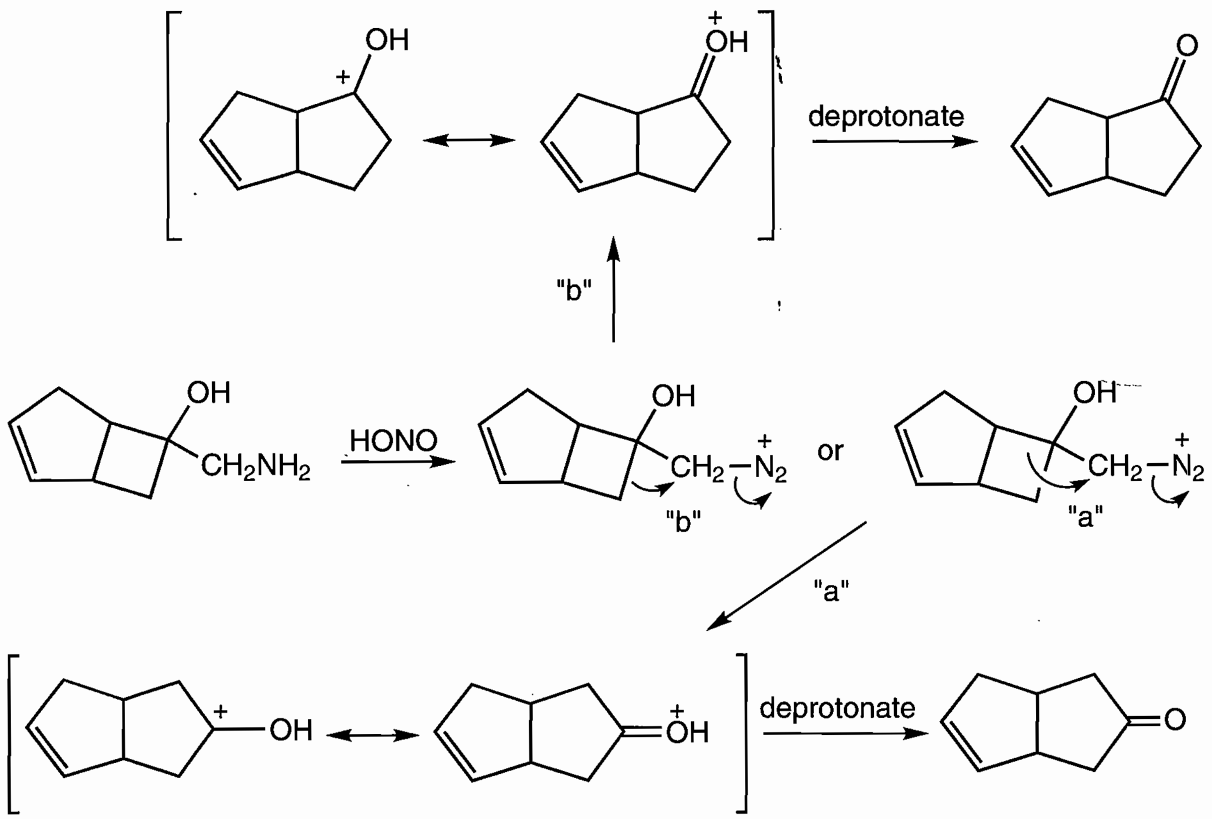


Problem 8.29 These reactions are examples of the Tiffeneau–Demyanov ring expansion. The first step in each case is the conversion of the amino group into a diazonium ion.

(a) Here, displacement of nitrogen, an excellent leaving group, by an adjacent carbon–carbon single bond forms the ring-expanded, resonance-stabilized carbocation **A**. Deprotonation of **A** by any base leads to cyclohexanone. Be careful not to form the primary carbocation **B**. *Remember*: Simple primary carbocations are very high in energy and are almost never formed. They serve as mechanistic “stop signs” in problems.



(b) In the second example, two different modes of ring expansion (a and b) are possible, as two different carbon–carbon bonds are in position to help displace the leaving group.



Problem 8.30 This is an E2 reaction. The rate of an E2 reaction of a secondary iodide is

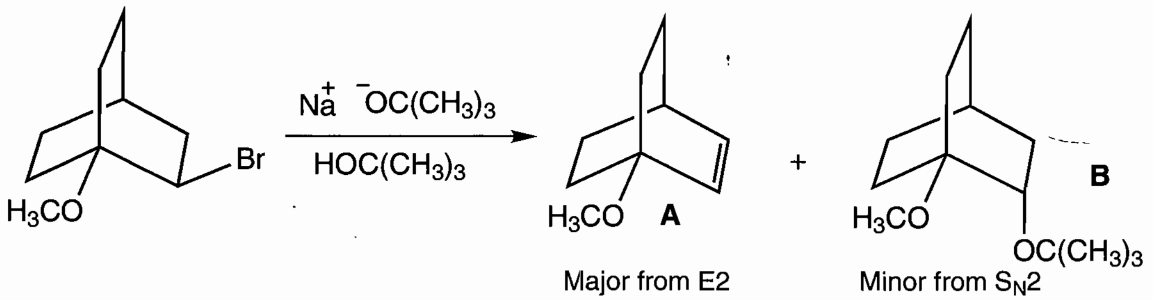
Rate = $\upsilon = k[\text{R—I}][\text{base}]$

If you double the concentration of base, the rate of the reaction will double. The rate of an E1 reaction of a secondary iodide is

Rate = $\upsilon = k[\text{R—I}]$

Therefore, if you double the concentration of base in an E1 reaction, there will be no change in the rate of the reaction.

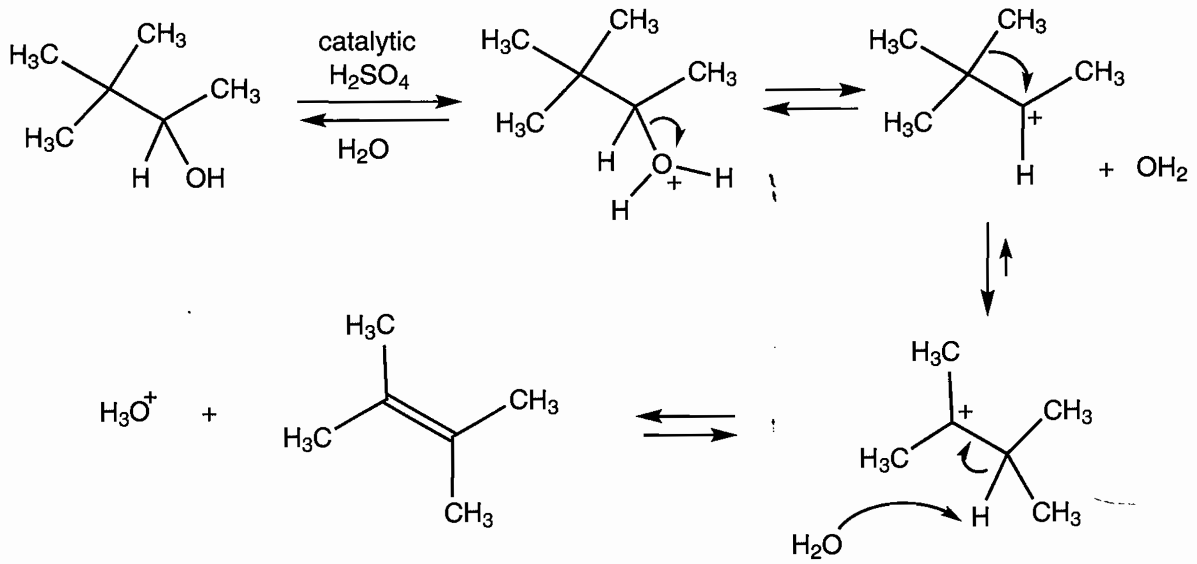
Problem 8.31 Task one is to see how the unwanted compound **B** is formed. It is pretty clearly the result of an S_N2 displacement with inversion. The S_N2 and E2 reactions are both sensitive to steric effects. However, the steric requirements for deprotonation (E2) are far less severe than those for the S_N2 reaction, which requires the approach of a nucleophile to the rear of the departing carbon-leaving group bond. In this case, our hopes of making alkene are being thwarted by the S_N2 displacement of bromide to give the dialkoxy compound. If we increase the size of the reactants, we should be able to prejudice the reaction in favor of the sterically less demanding E2 reaction. We can't do anything about the size of the substrate, the bromide, but we could increase the size of the base. *tert*-Butoxide, a branched alkoxide base, would be a good choice.



Problem 8.32 The hydrogens that are on the beta carbons (there are two beta carbons in this molecule) are in the anti position and have LUMO character. If you look at the 2-bromopropane shown at the beginning of the animation, the carbon–bromine bond is pointing down and the anti hydrogens on the beta carbons are both pointing up. The electrons in these carbon–hydrogen bonds overlap with the antibonding σ^* orbital of the carbon–bromine bond when they are lined up in this arrangement. This overlap of orbitals is called hyperconjugation.

Problem 8.33 There are three hydrogens that have the most LUMO character and are therefore most acidic. It is the hydrogens that are lined up with the *p* orbital of the carbocation that are acidic. This is because the electrons in these sigma bonds are best aligned with the empty *p* orbital. The electrons of the aligned sigma bonds feed into the empty *p* orbital, and that makes the hydrogens on those aligned bonds more acidic.

Problem 8.34 The steps involved in this E1 rearrangement reaction are shown on the next page. The methyl group that shifts in the third step of the reaction is the methyl group that is aligned with the empty *p* orbital of the carbocation. It is those electrons that can mix with the empty *p* orbital. The nucleophile is technically the electrons in the sigma bond and the electrophile is the *p* orbital of the carbocation. We might loosely say that the migrating methyl group is the nucleophile and the carbocation is the electrophile.



Problem 8.35 Note that there are several weak bases that could be involved in the deprotonation step. Water has been shown as the weak base in the scheme shown for the previous reaction. Another molecule of alcohol could be the weak base. Even the HSO_4^- is basic enough to deprotonate the hydrogen on the β carbon.

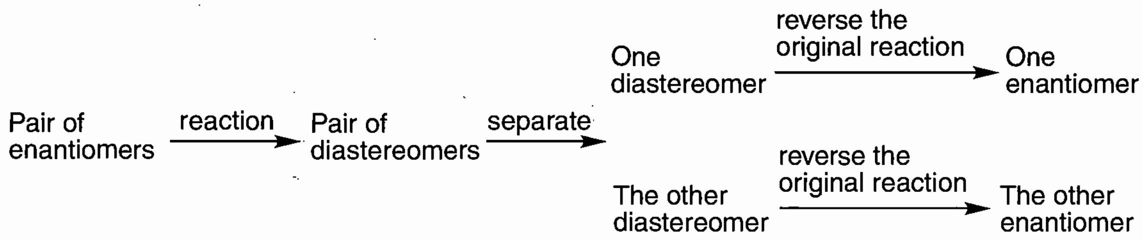
It is the β hydrogen that will give the most substituted alkene that is most acidic. The orbital that lines up best will be attached to the hydrogen that is most acidic. The transition state will be lowest for deprotonation of the aligned hydrogen because it is the hydrogen that is giving its electrons most effectively.

9

Analytical Chemistry: Spectroscopy

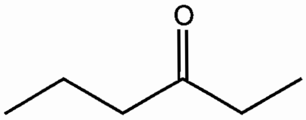
Solving spectral problems involves having a reasonable familiarity with the spectral techniques themselves, and then lots and lots of practice. You need to know what kinds of things each spectral technique can tell you: Mass spectrometry is different from nuclear magnetic resonance spectroscopy, for example. These early, in-chapter problems try to highlight what the techniques can do. The Additional Problems (Section 9.13) will go on to start you off on the actual solving of problems involving interpretation of spectra.

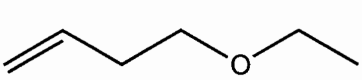
Problem 9.1 In Chapter 4, we discussed "resolution," which involves converting a pair of enantiomers (same physical properties) into a pair of diastereomers (different physical properties) by reaction with a single enantiomer of another molecule. The diastereomers can be separated and then the pair of enantiomers regenerated.

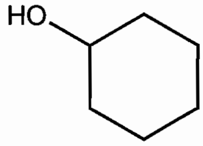


In Chapter 4, the technique of column chromatography was also introduced (p. 176). The chromatographic technique for separating enantiomers is a variation on the general theme. Diastereomeric *compounds* are not formed, but diastereomeric *complexes* are. The pair of enantiomers to be separated is passed though a column in which the stationary phase is constructed from a single enantiomer. As the pair to be separated passes through the column, the components will be adsorbed differently on the stationary phase because the complexes formed are diastereomeric. In this technique, the strong, covalent bonding of resolution is replaced with weaker partial bonding, or complexing, as the enantiomers are adsorbed on the material of the column.

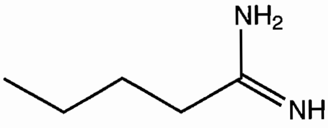
Problem 9.3 You know that the atomic weight of oxygen is 16. So you can start with the molecule C_7H_{16}, which has a molecular weight of 100, and replace one C and four H's with an oxygen. That will keep the MW at 100 because one C contributes 12 to the MW and four H's will contribute 4 to the MW ($12 + 4 = 16$). Therefore, $C_6H_{12}O$ has a molecular weight of 100 (so will $C_5H_8O_2$). The formula $C_6H_{12}O$ has 1 degree of unsaturation. Here are some isomers:

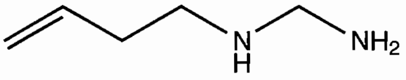


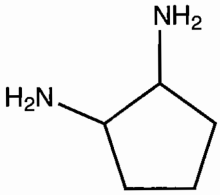




A molecule with a molecular weight of 100 and containing N will require a little more thinking. First, let's try doing the same kind of substitution we did with the oxygen. In this case, nitrogen has an atomic weight of 14. If we can start with C_7H_{16}, we will need to substitute one carbon and two hydrogens (12 + 2 = 14) with one nitrogen. That gives us a formula of $C_6H_{14}N$. But the degrees of unsaturation for this formula are $[(2 \times 6) + 2 - 14 + 1]/2$, which is equal to 1/2. There is no neutral molecule with $C_6H_{14}N$. Try drawing such a molecule and you will find that nothing works. It turns out that a neutral molecule with one nitrogen will have an odd MW. In fact, an organic molecule with an odd number of nitrogens will have an odd MW. An organic molecule with an even number of nitrogens will have an even MW. So let's try putting in two nitrogens. That will be the equivalent of a molecular weight of 28. We can get 28 by switching two carbons (24) and four hydrogens (4). So $C_5H_{12}N_2$ has a molecular weight of 100. The degrees of unsaturation for such a molecule are $[(2 \times 5) + 2 - 12 + 2]/2 = 1$. Here are some isomers:

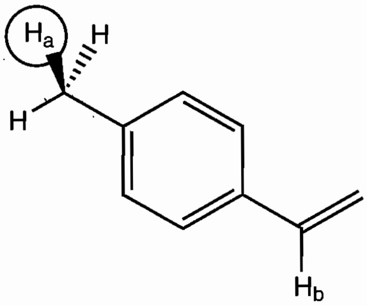




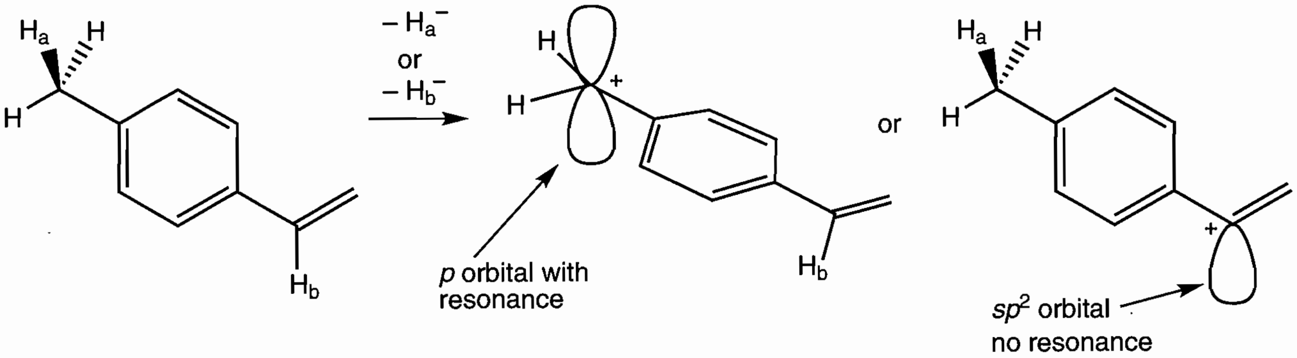


Problem 9.4

(a) The benzylic hydrogen (H_a) on the methyl group is most likely to be lost.



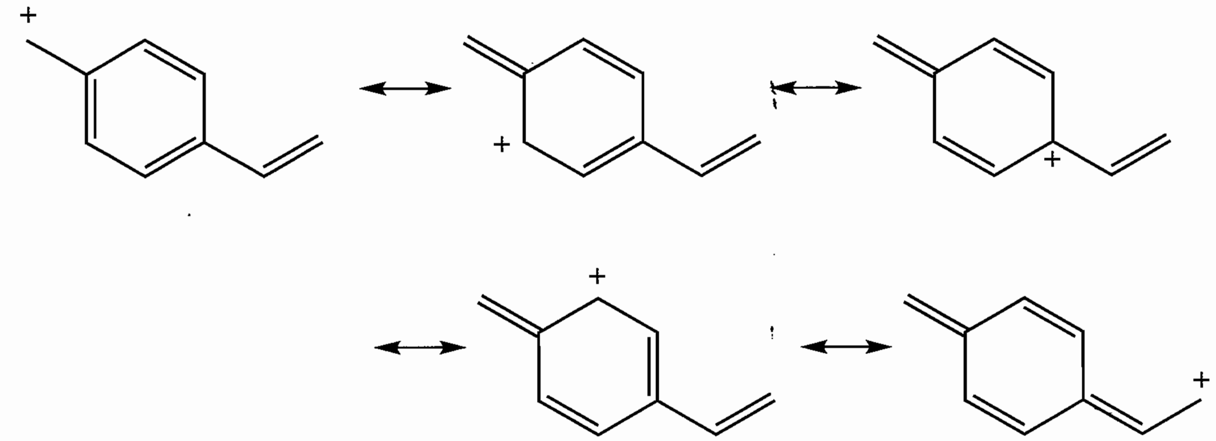
The hydrogen labeled H_b is not a likely candidate because the resulting empty sp^2 orbital does not "see" into the aromatic ring. There are no resonance structures for that potential carbocation. Also, vinyl cations are even less stable than primary cations.



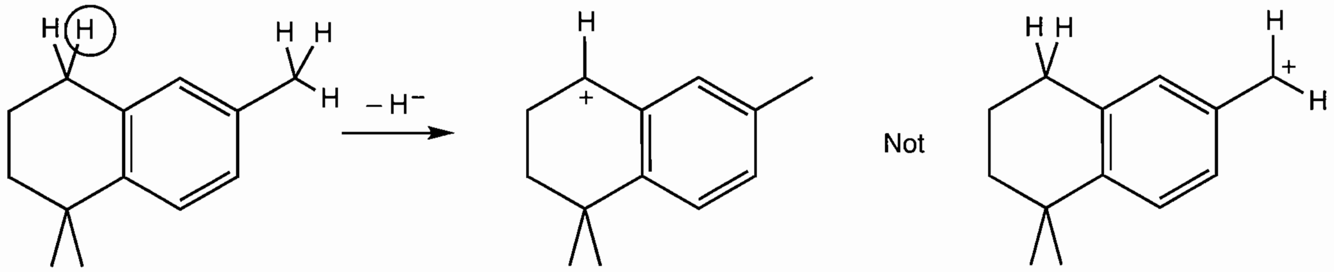
(continued)

Problem 9.4 *(continued)*

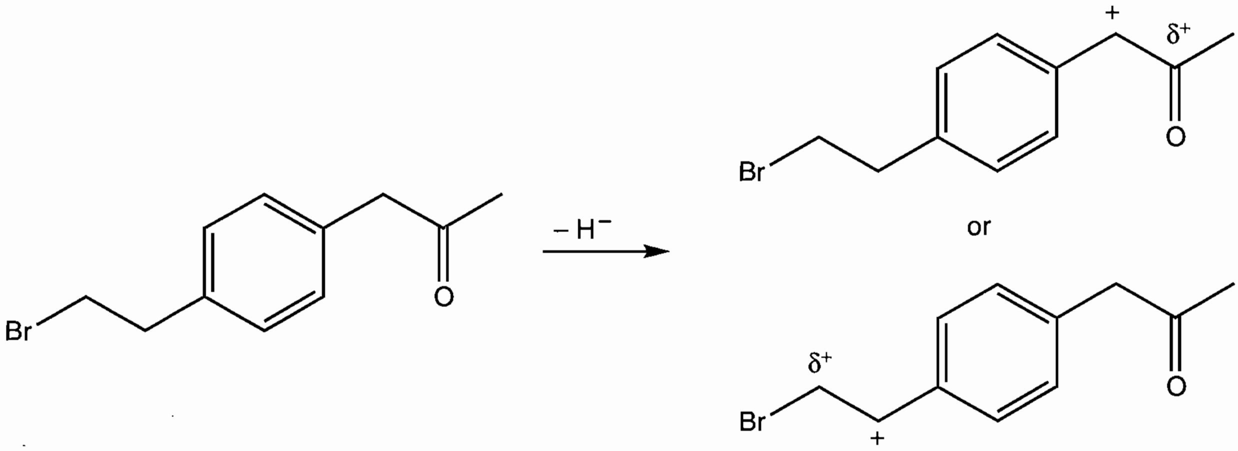
Loss of the H_a benzylic hydrogen gives a carbocation that has many stabilizing resonance structures.



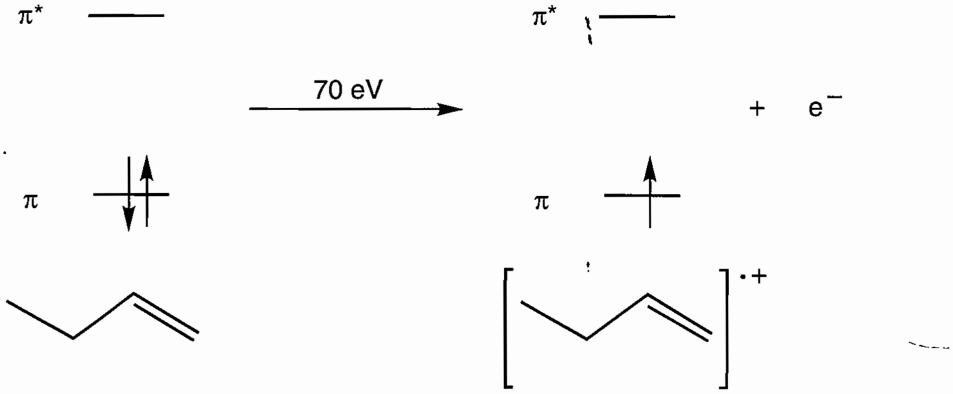
(b) The secondary benzylic cation would be more stable than a primary benzylic cation. We predict loss of one of the CH_2 benzylic hydrogens.



(c) The carbocation on the carbon adjacent to a carbonyl is destabilized because the carbonyl carbon is significantly electron deficient. We can predict that the more stable carbocation would be the benzylic CH_2 on the left. However, the carbon bonded to bromine is also somewhat electron deficient. In this case, it is more important to notice all the issues than it is to get the right answer.



Problem 9.5 In any alkene, the bonding π molecular orbital is filled with two electrons and the antibonding π* orbital is empty. When a π electron is ejected in the mass spectrometer, it will come from the highest occupied MO, which is the filled π orbital.



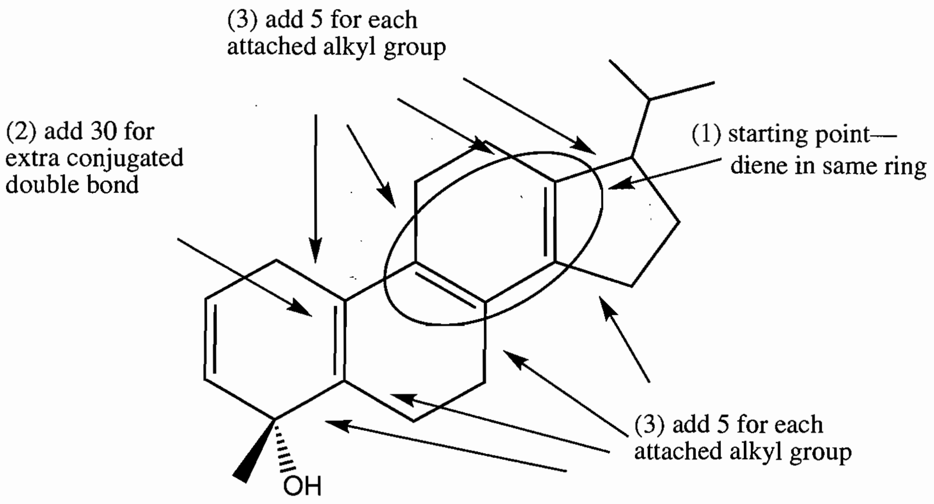
Problem 9.7

E = Nhc/λ and the quantity Nhc = 28.6 × 10^3 (p. 382).

So, E = (28.6 × 10^3)/200 = 143 kcal/mol at 200 nm and E = (28.6 × 10^3)/800 = 35.8 kcal/mol at 800 nm.

Problem 9.8

(b)



253 starting point
30 additional double bond
40 for the 8 alkyl groups
323 nm predicted λ_{max}

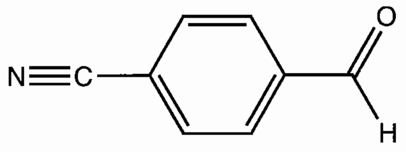
Problem 9.9 In Problem 9.9(b), the giveaway is the broad band above 3000 cm^{-1}. This band can only result from an OH. There is a strong band at 1720 cm^{-1}; a carbonyl group is present. The combination of these two bands means that you should think of a carboxylic acid, RCOOH. The appropriate strong C—O stretching vibrations are present between 1400 and 1200 cm^{-1}. As there are only two carbons in this molecule, the structure must be acetic acid, CH_3COOH.

In Problem 9.9(c), the band at 2220 cm^{-1} is in a region of few absorptions in the IR. As the compound contains nitrogen, it is very likely that the compound is a nitrile. There are C—H stretching bands above 3000 cm^{-1}. These bands reveal the presence of either "olefinic" or "aromatic"

(continued)

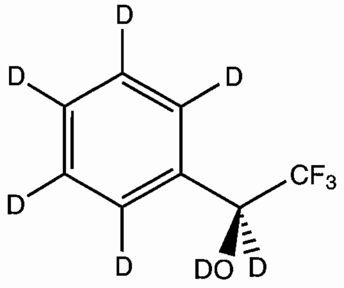
Problem 9.9 *(continued)*

hydrogens. There is a strong band at 1710 cm^{-1}, indicating that a carbonyl group is present. The band at about ~2740 cm^{-1} tells us that the carbonyl group is an aldehyde. The sequence of medium-to-weak bands at about 1600 cm^{-1} indicates that the molecule is aromatic. A reasonable guess would be an aromatic ring with an aldehyde and a nitrile. This one turns out to be a 1,4-disubstituted aromatic ring as indicated by the strong band at about 830 cm^{-1}.

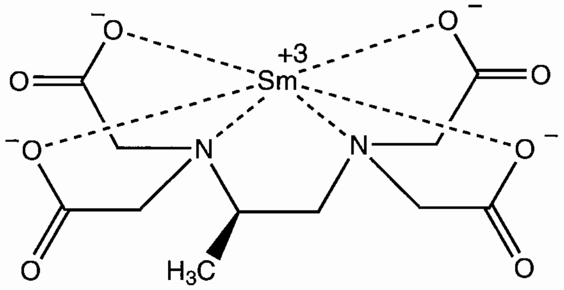


Problem 9.13 We can have a chiral environment in an NMR tube by using a chiral solvent. There aren't many chiral solvents available. A deuterated solvent would be best, so that the NMR spectrum of the solvent doesn't overwhelm the desired sample spectrum.

Another method is adding a small amount of a chiral reagent into the NMR tube. This practice is fairly common. The material added is called a chiral shift reagent. Here are examples of a possible solvent and a useful shift reagent.



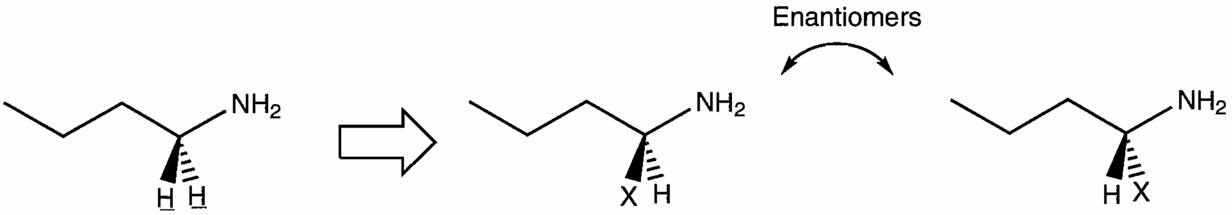
A possible chiral NMR solvent



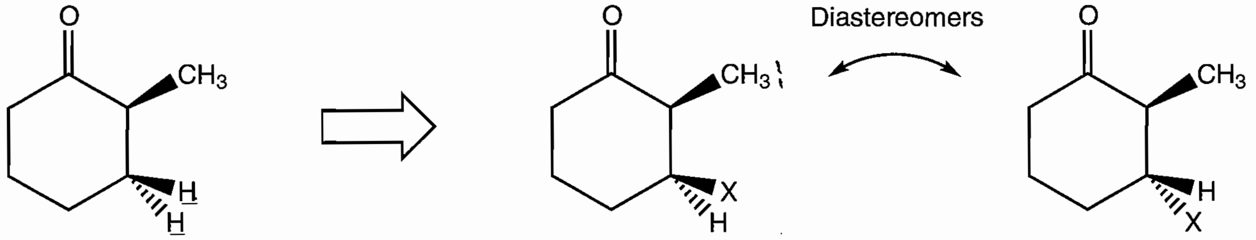
A commercially available chiral shift reagent

Problem 9.14

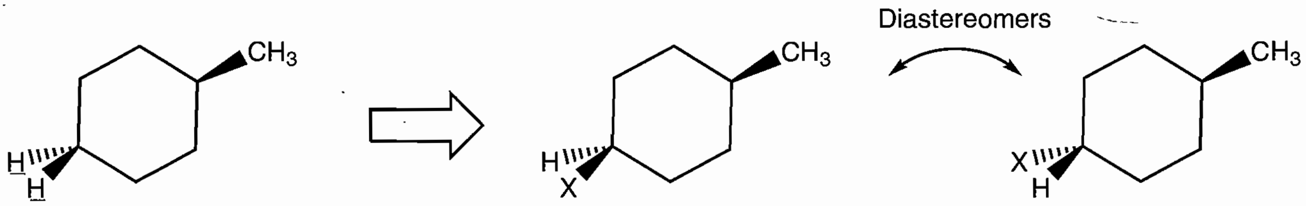
(a) The underlined hydrogens in 1-butanamine are enantiotopic. Replace one underlined H by an X and we get the enantiomer of replacing the other underlined H by an X.



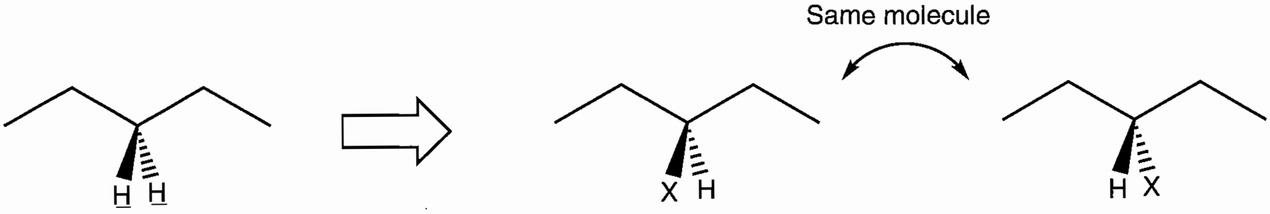
(b) The underlined hydrogens are diastereotopic. Replacing one underlined H by an X gives a diastereomer of the molecule obtained by replacing the other underlined H by an X.



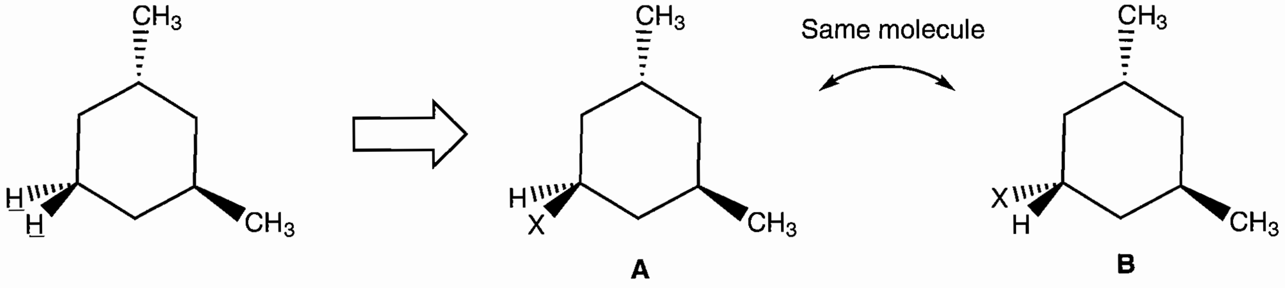
(c) The underlined hydrogens are diastereotopic. Replacing one underlined H with an X gives a diastereomer of the molecule obtained by replacing the other underlined H with an X.



(d) The underlined hydrogens in pentane are homotopic. Replacing one underlined H with an X gives the same molecule as obtained by replacing the other underlined H with an X.



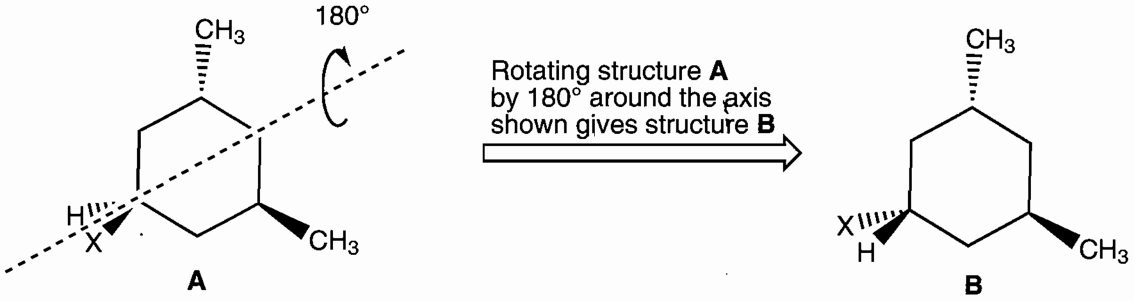
(e) This question is more difficult. It turns out that the underlined hydrogens in *trans*-1,3-dimethylcyclohexane are homotopic. Replacing one underlined H with an X gives the same molecule as obtained by replacing the other underlined H with an X.



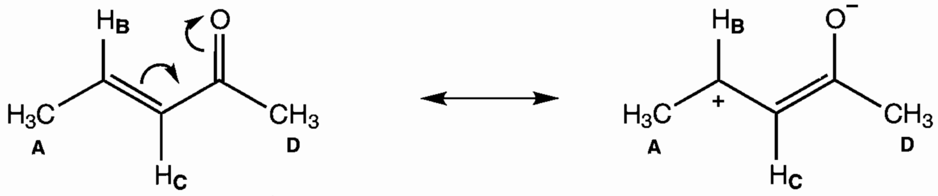
(continued)

Problem 9.14 *(continued)*

The first structure (**A**) can be rotated by 180° to give the second structure (**B**).

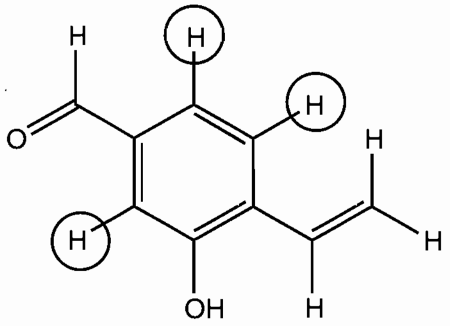


Problem 9.15 The vinyl hydrogens should be about δ 5.5 ppm. The H_B signal will be even further downfield because of the contribution of the resonance structure shown here. The position of H_B should be about δ 7.0 ppm. The H_C signal appears shifted further downfield because of the inductive effect of the carbonyl group (Table 9.5 on p. 400), about δ 2.7 ppm, and without the carbonyl, a CH appears about δ 1.5 ppm (both of these shifts come from Table 9.5). The effect of being α to a carbonyl is the difference (2.7 – 1.5 = 1.2). We can add the effect of being α to a carbonyl to our starting point of δ 5.5 in order to get our approximation of the chemical shift for H_C of δ 6.7 ppm. The next signal will be H_D. In Table 9.5 we see that a CH_3 that is α to a carbonyl will be at δ 2.0 ppm. Finally, H_A is an allylic methyl group. From Table 9.5 we see that an allylic methyl will have a chemical shift of δ 1.7 ppm. A good estimate for this molecule is H_B at δ 7.0, H_C at δ 6.7, H_D at δ 2.0, and H_A at δ 1.7. The actual values obtained from the literature are H_B at δ 6.9, H_C at δ 6.1, H_D at δ 2.2, and H_A at δ 1.9. We were pretty close, but most important, we have the right order of the signals.

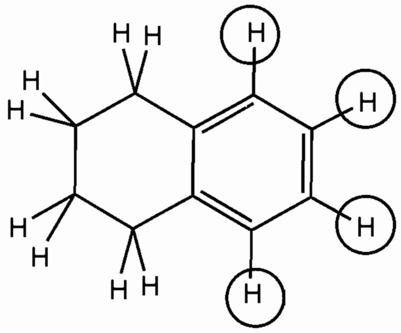


Problem 9.17

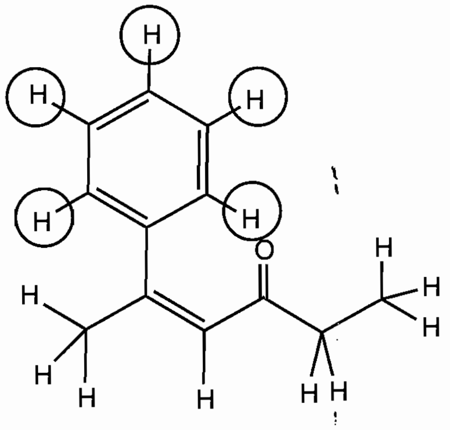
(a)



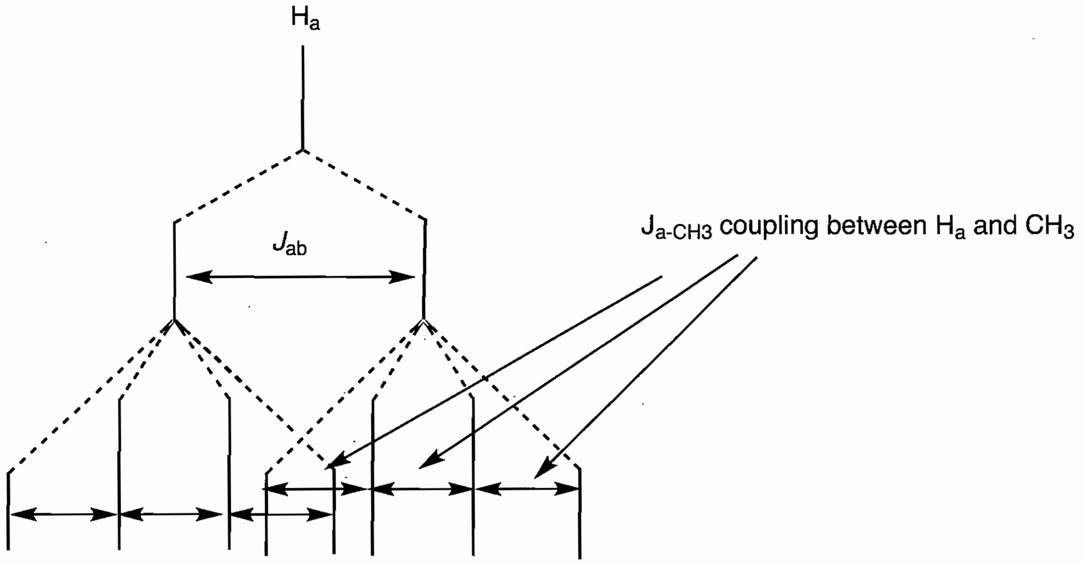
(b)



(c)



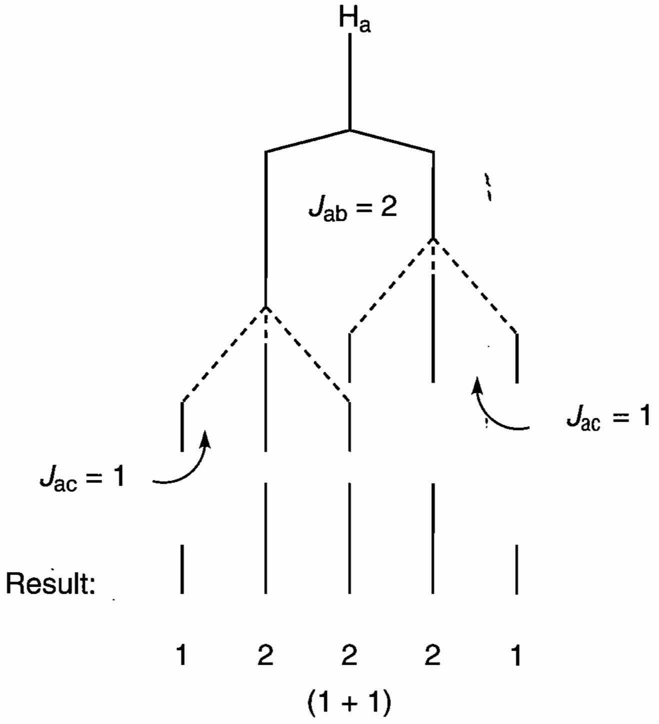
Problem 9.18 The only coupling that we will typically consider is 3-bond coupling. That means that we only need to consider the coupling (1) between H_a and the vinyl methyl, which will make H_a a quartet, and (2) between H_a and H_b, which will make H_a a doublet. Because H_a will be coupling to both H_b and the vinyl methyl group at the same time, the signal will be a doublet of quartets. You will see on page 411 of the text that the coupling between H_a and H_b (about 16 Hz) is larger than the value for the coupling between H_a and the methyl group (about 7 Hz).



Problem 9.19 In this case, there will be overlapping, and a pattern of five lines in the ratio 1:2:2:2:1 will appear. The single H_b will produce two lines, each of which will be split into a 1:2:1 triplet by the pair of H_c's. With the coupling constants set as they are in the problem, the lines of the triplets reinforce each other.

(continued)

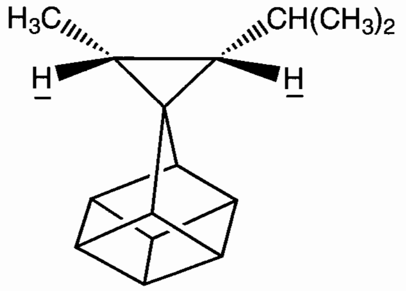
Problem 9.19 *(continued)*



Problem 9.20 2-Methoxypropane should present no problems. The underlined hydrogen is flanked by six equivalent hydrogens and so must appear as a septet (n +1 rule). 1,3-Dichloro-2-methoxypropane is much harder. It might seem that there should be five lines as there are four equivalent hydrogens adjacent to the underlined hydrogen. But those hydrogens come in diastereomeric pairs, so the correct answer is that the signal would be a triplet of triplets.

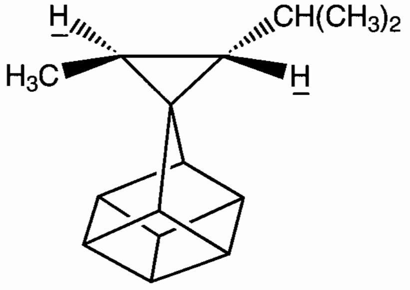
Problem 9.21

The dihedral angle between
the two cyclopropane
carbon–hydrogen bonds is 0°



J = 8.4 Hz

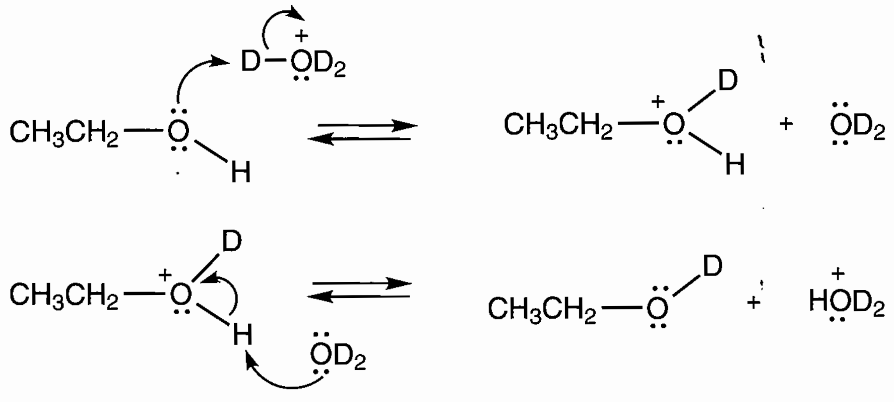
The dihedral angle between
the two cyclopropane
carbon–hydrogen bonds is about 120°



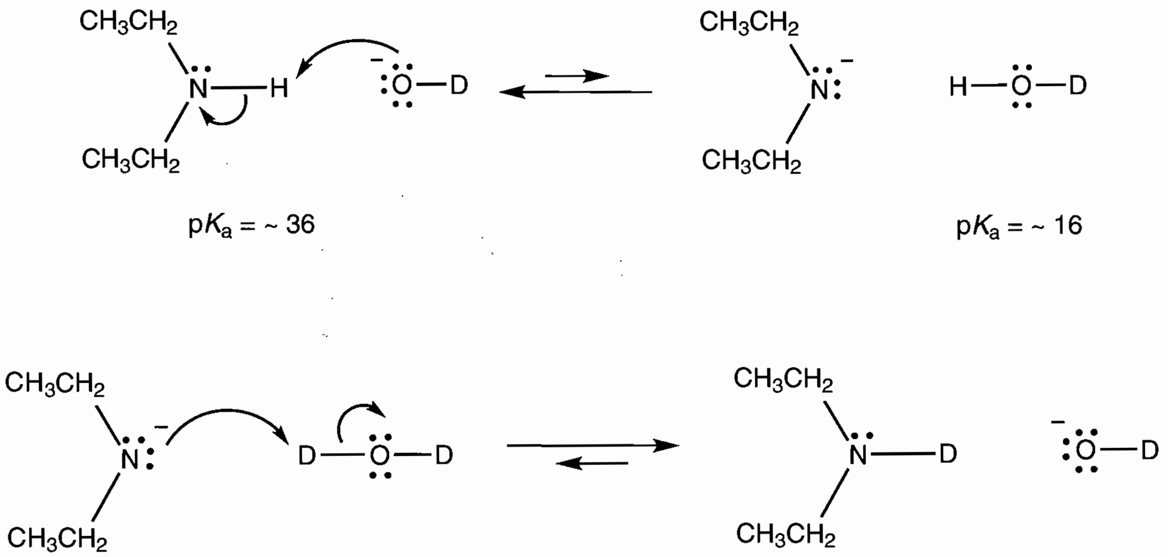
J = 5.3 Hz

A look at the Karplus curve (Figure 9.53) shows that the cis (0°) compound should have a larger coupling constant than the trans (120°) compound. This is exactly how the stereochemical assignment was made in the research paper describing these two compounds.

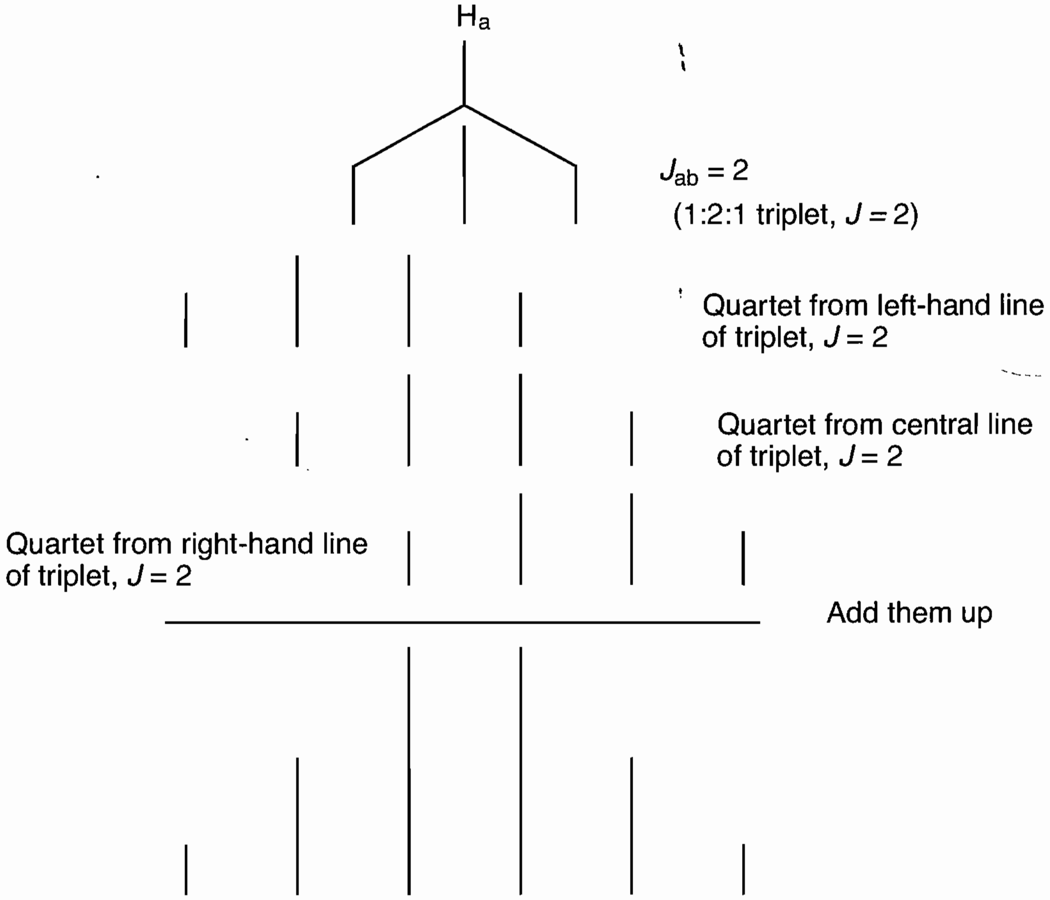
Problem 9.22 Here is an "arrow-pushing" problem deep in the middle of a spectroscopy chapter. It is a reminder that you never outgrow your need to push arrows.



The arrow pushing for NaOD-catalyzed exchange of diethylamine is shown here. We don't really expect these conditions to lead to rapid exchange. The hydroxide base is not strong enough to deprotonate the amine (p*K*a ~ 36) appreciably. Acidic conditions will be more effective for the exchange of the N—H.



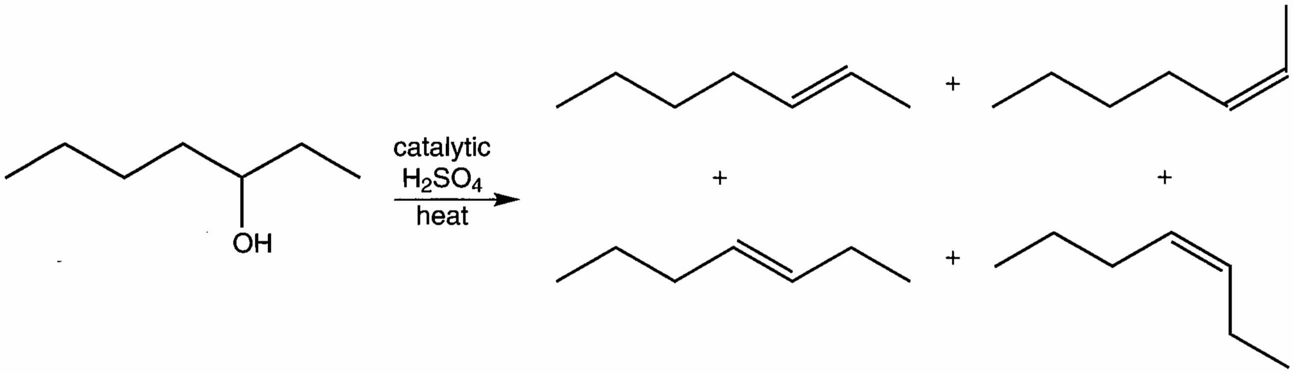
Problem 9.23 If we let the coupling constants be equal, the triplet of quartets (12 lines) we "expect" simplifies to six lines because of overlaps. The line intensities are not drawn to scale for clarity.



Problem 9.24 Use the correlation chart. The electron-withdrawing carbonyl group (recall the δ+ on the carbonyl carbon) reduces the shielding around the hydrogens on the adjacent carbon, which come into resonance at relatively low field.

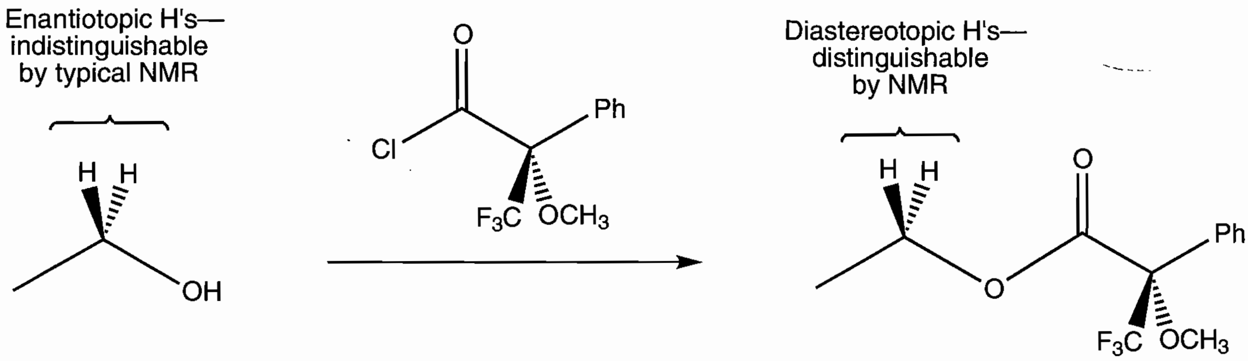
Problem 9.26 Yes, we could use ^{13}C NMR for Problem 9.25. Compound **A** will have three carbon signals, compound **B** will have five carbon signals, and compound **C** will have seven signals. We could not use the aromatic signals of the ^{1}H NMR spectrum to distinguish the three compounds. In each molecule, the aromatic C—H signal is a 2H singlet due to symmetry.

Problem 9.27

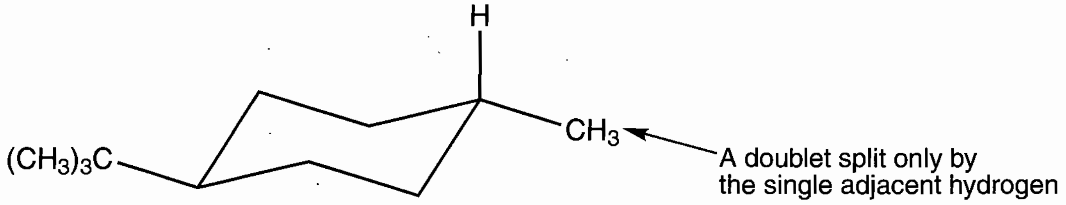


Perhaps a ^{13}C NMR expert could differentiate these molecules. But it isn't going to be an easy task, for sure. All four isomers will show seven signals in their ^{13}C NMR spectra. Just separating the molecules in order to get a clean spectrum for each would be a significant challenge.

Problem 9.31 In Problem 9.13 you considered two ways to differentiate enantiomers in an NMR sample. We can use a chiral solvent or add a chiral shift reagent. In a chiral environment, the enantiotopic hydrogens of ethanol will be different. Using a chiral solvent is very expensive and does not always give significant differences in signals of enantiotopic groups. Adding a chiral reagent to the NMR sample is also expensive, although much more reliable. A third method is similar to resolution (p. 174 of the text). We can make the hydrogens diastereotopic by using a chiral derivatizing agent as shown below.



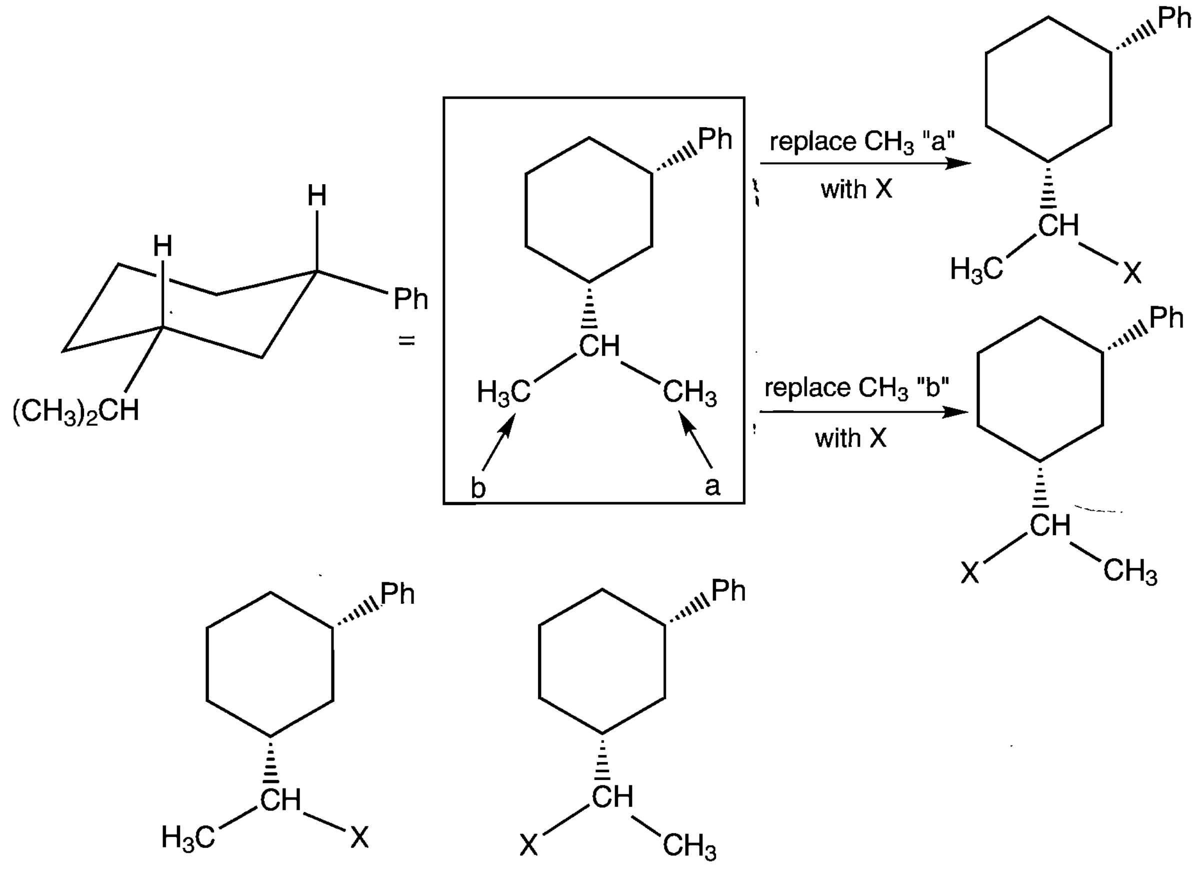
Problem 9.33 The first compound is easy. The *tert*-butyl and methyl groups will be largely in equatorial positions. There is only a single hydrogen on the carbon adjacent to the methyl group, and by the $n + 1$ rule the methyl hydrogens will apear as a doublet.



The second compound is more interesting. The methyl groups are diastereotopic and must give rise to different signals. Each methyl group will appear as a doublet in the NMR. Use the technique of replacing each methyl group with X to see this.

(continued)

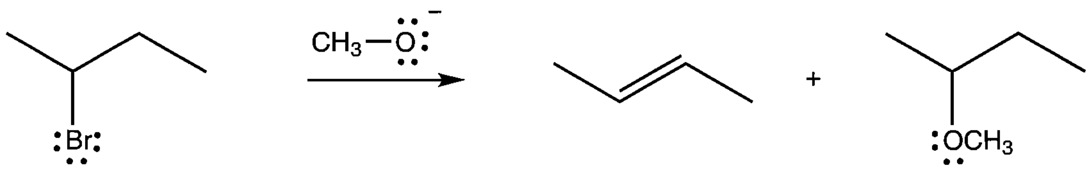
Problem 9.33 *(continued)*



These are not the same! They are diastereomers and the methyl groups are diastereotopic

Additional Problem Answers

Problem 9.34 The S_N2 product is 2-methoxybutane. The major E2 product is (*E*)-2-butene.



The easiest IR data to use would be the *sp*^{2} C—H stretch for the alkene at approximately 3010 cm^{-1}. The ether would not have such a band. The C=C stretch will not be visible in (*E*)-2-butene because there is no net change in the dipole in this symmetrical molecule. So we can't use the C=C stretch to distinguish the two products. There is an alkene C—H bend at 975–965 cm^{-1} for a trans alkene that might be useful for distinguishing these two products.

Problem 9.35

(a) This cyclic ester has one double bond and a ring. Therefore there are 2 degrees of unsaturation.

(b) This aromatic ketone has four double bonds and one ring. There are 5 degrees of unsaturation.

(c) This molecule has an alkene. There is only 1 degree of unsaturation.

(d) The triple bond contributes 2 degrees of unsaturation. Therefore, the alkyne and the alkene in the same molecule give 3 degrees of unsaturation.

(e) There are two alkenes and one ring in this molecule. It has 3 degrees of unsaturation.

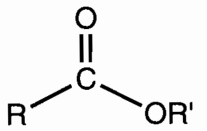
(f) There are no degrees of unsaturation in 3-methoxyhexane.

(g) Pyridine has 4 degrees of unsaturation (three double bonds and one ring).

Problem 9.36 All the structures are consistent with the O—H or N—H stretching band centered roughly at 3235 cm^{-1}, so no distinction is possible through use of this band. (Actually, the IR maven might object that primary amines and amides should show two bands in this region, but this seems a fine point.) Structures **A** and **C** can be eliminated because of the absence of a C═O stretch in the 1700 cm^{-1} region. So, the choice is between **B** and **D**. The band at 2240 cm^{-1} is consistent with a cyanide group (C≡N triple bond stretch), and so the structure must be **B**.

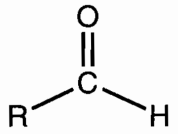
Problem 9.37

Compound 1 The IR spectrum of compound **1** exhibits an intense carbonyl stretch at 1750 cm^{-1}. By itself, this does not help much; however, the presence of a C—O stretch at 1200 cm^{-1} suggests the possibility of an **ester**. Anhydrides and carboxylic acids also show C—O stretches, but these can be ruled out by the absence of a second carbonyl stretch or the absence of an O—H stretch, respectively. Furthermore, the frequency of the carbonyl stretch for compound **1** suggests that it is probably not a conjugated ester (i.e., not an α,β-unsaturated or aryl ester).



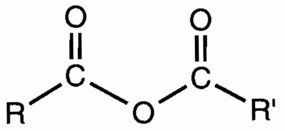
Ester

Compound 2 The IR spectrum of compound **2** displays a strong carbonyl stretch at 1710 cm^{-1}. The important additional bands in this spectrum are the weak C—H stretching absorptions at 2810 and 2715 cm^{-1}, which are characteristic of **aldehydes**. (The higher-frequency band is often obscured by overlapping aliphatic C—H stretches.) In addition, the frequency of the carbonyl stretch for compound **2** suggests that this compound is probably not a conjugated aldehyde.



Aldehyde

Compound 3 The IR spectrum of compound **3** shows two carbonyl stretches at 1855 and 1785 cm^{-1}. This pair of bands suggests that the compound is an **anhydride**. Anhydrides should also exhibit a C—O stretching band. Does this one?

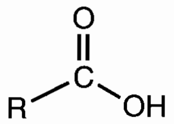


Anhydride

(continued)

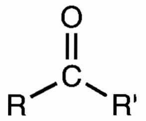
Problem 9.37 *(continued)*

Compound 4 The IR spectrum of compound **4** exhibits a strong carbonyl stretch at 1720 cm^{-1}. The diagnostic absorption in this spectrum is the very broad, intense absorption at 3600–2500 cm^{-1}, characteristic of the O—H stretch of **carboxylic acid** dimers.



Carboxylic acid

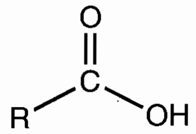
Compound 5 The IR spectrum of compound **5** displays a strong carbonyl stretch at 1710 cm^{-1}. This spectrum must belong to the **ketone**. Note the absence of a second carbonyl stretch, the aldehyde C—H stretching doublet, an O—H stretch, or a C—O stretch. The frequency of the carbonyl stretch suggests that compound **5** is probably not a conjugated ketone.



Ketone

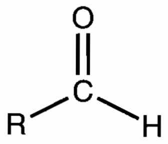
Problem 9.38

Spectrum 1 The choices for spectrum **1** are alcohol, carboxylic acid, or phenol.
All three classes would be expected to show an O—H stretch. For the alcohol and phenol, this absorption occurs in the 3400–3200 cm^{-1} region of the IR spectrum, whereas for the carboxylic acid, a broad, intense O—H stretch occurs in the 3300–2400 cm^{-1} region. The IR spectrum of compound **1** is most consistent with the latter values. Even stronger evidence for the carboxylic acid is the strong carbonyl stretch at 1720 cm $^{-1}$. This band would not be expected for the alcohol or phenol. Therefore, the IR spectrum of compound 1 is certainly that of a **carboxylic acid**.



Carboxylic acid

Spectrum 2 The carbonyl stretch at 1715 cm^{-1} could be diagnostic for an aldehyde, an ester, or a ketone. So, we will have to look elsewhere for a means of differentiating between these classes. An ester would be expected to display an intense C—O stretch in the 1300–1000 cm^{-1} region of the IR spectrum. Such a band is absent in the spectrum of **2**. The important additional bands in the spectrum of **2** are the weak C—H stretching absorptions at 2810 cm^{-1} and 2700 cm^{-1}, character-istic of **aldehydes**. (The higher-frequency band is often obscured by overlapping aliphatic C—H stretches.)



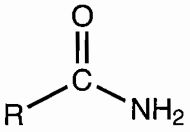
Aldehyde

Spectrum 3 The weak band at 2220 cm^{-1} could be from the C≡C stretch of a 1-alkyne or the C≡N stretch of a nitrile (cyanide). However, symmetrically disubstituted alkynes do not exhibit a C≡C stretch because this vibration does not result in a dipole moment change. 1-Alkynes also display a characteristic $\equiv$C—H stretch at about 3300 cm^{-1}, absent in the IR spectrum of compound **3**. Accordingly, this leaves the **nitrile** as the best fit for spectrum **3**.

$$R—C\equiv N$$

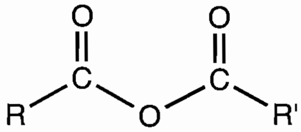
Nitrile

Spectrum 4 The intense bands at 3350 cm^{-1} and 3180 cm^{-1} are consistent with the N—H stretches of either a primary amine or primary amide, but not with a nitro compound. To differentiate between the amine and the amide, look for the presence or absence of a carbonyl stretch. The IR spectrum **4** shows an absorption centered at 1650 cm^{-1}, the result of a combination of a carbonyl stretch and an N—H bend. Therefore, the IR spectrum **4** is probably that of a **primary amide**.



Primary amide

Spectrum 5 The carboxylic acid can be eliminated immediately because of the absence of the diagnostic broad, intense O—H stretch in the 3300–2400 cm^{-1} region of the IR spectrum. Both anhydrides and esters display a strong C—O stretch in the 1300–1000 cm^{-1} region (present in this case at 1040 cm^{-1}). However, esters normally exhibit only a single carbonyl stretch, whereas anhydrides display two carbonyl stretches. The presence of two carbonyl absorptions at 1810 cm^{-1} and 1750 cm^{-1} in the IR spectrum **5** is strong evidence for an **anhydride**.



Anhydride

Problem 9.39 Alkene isomers are traditionally distinguished through the use of the $=$C—H out-of-plane bending vibrations. The third spectrum has a band at 697 cm^{-1}, the position typical of cis alkenes. This molecule is *cis*-2-octene.

Spectrum **2** has a strong band at 966 cm^{-1}, a typical position for a trans alkene. This molecule is *trans*-2-octene. Notice that in the IR spectrum for this relatively symmetrical molecule, there is no visible band for the C$=$C stretch. By contrast, in the IR spectrum of the less symmetrical cis isomer **3**, this band appears at ~1650 cm^{-1}.

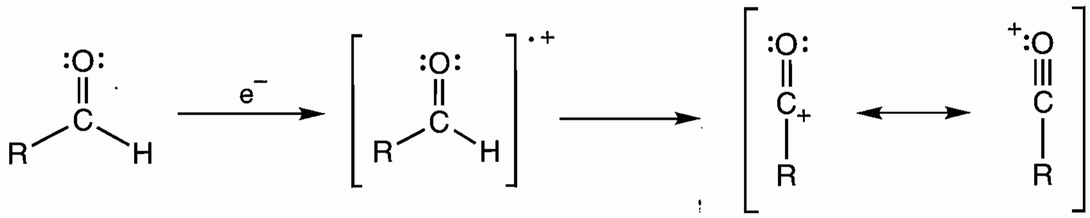
Spectrum 1 must belong to 1-octene by a process of elimination, but let's look at the spectrum anyway to make certain. The two bands for a vinyl group (HC$=$CH$_2$) appear at 991 cm^{-1} and 909 cm^{-1}, and there is a peak for the C$=$C stretch at about 1640 cm^{-1}.

Problem 9.40 The keys to this problem are the bands in spectrum **2** at 3333 cm^{-1} and 2128 cm^{-1} for the stretching of the alkyne terminal carbon–hydrogen bond and the triple bond, respectively. In the first spectrum, there is no visible band for either the alkyne carbon–hydrogen bond or the carbon–carbon triple bond. The first molecule is 6-phenyl-2-hexyne, a disubstituted acetylene too symmetrical to show a C$\equiv$C stretch. The second is the 1-alkyne, 5-phenyl-1-pentyne.

Problem 9.41 Ethanol has a broad O—H band at ~3400 cm^{-1}, and this band will disappear during the reaction. The aldehyde product has a strong C$=$O stretch at about 1730 cm^{-1}, and this band will appear during the oxidation of ethanol. One could monitor this biochemical process by following either IR band. The O—H band might be complicated by the presence of water, so the carbonyl band at ~1730 cm^{-1} is the more logical choice.

Problem 9.42 As Table 9.1 shows, natural bromine has two common isotopes, ^{79}Br and ^{81}Br, in nearly equal amounts. The two ions come from the two molecules, $C_8H_7{}^{79}BrO_2$ ($m/z = 214$) and $C_8H_7{}^{81}BrO_2$ ($m/z = 216$).

Aldehydes generally show very intense (M – 1) peaks as a hydrogen atom is easily lost to give the resonance-stabilized acylium ion.



Of course, in this case the acylium ion still contains bromine, and two peaks will be observed, $C_8H_6{}^{79}BrO_2$ ($m/z = 213$) and $C_8H_6{}^{81}BrO_2$ ($m/z = 215$).

Problem 9.43 Our first task is to derive the empirical formula from the elemental analysis data. If you are unsure of these calculations, be sure to review the problems in Chapter 3 (p. 148). We can find the percentage of oxygen easily, 100 – (80.00 + 6.70) = 13.30.

$$\text{C} \quad \frac{80.00}{12.01} = 6.66 \qquad \text{H} \quad \frac{6.70}{1.01} = 6.63 \qquad \text{O} \quad \frac{13.30}{16.00} = 0.831$$

Now we divide by the smallest value, 0.831:

$$\text{C} \quad \frac{6.66}{0.831} = 8.01 \qquad \text{H} \quad \frac{6.63}{0.831} = 7.98 \qquad \text{O} \quad \frac{0.831}{0.831} = 1.00$$

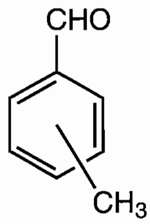
So, the empirical formula is C_8H_8O and formula weight is 120 g/mol.

A quick look at the mass spectrum shows that the highest peak, likely to be the molecular ion, is at $m/z = 120$. Accordingly, the empirical formula and the molecular formula are the same, C_8H_8O.

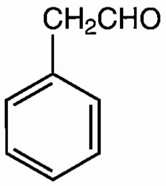
Next, it is useful to work out the degrees of unsaturation (Ω) in this molecule. Remember, $\Omega = [(2n + 2) - (\text{No. of hydrogens})]/2$.

Here, $\Omega = [18 - 8]/2 = 5$. There is a total of five rings and/or π bonds in this molecule. For this small a molecule, this many degrees of unsaturation almost certainly means there will be a benzene ring (four unsaturations) in the molecule.

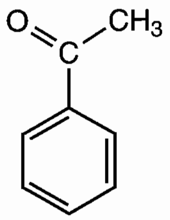
Now it is finally time to analyze the IR spectrum. The presence of a strong band at 1690 cm^{-1} suggests a carbonyl group. Taken together with the formula and the notion that a benzene ring is present, this limits the choices to the following five possibilities.



Three possible isomers of tolualdehyde



Phenylacetaldehyde



Acetophenone

The strong bands at 758 cm^{-1} and 690 cm^{-1} indicate a monosubstituted benzene, eliminating the three isomers of tolualdehyde. All aldehydes are eliminated by the lack of the two characteristic bands for the aldehyde C—H stretch at 2900–2700 cm^{-1}. Only acetophenone, the last possibility, remains.

Problem 9.44 First, we need to know the amount of oxygen in this molecule. A little addition and subtraction does the job.

$$\begin{array}{lr} \text{C} & 70.60 \\ \underline{\text{H}} & \underline{5.90} \\ & 76.50 \end{array} \qquad 100 - 76.50 = 23.50 = \%\ \text{oxygen in the compound}$$

The calculation of the empirical formula is now as follows:

$$\text{C} \quad \frac{70.60}{12.00} = 5.88 \qquad \text{H} \quad \frac{5.90}{1.01} = 5.84 \qquad \text{O} \quad \frac{23.50}{16.00} = 1.47$$

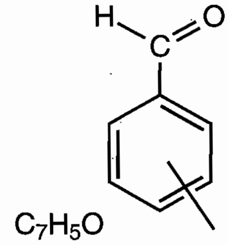
Now we divide by the smallest value, 1.47:

$$\text{C} \quad \frac{5.88}{1.47} = 4.00 \qquad \text{H} \quad \frac{5.84}{1.47} = 3.97 \qquad \text{O} \quad \frac{1.47}{1.47} = 1.00$$

So, the empirical formula is C_4H_4O and formula weight is 68 g/mol.

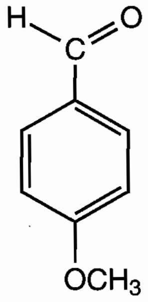
The mass spectrum shows that the molecular formula is twice the empirical formula as the molecular ion is 136, (2 × 68). So the molecular formula is $C_8H_8O_2$.

The degrees of unsaturation can now be calculated: $\Omega = (18 - 8)/2 = 5$. A benzene ring is suggested and would account for 4 degrees of unsaturation. The IR spectrum reveals a strong band at 1685 cm^{-1}. This absorption shows that a carbonyl group is present as the fifth unsaturation. The pair of peaks at 2820 cm^{-1} and 2720 cm^{-1} is diagnostic for aldehydes. The low-frequency position of the carbonyl band suggests that the carbonyl group is conjugated and, in combination with the presence of a benzene ring, indicates a benzaldehyde. An atom inventory shows that we are now short CH_3O, probably a methoxy group.



$C_8H_8O_2$ less C_7H_5O leaves CH_3O

It is tempting at this point to imagine that compound **A** is a methoxybenzaldehyde, and the only real question left is the position of substitution on the ring. The single band at 833 cm^{-1} is diagnostic for para substitution, and, indeed, this compound is *p*-methoxybenzaldehyde.



Problem 9.45 It is our first task to determine the molecular formulas for isomers **A**, **B**, and **C**. Is there any oxygen? No, the percentages of C, H, and N add up to 100.

$$\begin{array}{lr} \text{C} & 71.17 \\ \text{H} & 5.12 \\ \underline{\text{N}} & \underline{23.71} \\ & 100.00 \end{array}$$

There is no oxygen present!

To determine the molecular formula, apply the usual calculation:

$$\text{C} \quad \frac{71.17}{12.01} = 5.92 \qquad \text{H} \quad \frac{5.12}{1.01} = 5.07 \qquad \text{N} \quad \frac{23.71}{14.01} = 1.69$$

$$\text{C} \quad \frac{5.92}{1.69} = 3.50 \qquad \text{H} \quad \frac{5.07}{1.69} = 3.00 \qquad \text{N} \quad \frac{1.69}{1.69} = 1.00$$

Therefore, the empirical formula = $2(C_{3.50}H_{3.00}N_{1.00}) = C_7H_6N_2$, and the formula weight is $(C_7H_6N_2) = 118$ g/mol.

So, the empirical formula = the molecular formula, as the molecular ion in the mass spectrum is 118.

Now let's determine the degrees of unsaturation, Ω.

$$\Omega = \frac{2(7+2)+2-2-6}{2} = 6$$

Six degrees of unsaturation suggests the possibility of a benzene ring.

Now it is time to see where we are by doing an atom inventory:

$$\begin{array}{ll} C_7H_6N_2 & \text{Formula} \\ \underline{-\,C_6} & \text{Benzene ring} \\ CH_6N_2 & \text{Remaining} \end{array}$$

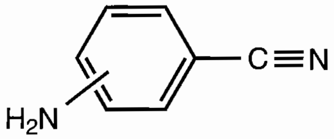
The IR spectra of isomers **A**, **B**, and **C** all show an absorption at about 2220 cm^{-1}. This band could be the result of a C$\equiv$C stretch of an alkyne or the C$\equiv$N stretch of a nitrile. Assuming that our conjecture that these isomers contain a benzene ring is correct, the alkyne C$\equiv$C stretch can be ruled out because the atom inventory shows only one residual carbon atom. Also note that the nitrile C$\equiv$N accounts for the remaining two degrees of unsaturation.

$-C\equiv N$ Two degrees of unsaturation

The IR spectra of isomers **A**, **B**, and **C** also exhibit doublets at about 3490 cm^{-1} and 3390 cm^{-1}. These are N—H stretches indicative of a primary amine, which shows two N—H stretches.

$R-NH_2$ primary amine

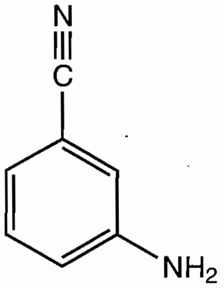
All the available information suggests that isomers **A**, **B**, and **C** are the three possible aminobenzonitriles; that is,



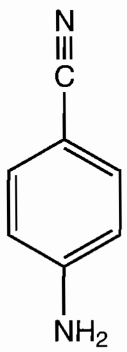
Isomer **A**. The IR spectrum of isomer **A** exhibits three peaks at 860 cm^{-1}, 780 cm^{-1}, and 680 cm^{-1}, which indicates 1,3- or meta-disubstitution. Thus isomer **A** is 3-aminobenzonitrile.

Isomer **B**. The IR spectrum of isomer **B** displays a band at 835 cm^{-1}, which suggests 1,4- or para-disubstitution. Isomer **B** is 4-aminobenzonitrile.

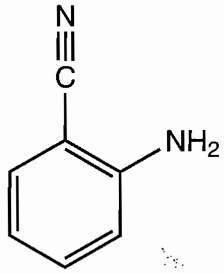
Isomer **C**. Finally, the IR spectrum of isomer **C** shows only an intense peak at 750 cm^{-1}, indicative of 1,2- or ortho-disubstitution. Isomer **C** is 2-aminobenzonitrile (anthranilonitrile).



A



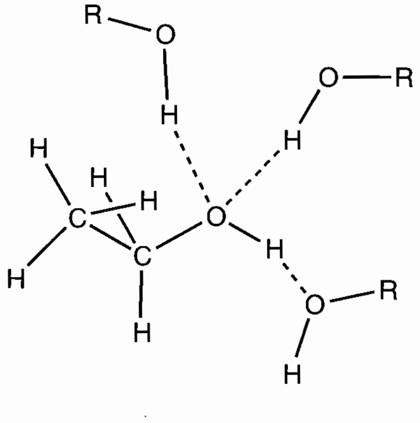
B



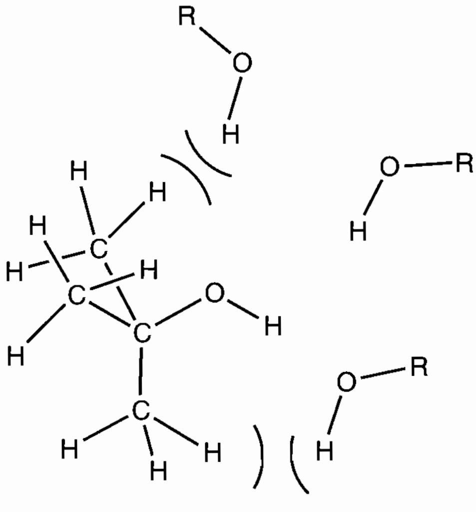
C

Problem 9.46 The IR band for the O—H stretch in an alcohol will sharpen upon dilution because the amount of hydrogen bonding diminishes. There are fewer neighboring molecules with which hydrogen bonding can occur. The typical broad band of the O—H stretch between 3200 and 3600 cm^{-1} is due to the many different types of hydrogen-bonded species (dimers, trimers, tetramers, etc.). The O—H stretching frequency of the isolated monomer appears at approximately 3600 cm^{-1}.

The O—H stretching frequency for *tert*-butyl alcohol is often sharp because the *tert*-butyl makes the area around the O—H group congested. There is less hydrogen bonding possible. The O—H stretching frequency appears at approximately 3600 cm^{-1}.



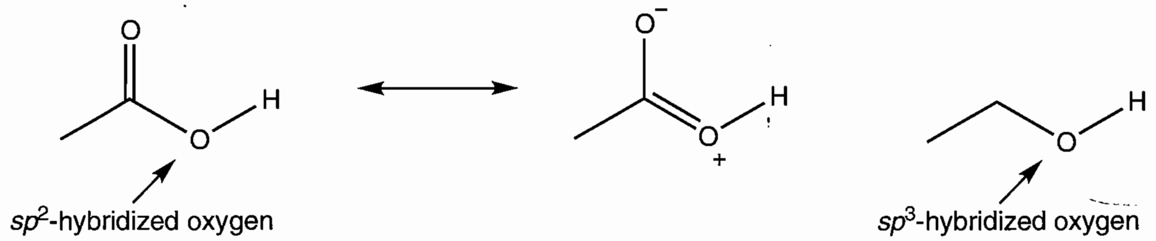
Primary alcohol—with H-bonding



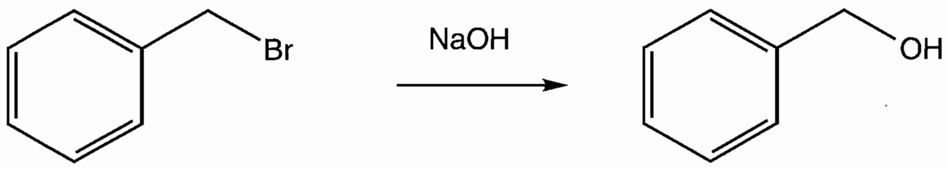
tert-Butyl alcohol—fewer H-bonds

Problem 9.47 The O—H stretch for a carboxylic acid is 3200–2800 cm^{-1}. The O—H stretch for an alcohol is 3550–3300 cm^{-1}. One reason for the difference between the two O—H stetches is that the OH hydrogen of the carboxylic acid is more acidic than the OH of an alcohol. Therefore, it is more strongly involved in hydrogen bonding.

Another reason for the difference is that the oxygen of the O—H in the carboxylic acid has a different hybridization. The carboxylic acid is stabilized by resonance. Therefore, the hybridization of the O—H oxygen is close to *sp*^{2}. There is no resonance for the alcohol oxygen, so its oxygen is close to *sp*^{3}.

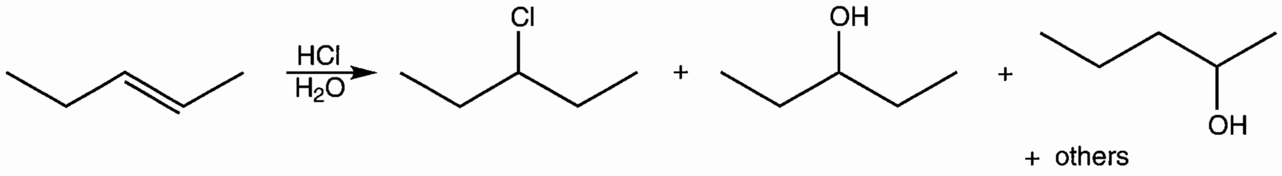


Problem 9.48 Benzyl bromide will react with NaOH in an S$_N$2 reaction to give benzyl alcohol.



Both the starting material and product should show IR bands for a monosubstituted aromatic ring (Table 9.4, p. 391). The major difference will be that the starting bromide will not show an OH stretching band at 3500–3300 cm^{-1} and a C—O stretching absorption at 1260–1000 cm^{-1}, whereas the product alcohol will.

Problem 9.49 IR spectroscopy is a great tool that can be used to distinguish between an alkyl halide (such as 3-chloropentane) and an alcohol (such as 3-pentanol). The broad band at 3400 cm^{-1} that is a characteristic of the O—H stretch of an alcohol will be observed for the 3-pentanol but not for 3-chloropentane.



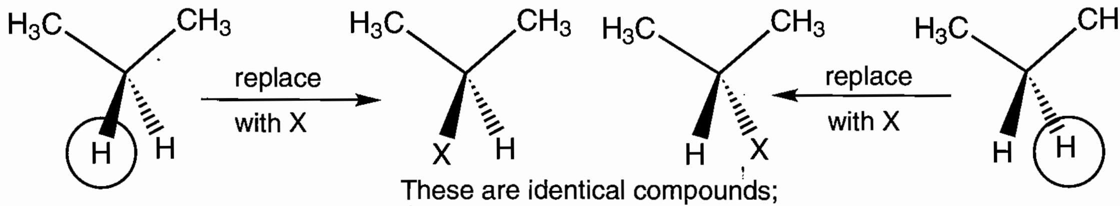
IR spectroscopy is not a good tool for distinguishing between 3-pentanol and 2-pentanol. NMR would be a better tool for such a challenge (see Problem 9.64).

Problem 9.50 The formula is $C_2H_4Br_2$. The C_2H_4 part is constant and has a mass of 28. Each bromine has a 50:50 chance to be 79 or 81. Thus, both bromines can be 79, both bromines can be 81, and there are two ways that one bromine can be 79 and one 81. So we should see three molecular ions in the ratio 1:2:1.

28	28	28	28
79	81	79	81
79	79	81	81
186	188	188	190

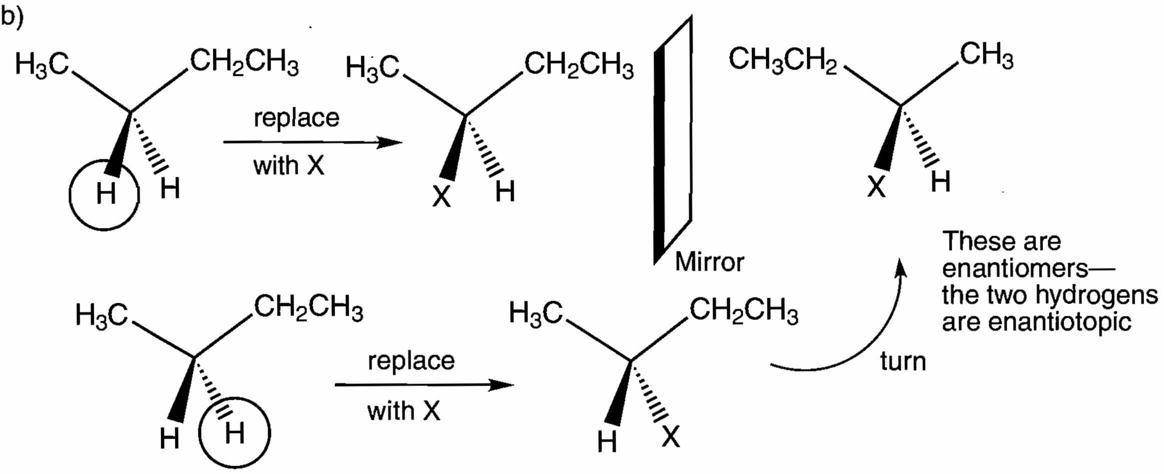
Problem 9.51 We will use the technique outlined in the chapter (p. 401). Simply replace the hydrogens in question one by one with X and determine the relationship between the two "new compounds." If they are identical, the two hydrogens are homotopic; if the "new compounds" are enantiomers, the two hydrogens are enantiotopic; and if they are different compounds entirely, the two hydrogens are diastereotopic. The first three cases are quite easy:

(a)



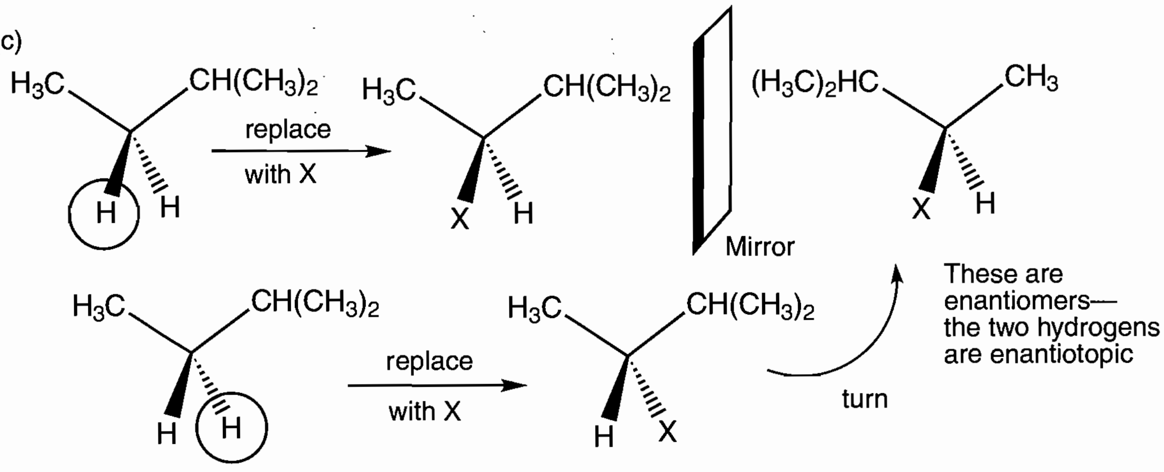
These are identical compounds; the two hydrogens are homotopic

(b)



These are enantiomers—the two hydrogens are enantiotopic

(c)

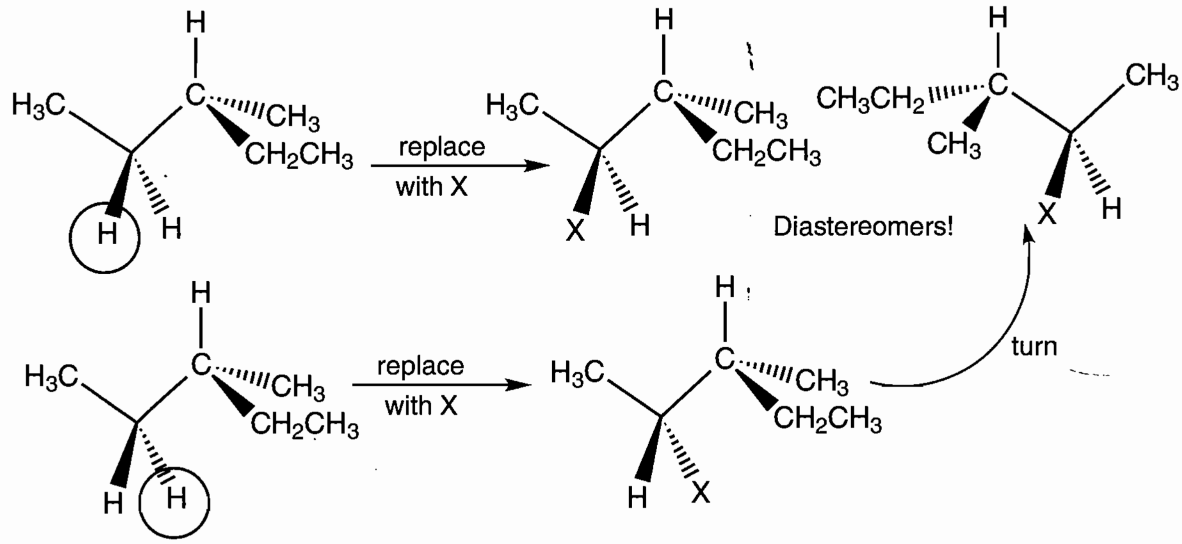


These are enantiomers—the two hydrogens are enantiotopic

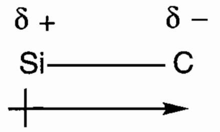
(continued)

Problem 9.51 *(continued)*

Part (d) is the most interesting case. The "replacement technique" leads to diastereomers. The two hydrogens in question are diastereotopic.



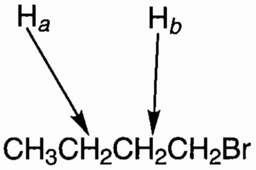
Problem 9.52 Silicon is less electronegative than carbon; thus the dipole arrow runs as follows:



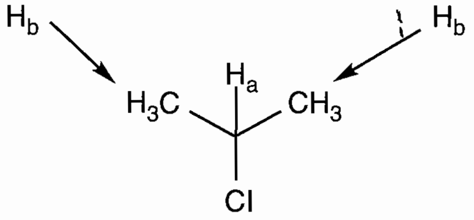
The "extra" electrons around carbon shield the hydrogens, which are shifted upfield as a result.

Problem 9.53 There are four factors that can have an impact on the chemical shift:
(1) electronegativity, (2) hybridization, (3) aromaticity, and (4) delocalization. A cyclopropane has no electronegative groups. The ring is not aromatic, and there is no delocalization possible in the molecule, so the most logical reason for a different chemical shift is hybridization. In fact, that is the explanation found in the literature.

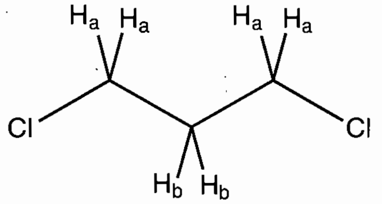
Problem 9.54 The 300-MHz spectrum is nearly first order. The 60-MHz spectrum is not and is therefore much more complicated and difficult to interpret. Remember, for a first-order spectrum to appear for two different coupled hydrogens such as H_a and H_b, the difference in Hz in the chemical shifts (δ_{ab}) must be about 10 times greater than their coupling constant (J_{ab}). At 60 MHz this condition is not satisfied, but at 300 MHz it is.



Problem 9.55 There are only two kinds of hydrogen in 2-chloropropane. H_a will appear as a septet (six adjacent equivalent hydrogens, $n + 1$ rule) at about $\delta = 3.8$ ppm, the position appropriate for a hydrogen on a methine carbon bearing a chlorine atom. The six methyl hydrogens (H_b) will be a doublet (only one adjacent hydrogen) at about $\delta = 1.5$ ppm, the position for a methyl hydrogen β to a chlorine.



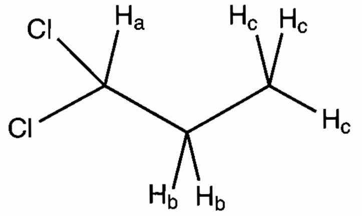
Problem 9.56 The first step for predicting a ^1H NMR spectrum is to identify the different signals. For 1,3-dichloropropane, there will be only two signals. The signals will be from the four equivalent H_a's and the two H_b's. The chemical shift for H_a will be δ 3.5 ppm because these hydrogens are on a C that is directly attached to a chlorine. The H_a CH_2 on the left is too far from the chlorine on the right to be further deshielded. The limit for deshielding by electronegativity is three bonds. So the hydrogens on the α carbon (CH_2 directly attached to the electronegative group) will be strongly deshielded, and the hydrogens on the β carbon (CH_2 once removed from the electronegative group) will be weakly deshielded. The hydrogens on a γ carbon (CH_2 twice removed) are not substantially shifted by the electronegative group. They are too far away. The H_b hydrogens are once removed from both chlorines. The chemical shift for a CH_2 once removed from a chlorine is about δ 1.8 ppm. In order to determine the chemical shift of H_b, we have to add the **effect** of the second chlorine. We cannot simply add the chemical shifts. To determine the **effect** of being a CH_2 once removed from a chlorine, we simply compare such a CH_2 with and without the chlorine. A typical CH_2 appears at a chemical shift of about δ 1.3 ppm. The CH_2 once removed from a chlorine is about δ 1.8 ppm. Therefore, the effect of the chlorine is the difference, which is 1.8 ppm – 1.3 ppm = 0.5 ppm. That is the value we can add to take into account the second chlorine. We predict a chemical shift of δ 1.8 ppm for the chlorine on one side, and we add 0.5 ppm for the chlorine on the other side to get δ 2.3 ppm for our predicted chemical shift of H_b.



For the coupling of the two signals, we predict that H_a will be a triplet because they will "see" two H_b hydrogens. The H_b signal will be a quintet (or pentet) because there are four equivalent vicinal H_a hydrogens.

Problem 9.57

(a) The chemical shift for the H_a signal will be the furthest downfield, which means the shift of δ 5.72 ppm. H_a will be a triplet because there are two hydrogens (H_b) on the adjacent carbon.



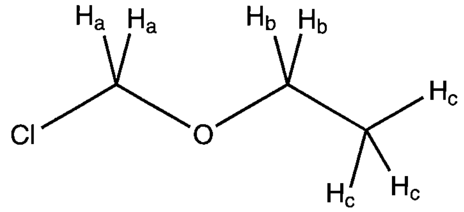
(continued)

Problem 9.57 *(continued)*

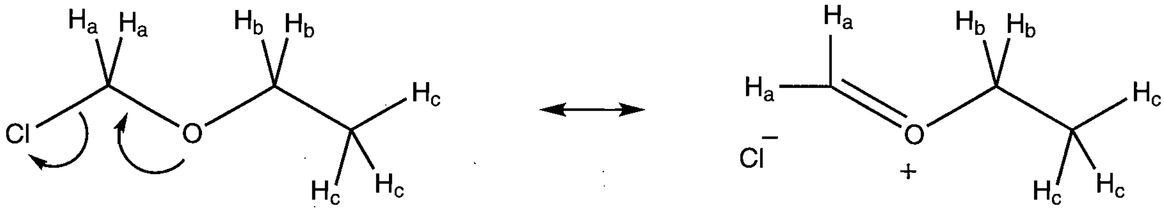
The chemical shift for H_b is the next most deshielded signal, which means it must be at δ 2.22 ppm. We would predict a shift of about δ 2.3 ppm (see Problem 9.56). The coupling for H_b will be a quintet (or pentet) because the rapid rotation around the single bonds will result in nearly the same coupling constant with the four hydrogens (one H_a and three H_c). Predicting a doublet of quartets is also an acceptable answer.

The chemical shift for the CH_3 will be δ 1.10 ppm. The CH_3 is twice removed from the chlorines, which is too far away to have much deshielding. A typical CH_3 appears at a chemical shift of about δ 0.9 ppm (see Table 9.5). The methyl signal will be coupled to the H_b hydrogens on the adjacent carbon. Therefore it will be a triplet.

(b) The CH_2 between the chlorine and the oxygen is directly attached to the two electronegative groups. It will be the signal furthest downfield, which is δ 5.5 ppm. The H_a signal will be a singlet because there are no hydrogens on the adjacent atoms.

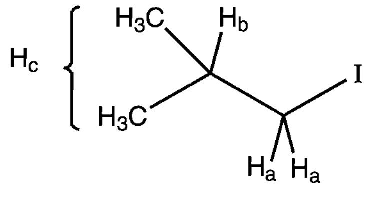


We predict the H_b hydrogens to be at δ 3.5 ppm because that CH_2 is directly attached to an oxygen, which produces the same chemical shift as a CH_2 directly attached to a chlorine. The fact that the H_b hydrogens are at δ 3.75 ppm in this molecule suggests that this particular oxygen is a little bit more deshielding. This is undoubtedly due to the resonance contribution shown here. A positively charged oxygen is more electronegative. The coupling for H_b would be a quartet because there are three hydrogens on the adjacent carbon.



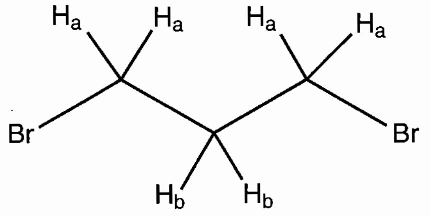
We can assign the H_c signal to the δ 1.28 ppm. The methyl group is once removed from the electronegative oxygen. The H_c signal will be a triplet because there are two H_b hydrogens on the adjacent carbon.

(c) The chemical shift for H_a would be furthest downfield. Because the methylene group is next to an iodine, we predict that shift to be about δ 3.2 ppm (see Table 9.5). That fits nicely with the observed δ 3.16 ppm signal. The CH that is once removed from the iodine should be at δ 1.5 ppm because it is a methine and a little further downfield because the iodine is electronegative and deshielding on the once-removed position. That fits well with the δ 1.72 ppm signal. The six H_c hydrogens are equivalent. They are more removed from the iodine and should appear at δ 0.9 ppm, if the iodine has no effect on them. It isn't too surprising to find that there is a small downfield shift on H_c, so δ 1.03 ppm is a reasonable chemical shift.



The signal for H_a would be a doublet because of the single H_b that is on the only adjacent carbon. The H_c methyls would also be a doublet because of the single H_b. The H_b signal could appear as a nonet (nine lines) if the rotation around the C—C bonds makes the coupling constant between H_a and H_b (J_{ab}) the same as the coupling constant between H_b and Hc (J_{bc}). In that case, H_b would be split by the eight vicinal hydrogens. It is possible that the H_b splitting will appear as a triplet of septets, although that would be difficult to ascertain.

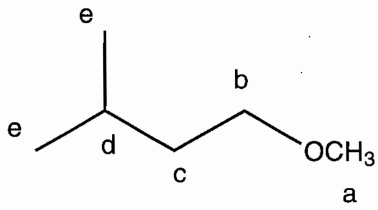
(d) The first thing to notice about 1,3-dibromopropane is that the molecule is symmetrical. There are four equivalent H_a hydrogens. Based on Table 9.5, the chemical shift for H_a should be δ 3.4 ppm, the chemical shift for a methylene attached to a bromine. The δ 3.59 ppm signal indicates that each of the methylenes is shifted by the attached bromine in addition to the bromine that is two carbons away. The H_b hydrogens should be at a chemical shift of about δ 2.3 ppm because the methylene, which has a chemical shift of δ 1.3 ppm, is once removed from two bromines. Each bromine has about a δ 0.5 ppm effect when once removed. Thus, δ 1.3 + 0.5 + 0.5 = 2.3 ppm. The observed δ of 2.36 ppm fits nicely with where we would predict the H_b methylene signals to appear.



The coupling for the H_a signal would be a triplet due to the two H_b hydrogens that are vicinal. The H_b signal would be a quintet (five lines) because of the four equivalent vicinal H_a hydrogens.

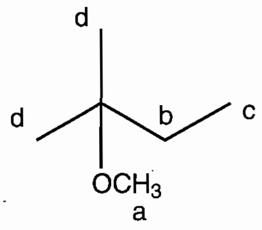
Problem 9.58 For each of these problems, it is good to keep the following chemical shifts in mind. A CH_3 directly attached to an oxygen has a typical chemical shift of δ 3.2 ppm. A CH_2 directly attached to an oxygen has a chemical shift of about δ 3.5 ppm. A CH directly attached to an oxygen has a chemical shift of approximately δ 3.8 ppm. The chemical shift for being β (once removed) from an oxygen is about δ 1.9 ppm for a CH, δ 1.6 ppm for a CH_2, and δ 1.3 ppm for a CH_3. We will ignore the effect of an electronegative group for hydrogens on the γ carbon (twice removed).

(a)



	δ	#H	coupling
a	3.2	3	singlet
b	3.5	2	triplet
c	1.8	2	quartet (or doublet of triplets)
d	1.5	1	nonet (or triplet of septets)
e	0.9	6	doublet

(b)

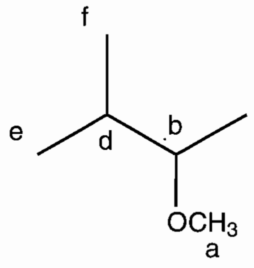


	δ	#H	coupling
a	3.2	3	singlet
b	1.8	2	quartet
c	0.9	3	triplet
d	1.3	6	singlet

(continued)

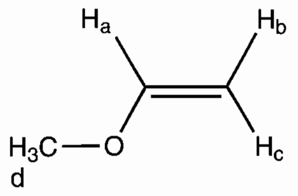
Problem 9.58 *(continued)*

(c) The methyl groups e and f are not equivalent because of the stereogenic carbon in the molecule. They are diastereotopic. Each will have a slightly different shift. The result is that the signal for H_d will be very messy.



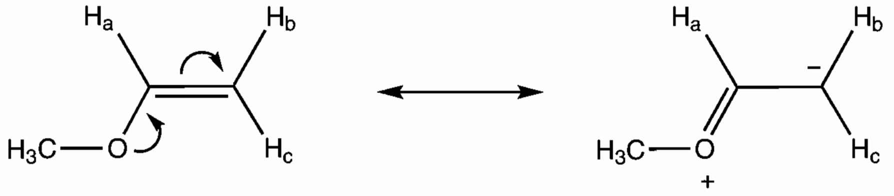
	δ	#H	coupling
a	3.2	3	singlet
b	3.8	1	quintet (or doublet of quartets)
c	1.3	3	doublet
d	1.9	1	multiplet
e	0.9	3	doublet
f	0.9	3	doublet

Problem 9.59 A vinyl hydrogen will have a chemical shift of about δ 5.5 ppm. In methoxyethene, the H_a vinyl hydrogen will also feel the effect of the directly attached oxygen. Therefore, the δ 6.4 ppm signal must belong to H_a. The coupling for H_a will be a doublet because of H_b and a doublet because of H_c. Because the coupling to each of those hydrogens will be different (trans coupling is larger than cis coupling), the signal will be a doublet of doublets.



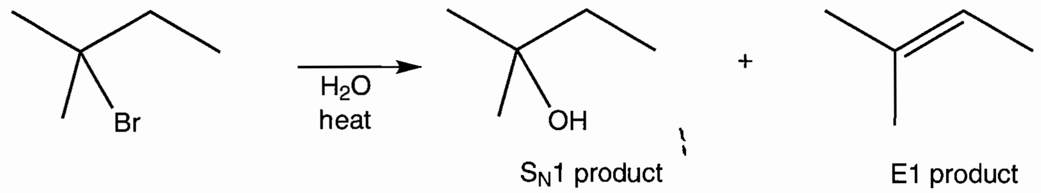
	δ	#H	coupling
a	6.4	1	dd (doublet of doublets)
b	3.9	1	d (with small coupling to H_c)
c	4.0	1	d (with small coupling to H_b)
d	3.2	3	singlet

A methyl group attached to an ether oxygen appears at δ 3.2 ppm. Therefore H_d will be at δ 3.2 ppm, and it will be a singlet because there are no hydrogens on the adjacent atom. The chemical shift for the H_b and H_c hydrogens will be upfield from the typical δ 5.5 ppm chemical shift of a vinyl hydrogen because the oxygen contributes electron density to the β carbon of the alkene (see the resonance structure). Therefore we expect these hydrogens to appear around δ 4.0 ppm.



Deciding which signal is H_b and which is H_c is not critical. The hydrogen that is cis to the oxygen might have a little more deshielding, but the difference is very small. We don't usually try to assign the chemical shifts of such hydrogens. This is why the question asks you to assign these signals "as accurately as possible." Both H_c and H_b will couple to H_a. So they will be doublets. A well-tuned high-field NMR will show the small coupling (J = ~ 1 Hz) between H_c and H_b.

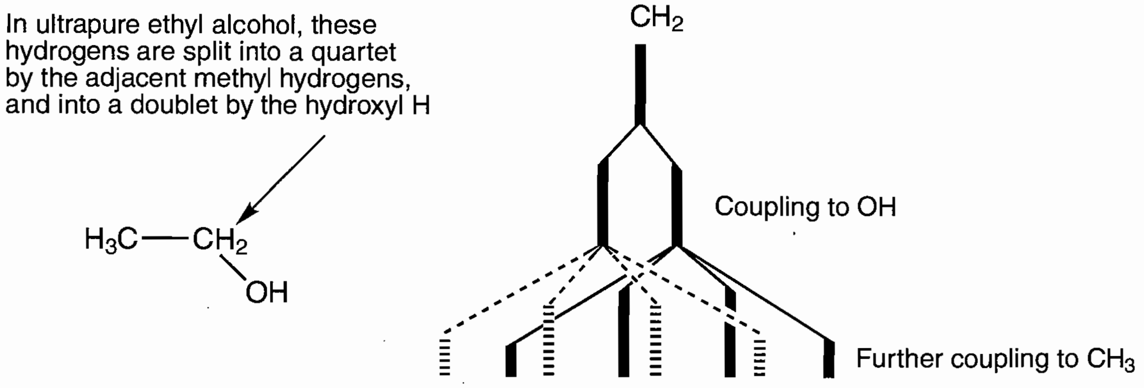
Problem 9.60



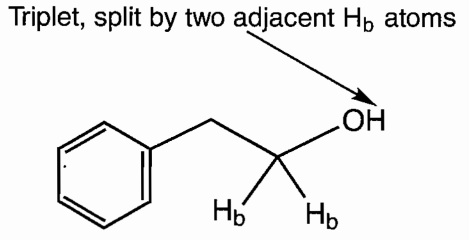
The ^1H NMR spectrum of the alkene product will have a vinyl hydrogen near δ 5.5 ppm. It will appear as a quartet. The alcohol product will have a CH_2 quartet near δ 1.8 ppm. There are other differences that can be used to distinguish these two products.

Problem 9.61 The four compounds, **A**, **B**, **C**, and **D**, divide into pairs. Compounds **B** and **D** have only one kind of hydrogen attached to the four-membered ring and thus must share structures 2 and 3. Compounds **A** and **C** have two kinds of ring hydrogen and thus share structures 1 and 4. Compound 2 is more polar than compound 3 and thus must have the cis OH groups (dipoles reinforce) and is **B**. Compound 3 must be **D**. Compound 4 is more polar than compound 1 and thus must be **C** with cis OH groups. By elimination, compound 1 must be **A**.

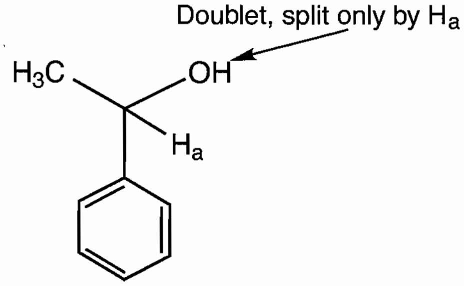
Problem 9.62 The figure shows the spectrum of ultrapure ethyl alcohol. The methylene group appears as a doublet of quartets (or, equivalently, a quartet of doublets).



Problem 9.63 The clue in this problem is the words “scrupulously dry.” Alcohols generally show no coupling of the OH hydrogens because of the rapid exchange catalyzed by small amounts of water. If essentially all the water is removed, one sees the first-order spectrum (p. 414). In **A**, we see a doublet, and there is only one hydrogen in either molecule that can appear as a doublet, the OH of 1-phenylethanol. The OH of the other molecule, 2-phenylethanol, appears as a triplet as it is split by the two equivalent adjacent methylene hydrogens, as in **B**.



Spectrum **B**, 2-phenylethanol



Spectrum **A**, 1-phenylethanol

When water is added, the acid-catalyzed exchange reaction effectively decouples the OH hydrogen from all adjacent hydrogens. The OH appears as an average signal, a broad singlet.

Problem 9.64 To distinguish between 3-pentanol and 3-chloropentane, one would need to look for the alcohol signal. There will not be any major difference in the chemical shifts of the other hydrogens. Sometimes the OH hydrogen is difficult to see in a ^{1}H NMR spectrum. To determine if the unknown material is an alcohol, you can (1) obtain the spectrum of your compound and then (2) add a drop of D_2O to your sample and obtain a second NMR spectrum of your compound. Now compare the spectra. If there are no significant shifts between the two, it is not an alcohol. If one of the signals shifts significantly (> 0.2 ppm), it is an alcohol.

To distinguish between 3-pentanol and 2-pentanol, look at the methyl signals. The 3-pentanol methyls will be 6H, δ ~0.9 ppm, triplet. The 2-pentanol methyls will be 3H, δ 0.9 ppm, triplet and 3H, δ ~1.2 ppm, doublet.

Problem 9.65 We use Equation (9.7) (p. 396), $\upsilon = \gamma B_o/2\pi$

for ^{1}H:

$\nu = (2.7 \times 10^8 \text{ rad T}^{-1}\text{s}^{-1})(4.7 \text{ T})/2(3.14 \text{ rad})$
$\nu = 2.02 \times 10^8 \text{ s}^{-1} = 200 \text{ MHz}$

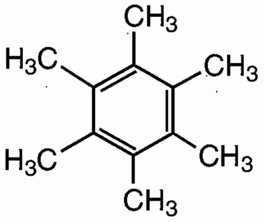
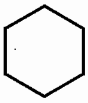
for ^{2}H:

$\nu = (0.41 \times 10^8 \text{ rad T}^{-1}\text{s}^{-1})(4.7 \text{ T})/2(3.14 \text{ rad})$
$\nu = 3.07 \times 10^7 \text{ s}^{-1} = 31 \text{ MHz}$

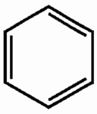
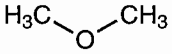
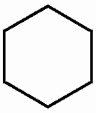
for ^{13}C:

$\nu = (0.67 \times 10^8 \text{ rad T}^{-1}\text{s}^{-1})(4.7 \text{ T})/2(3.14 \text{ rad})$
$\nu = 5.01 \times 10^7 \text{ s}^{-1} = 50 \text{ MHz}$

Problem 9.66 This problem should be especially easy.

	A	**D**	**B**	**E**	**C**
δ	7.3	2.25	1.42	0.90	0.04
				$C(CH_3)_4$	$(H_3C)_3Si{-}Si(CH_3)_3$
	"Aromatic hydrogens" are especially downfield	Benzylic methyl groups	Normal methylene group	Normal methyl group	Like TMS, these methyl hydrogens are far upfield

Problem 9.67

	A	**B**	**C**	**D**
δ	128.5	59.7	26.9	− 2.9
				
	Carbons on aromatic ring are sp^2 hybridized	Carbons attached to oxygen are deshielded and appear downfield	Normal methylene carbon	Cyclopropane carbons are upfield

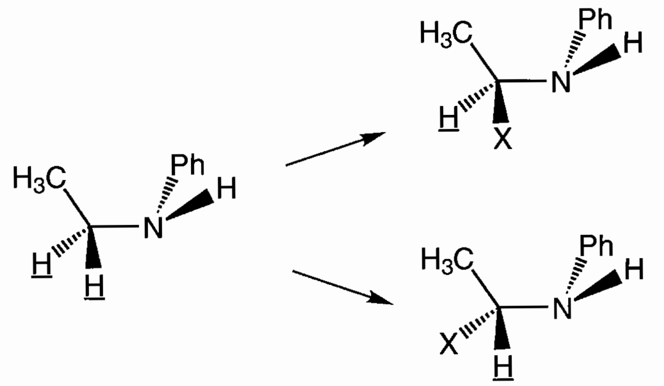
Problem 9.68 Oxygen is more electronegative than nitrogen and will withdraw electrons more effectively, making the adjacent carbon more electron deficient (greater δ^+). All other effects being more or less equal, the adjacent hydrogens are more shielded in the amines than they are in the alcohols and will appear at higher field.

The smaller dipole means that the hydrogens are more shielded than in the alcohols. They will appear upfield of the CH_2–O.

The greater dipole means that the hydrogens are deshielded more than the amines. They will appear downfield of the CH_2–N.

Problem 9.69 The two hydrogens are diastereotopic, and thus there should be two signals. Use the technique first outlined on page 401. To see how many signals should appear, replace each in turn with an "X" and see what the relationship is between those two hypothetical compounds.

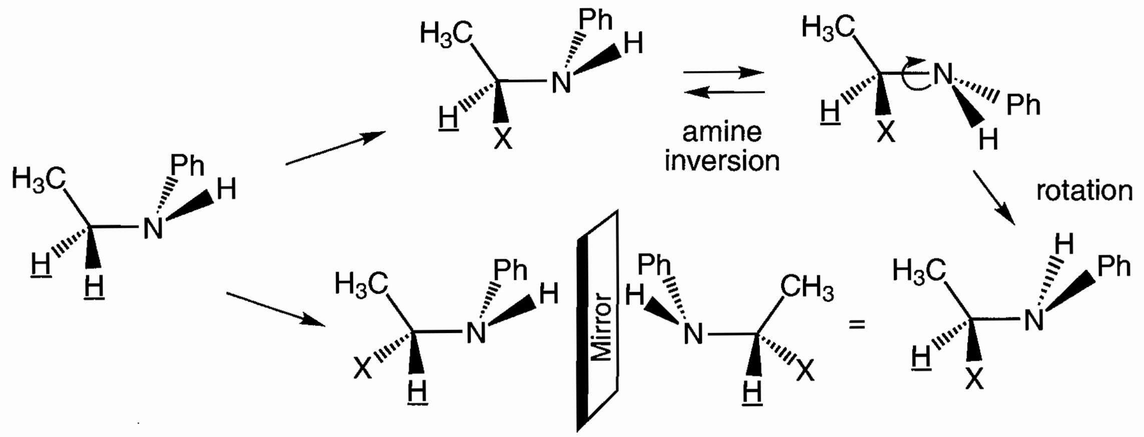
1



These are stereoisomers, but not mirror images; these two molecules are diastereomers. The two hydrogens replaced with "X" are diastereotopic, and must give different signals in the NMR spectrum.

If we obtain the NMR spectrum of compound **1** at room temperature, which is the normal temperature for an NMR experiment, we find that the underlined hydrogens are equivalent. The reason for this observation is that the amine undergoes rapid inversion. The underlined hydrogens are no longer diastereotopic when there is rapid inversion of the nitrogen.

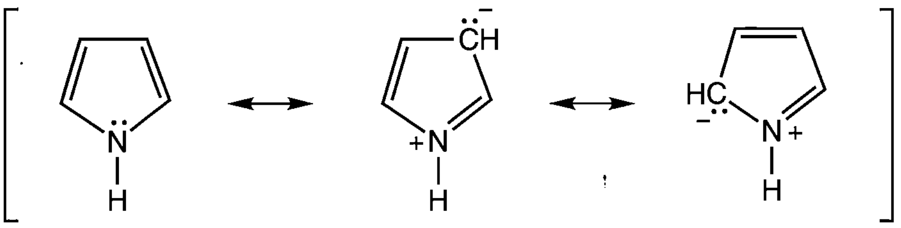
1



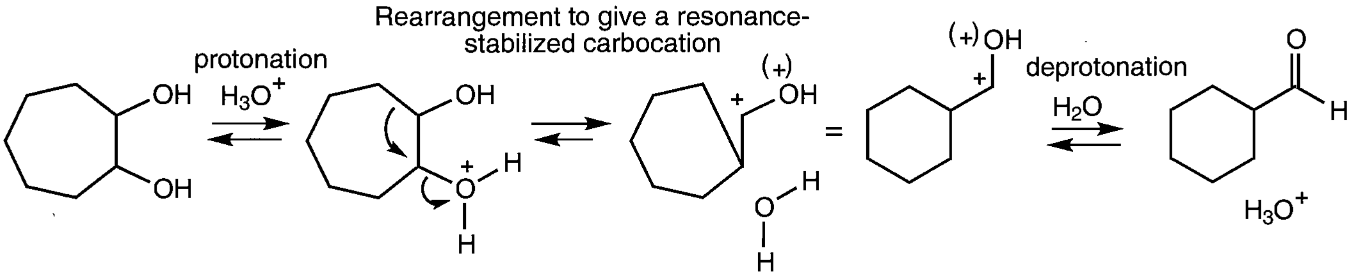
These are mirror images; these two molecules are enantiomers. The two hydrogens replaced with "X" are enantiotopic, and must give one signal in the NMR spectrum.

Problem 9.70 All of the hydrogens of cyclooctane appear as a single peak. This must mean that the hydrogens are equivalent. It is only possible if there is rapid conformational interconversion of the ring structure.

Problem 9.71 Not at all. Both kinds of ring carbon in pyrrole are partially negative. Those additional electrons will serve to shield nearby hydrogens and shift them upfield.

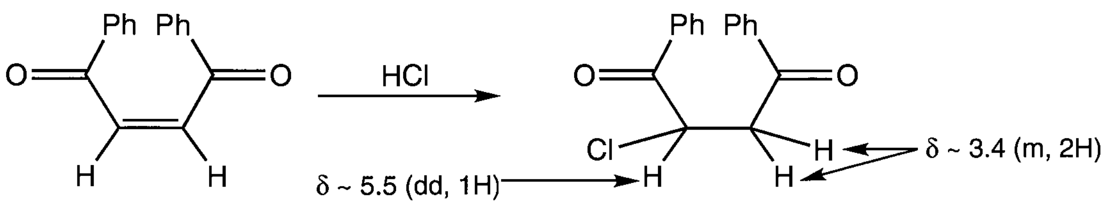


Problem 9.72 Vicinal (1,2) diols react in acid to give carbonyl compounds in what is called the pinacol rearrangement. If the 1,2-diol is cyclic, this reaction becomes a ring contraction process. The problem gives clues that an aldehyde is the product. Note the IR stretching frequency at 1729 cm^{-1} and the signal in the ^{1}H NMR spectrum at δ 9.5 ppm, a position diagnostic for aldehydes.

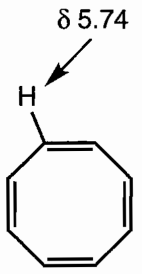


Problem 9.73 The assigned structure can't be correct. There is no hydrogen in the proposed structure that should absorb upfield of about δ ~ 7 ppm. This spectrum shows no fewer than three hydrogens upfield of this value. Indeed, one could also have pointed out that in the assigned structure there is no possible absorption for a single hydrogen. It's wrong.

Problem 9.74 Perhaps hydrogen chloride adds to the double bond of the proposed structure to give a chloride. If so, there should be a low-field dd exactly as appears in the spectrum. The lone hydrogen adjacent to the chlorine is split into doublets by the two different (diastereotopic) adjacent hydrogens of the methylene group. The new methylene group would be a complex multiplet, and the signal centered roughly at δ 3.4 ppm certainly qualifies for that description.

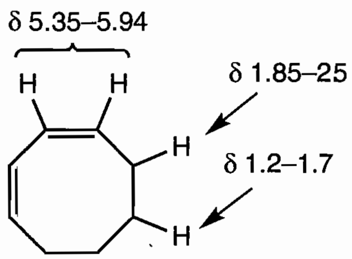


Problem 9.75 Compounds **A** and **B** should be easy because there are only single peaks. One, **B**, is in the range for hydrogens attached to a double bond, and the other, **A**, is in the range for saturated methylene groups. Compound **C** shows only two signals, one for the hydrogens attached to the double bonds, and the other for the allylic methylene groups. The last, most complicated spectrum must be **D**. The assignments follow.



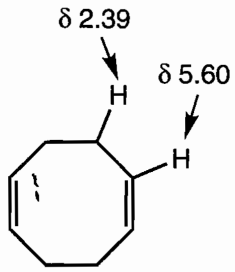
B

One hydrogen



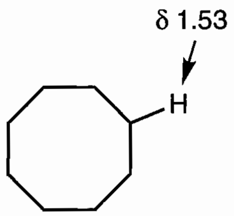
D

Four different hydrogens



C

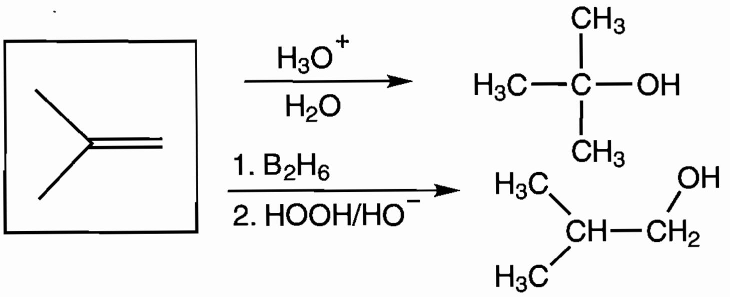
Two different hydrogens



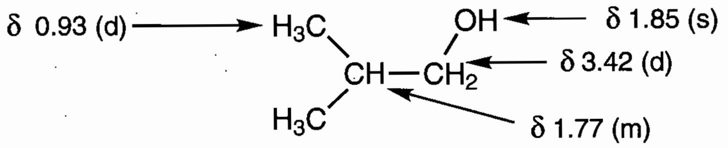
A

One hydrogen

Problem 9.76 Hydration gives the more substituted alcohol, in this case *tert*-butyl alcohol. The hydroboration–oxidation sequence gives the less substituted alcohol, in this case isobutyl alcohol.

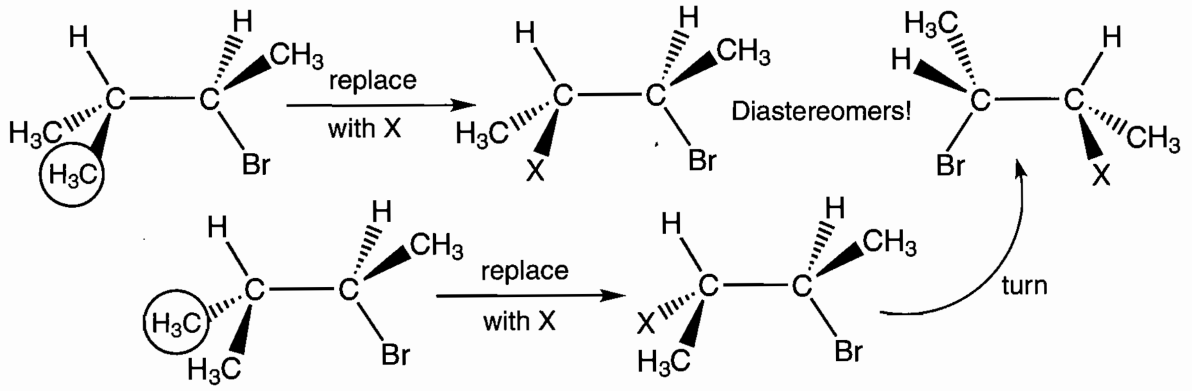


Spectrum **1** must be the more symmetrical *tert*-butyl alcohol. The hydroxyl hydrogen appears at δ 1.61 ppm and the nine methyl hydrogens at δ 1.28 ppm. The more complicated spectrum is that of isobutyl alcohol. The assignments are as follows:

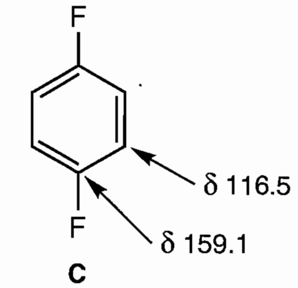


Addition of D_2O will replace the OH hydrogens with D and make HOD. The peak for the ROH hydrogen will become a peak for the HOD hydrogen, which will appear at a different chemical shift.

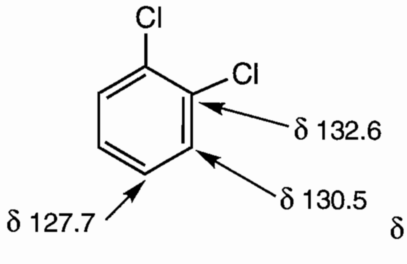
Problem 9.77 These methyl groups are diastereotopic. Use the "replacement technique" to see this. The two methyl groups are different, and each will give rise to a separate doublet signal.



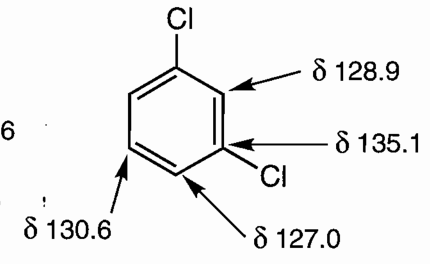
Problem 9.78 This problem should also be easy. There is no need to think about complete assignments of the signals. Instead one takes advantage of symmetry. 1,4-Difluorobenzene has only two different carbons and must have spectrum **C**. Similarly, 1,2-dichlorobenzene has three different carbon atoms and must have spectrum **B**. The remaining isomer, 1,3-dichlorobenzene, has four different carbons and must have spectrum **A**. The complete assignments are shown, but symmetry alone is enough to make the structural assignments.



C

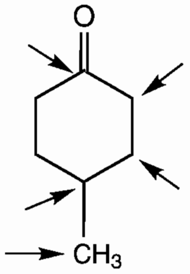


B

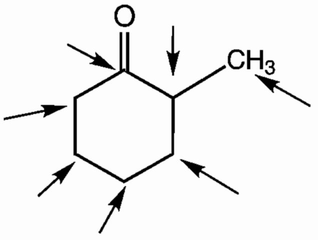


A

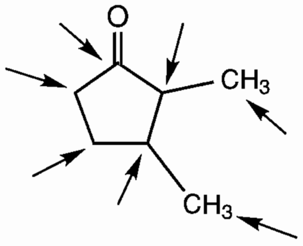
Problem 9.79 How far can we get using symmetry? The answer is "somewhere, but not all the way." We can tell which isomer is 4-methylcyclohexanone, but that's all. 4-Methylcyclohexanone has only five different carbons, whereas both 2-methylcyclohexanone and 2,3-dimethylcyclopentanone have seven different carbons. We can tell which isomer is 4-methylcyclohexanone, but we can go no further than this.



Five signals



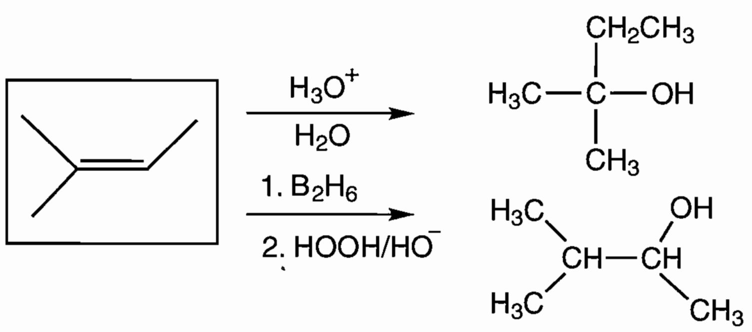
Seven signals



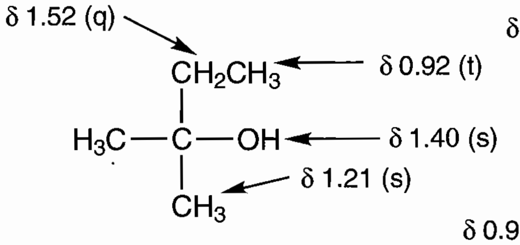
Seven signals

An examination of the hydrogen-coupled ^{13}C NMR spectra should allow us to distinguish the last two compounds. For example, 2-methylcyclohexanone will show one ^{13}C signal as a quartet, the methyl carbon attached to three hydrogens, whereas 2,3-dimethylcyclopentanone will show two such quartets.

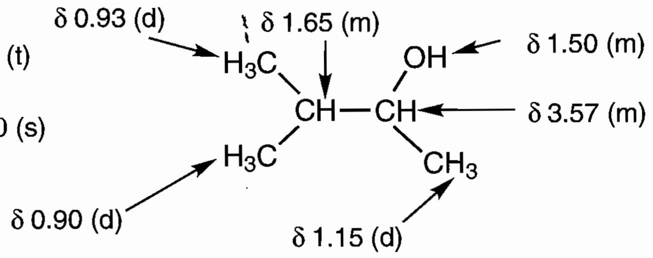
Problem 9.80 Hydration gives the more substituted alcohol, in this case 2-methyl-2-butanol. The hydroboration–oxidation sequence gives the less substituted alcohol, in this case 3-methyl-2-butanol.



The more symmetrical compound, 2-methyl-2-butanol, gives the simpler spectrum **1**. A critical point to notice is the six-hydrogen singlet for the two equivalent methyl groups. Note especially in spectrum **2** the downfield multiplet for the hydrogen adjacent to the oxygen atom.



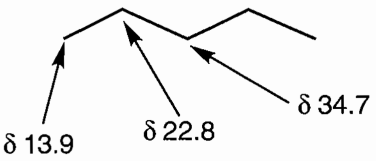
Spectrum **1**



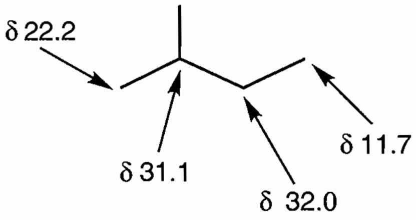
Spectrum **2**

Problem 9.81 The three isomers of pentane are pentane, isopentane, and neopentane. Neopentane is easy to assign, as it is the only isomer with only two different carbons. Isopentane has four different carbons and pentane three different carbons. So pentane is **A**, and isopentane is **B**. Note that it is not necessary in this case to be able to assign all the signals, just to count the numbers of different carbons. This practice is common for ^{13}C NMR spectra.

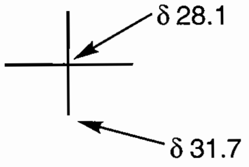
Pentane (**A**)



Isopentane (**B**)



Neopentane (**C**)



Problem 9.82 Isomer (b) shows a singlet for the two equivalent "aromatic hydrogens" and must be spectrum **1**. Isomer (a) shows two singlets for the two nonequivalent "aromatic hydrogens" and must be spectrum **2**. The other two isomers each show a typical AB quartet, but the spectrum for (c) is much more narrowly split than that for (d). Four-bond coupling is typically much smaller than adjacent, three-bond coupling. Compound (c) must have spectrum **3**, and compound (d) has spectrum **4**.

Problem 9.83

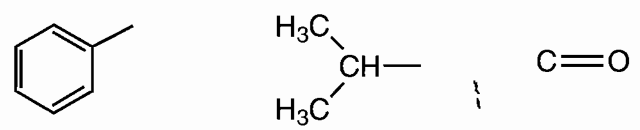
Compound A In this problem, we are given no information with which to determine the molecular formula. Although we have no elemental analysis data, we do have a mass spectrum, and this tells us the molecular weight of the compound, as the molecular ion is 148. We can also gain information from looking at the fragment ions, 105 and 77. These result from sequential losses of masses 43 (148 – 105) and 28 (105 – 77). At this point we can't be certain, but masses of 43 and 28 suggest C_3H_7 and CO, respectively.

The ^1H NMR spectrum shows five aromatic hydrogens (δ 7–8 ppm), and this in turn will surely make us think of a monosubstituted benzene. The septet integrating for a single proton looks very much like an "isopropyl" hydrogen [C$\underline{H}$(CH_3)$_2$], and its chemical shift implies that it is adjacent to an electronegative atom.

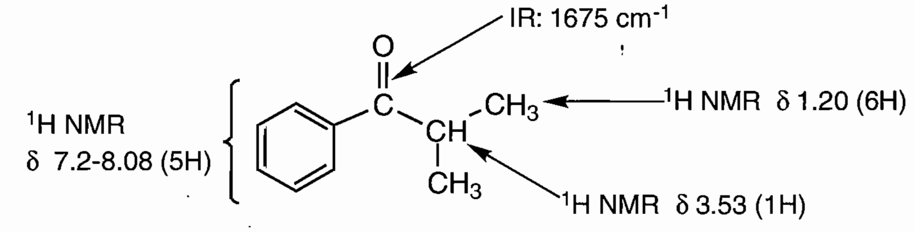
(continued)

Problem 9.83 *(continued)*

The IR spectrum shows a strong band at 1675 cm^{-1}, possibly a conjugated ketone, and is consistent with the loss of CO shown by the mass spectrum. Collecting the pieces leads to the following parts:



Do these parts add up to a molecule with a molecular weight of 148? Yes, just zip them together to give isobutyrophenone:

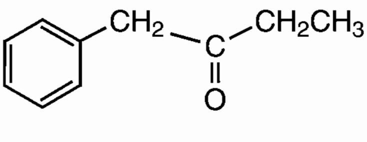


Note also that the mass spectrum becomes quite logical. If the isopropyl group is lost to give an acylium ion, we see loss of C_3H_7. Subsequent loss of CO leads to the fragment of molecular weight 77.

<u>Compound **B**</u> We know this molecule is isomeric with compound **A**, isobutyrophenone, so the formula is $C_{10}H_{12}O$. The IR spectrum shows a strong band at 1705 cm^{-1}, at substantially higher frequency than the carbonyl stretch of compound **A** and indicative of an unconjugated carbon–oxygen double bond. The ^{1}H NMR spectrum shows five "aromatic" hydrogens, and so a mono-substituted benzene ring is apparently present, as in compound **A**. The combination of an upfield triplet (3H) and a somewhat downfield quartet (2H) is always strongly suggestive of an ethyl group (CH_2CH_3). There is also an uncoupled 2H signal.

Now we can put the pieces together:

The combination is benzyl ethyl ketone:

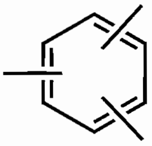


Problem 9.84 We have the formula $C_{11}H_{12}O_4$, so the first task is to work out the number of degrees of unsaturation (Ω) for **A** and **B**.
In this case,

$\Omega = [2(11) + 2 - 12]/2 = 6$

Six degrees of unsaturation strongly suggests the possibility of a benzene ring.

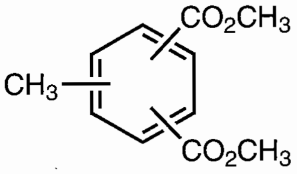
This surmise is supported by the ^{1}H NMR spectra. The ^{1}H NMR spectra for both compounds **A** and **B** are similar in several respects. Both spectra exhibit three aromatic hydrogens and three uncoupled methyl signals. Two of the methyl groups appear at about δ 3.9 ppm, indicating that they are attached to an electronegative substituent (for example, oxygen). The other methyl group appears at about δ 2.5 ppm, suggesting attachment to a carbonyl group or the benzene ring. At the very least, we might surmise that compounds **A** and **B** are trisubstituted benzene derivatives; that is,



The IR spectra of compounds **A** and **B** reveal the presence of an ester group as indicated by a strong carbonyl stretch at 1720 cm^{-1} and an intense C—O stretch at 1240–1245 cm^{-1}. The relatively low-frequency position of the carbonyl absorptions suggests the possibility of conjugation. Now let's do an atom inventory to see where we are:

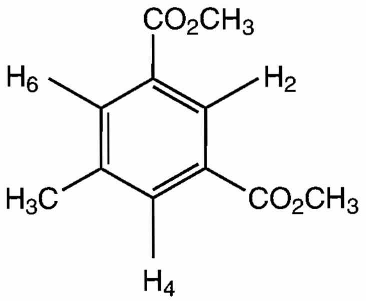
$C_{11}H_{12}O_4$	Formula
$-C_6\ H_3$	Trisubstituted benzene ring
$-C_3\ H_9$	Three methyl groups
$-C\ \ O_2$	One ester
$C\ \ O_2$	Remaining

The presence of a residual CO_2 suggests the presence of a second ester group, accounting for the last degree of unsaturation. This result is also consistent with the presence of two low-field methyl groups in the ^1H NMR spectra of **A** and **B**. Putting all the structural fragments together gives trisubstituted benzenes, in which the three substituents are two methyl esters and a methyl group. The ^1H NMR aromatic resonances of compounds **A** and **B** can be used to deduce the exact substitution patterns.



<u>Compound **A**</u> Two of the aromatic hydrogens are identical and have a chemical shift of δ 8.05 ppm, whereas the other aromatic hydrogen appears at δ 8.49 ppm. The small 2-Hz coupling constant is indicative of meta coupling. The only possible arrangement of substituents with only meta coupling is dimethyl 5-methylisophthalate. Note that H_4 and H_6 are identical and are each adjacent to one ester group. The H_2 is adjacent to two ester groups and accordingly appears at the lower field.

^1H NMR ($CDCl_3$): δ 2.46 (s, 3H)
3.94 (s, 6H)
8.05 (d, $J = 2$ Hz, 2H)
8.49 (t, $J = 2$ Hz, 1H)



Dimethyl 5-methylisophthalate

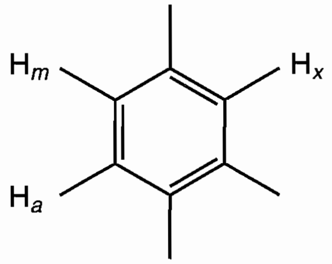
A

(continued)

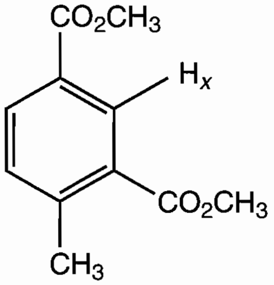
Problem 9.84 *(continued)*

Compound **B** The 8 Hz coupling constant is indicative of 1,2 coupling, whereas the 2 Hz coupling constant is appropriate for 1,3 coupling. This coupling pattern suggests a 1,2,4-trisubstituted benzene ring; that is,

^{1}H NMR (CDCl$_3$): δ 7.28 (d, J = 8 Hz, 1H) H$_a$
8.00 (dd, J = 8 Hz, J = 2 Hz, 1H) H$_m$
8.52 (d, J = 2 Hz, 1H) H$_x$



The aromatic hydrogen H$_x$, which exhibits only 1,3 coupling, is furthest downfield and should be flanked by both ester groups. Dimethyl 4-methylisophthalate is the only reasonable stucture for compound **B**.



Dimethyl 4-methylisophthalate

B

Problem 9.85 Our first task is to determine the molecular formulas of **A** and **B**. We can get the percentage of oxygen in the compounds by subtraction, and then work out the formula in the usual way.

C 63.15	100.00
<u>H 5.30</u>	<u>− 68.45</u>
68.45	31.55% O

C 63.15/12.01 = 5.26
H 5.30/1.01 = 5.25
O 31.55/16.00 = 1.97

C 5.26/1.97 = 2.67
H 5.25/1.97 = 2.66
O 1.97/1.97 = 1.00

$(C_{2.67}H_{2.66}O_{1.00}) \times 3 = C_{8.01}H_{7.98}O_{3.00}$

Empirical formula = $C_8H_8O_3$

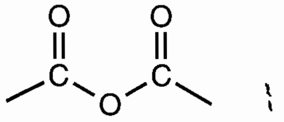
As we know the molecular weight from freezing point depression to be about 150 g/mol, we know that the empirical formula = molecular formula.

Second, let's work out the number of degrees of unsaturation, Ω. In this case,

$\Omega = [2(8) + 2 - 8]/2 = 5$

Although the presence of 5 degrees of unsaturation might suggest the presence of a benzene ring, the IR and NMR spectra of compounds **A** and **B** do not support this hypothesis, particularly in the case of compound **B**.

The presence of three oxygen atoms and two high-frequency carbonyl bands in the IR spectra of compounds **A** and **B** suggests the possibility of an anhydride; that is,



Two degrees of unsaturation

(A true IR maven would also recognize that the anhydrides are cyclic because the lower-frequency carbonyl band is more intense than the higher-frequency band.)

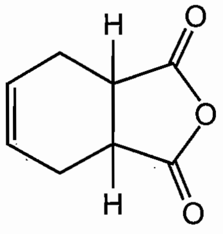
Now let's do an atom inventory:

$C_8H_8O_3$	Formula
$-C_2\ \ O_3$	Anhydride
C_6H_8	Remaining

There must be at least one carbon–carbon double bond (from the reaction that converts an alkene into an alkane), leaving 2 degrees of unsaturation unaccounted for, and suggesting the possibility of one or two rings. (Alternatively, a disubstituted alkyne and one ring could be present.)

The ^1H NMR spectra of compounds **A** and **B** should help with the structural assignments.

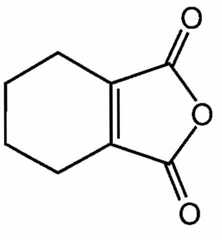
Compound **A** The ^1H NMR spectrum of compound **A** suggests the presence of two vinylic hydrogens (δ 5.65–6.25 ppm), two deshielded hydrogens (δ 3.15–3.70 ppm), possibly adjacent to the carbonyl groups, and four slightly deshielded hydrogens (δ 2.03–2.90 ppm), probably allylic. One possible way to join these fragments is shown. Note that the relative numbers of hydrogens given by the integral need to be multiplied by two to bring the hydrogen count to eight.



A

The 5 degrees of unsaturation are two carbonyl groups, one carbon–carbon double bond, and two rings. The type of ring juncture (cis or trans) is not obvious at this time.

Compound **B** The ^1H NMR spectrum of compound **B** shows the absence of vinylic hydrogens and the presence of four slightly deshielded hydrogens (δ 2.15–2.70 ppm)—possibly allylic—and four hydrogens with a "normal" aliphatic chemical shift (δ 1.50–2.10 ppm). It should also be noted that the carbonyl absorptions in the IR spectrum of compound **B** are about 15–20 cm^{-1} lower in frequency than those for compound **A**, indicating the possibility of conjugation. Putting all this information together suggests the following structure for compound **B**.

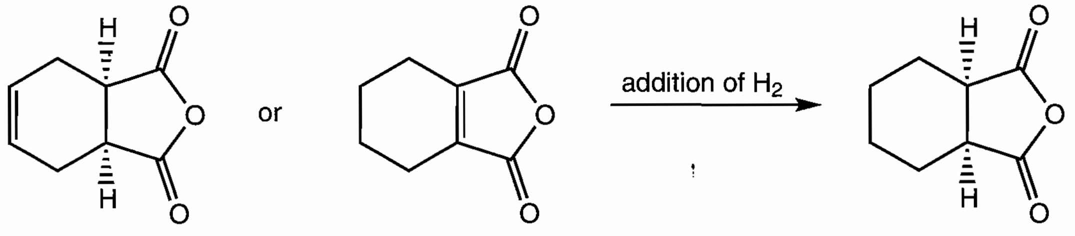


B

(continued)

Problem 9.85 *(continued)*

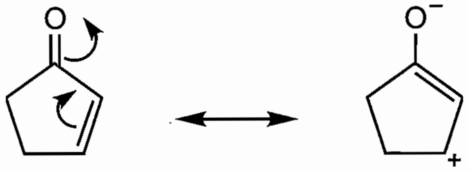
Compound C The reaction that converts an alkene into an alkane does so by adding hydrogens to the same face of the alkene. The experiments in this case imply that compound **C** is *cis*-1,2-cyclohexanedicarboxylic anhydride. This structure is consistent with the ^1H NMR spectrum, which exhibits eight hydrogens with a "normal" aliphatic chemical shift (δ 1.10–2.30 ppm) and two deshielded hydrogens (δ 3.05–3.55 ppm) adjacent to the carbonyl groups. Notice also that as **C** must have a cis ring juncture (from the reaction of **B**), then compound **A**, which gives **C**, must also have a cis ring junction.



A **B** **C**

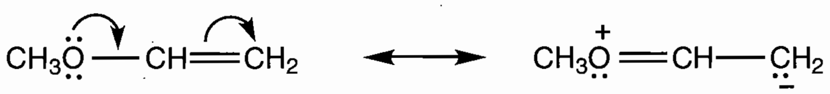
Problem 9.86

(a) The ^{13}C NMR chemical shift of the β carbon of α,β-unsaturated ketones such as **A** can be rationalized on the basis of the lower electron density at this position. The resonance formulation shows it well.



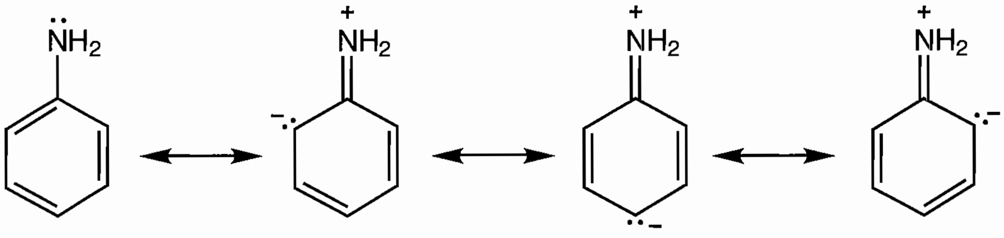
A

Similarly, the ^{13}C NMR chemical shift of the β carbon of vinyl ethers such as **B** occurs further upfield because of the greater electron density at this position.



B

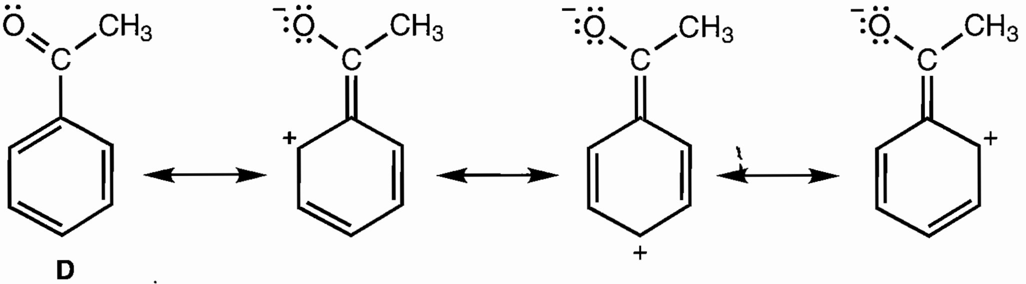
(b) The ^1H NMR chemical shifts of the ring hydrogens of aniline (**C**) can also be correlated by considering the appropriate resonance contributors.



C

Therefore, the C(2), C(4), and C(6) hydrogens of **C** appear at a higher field than the C(3) and C(5) hydrogens because of the greater electron density at these positions.

A similar treatment of acetophenone (**D**) would predict that the C(2), C(4) and C(6) hydrogens would be deshielded because of the lower electron density at these positions.



D

However, **D** shows only two deshielded aromatic hydrogens, not three, as predicted by this resonance argument. Clearly, there must be another factor (or factors) operating here. We already know that the hydrogens on a benzene ring are deshielded because of the induced field of the π ring current. The carbon–oxygen double bond in **D** also has an induced field of circulating π electrons. Because the carbonyl bond and the benzene ring of **D** are coplanar, the ortho protons lie in the deshielding zone of the adjacent carbonyl group. As a result, the two ortho protons are shifted further downfield than the other three ring protons. The ortho protons of **D** may also be inductively deshielded by the adjacent carbonyl group.

For chlorobenzene (**E**), the ^{1}H NMR chemical shifts of the aromatic protons can be rationalized by a consideration of inductive and resonance effects. In this case, these two effects, which oppose each other, are apparently roughly in balance. By contrast, in alkyl chlorides, the chlorine substituent is deshielding because only the inductive effect is operative, as there can be no resonance effect.

The ^{13}C NMR chemical shifts of **C** and **E** are, in general, consistent with the proton chemical shifts for these compounds. For example, note the upfield chemical shifts of C(2) and C(4) in aniline (**C**). Finally, note that the ^{13}C NMR chemical shifts for C(1) of compounds **C** and **E** are good indications of the inductive effect of the attached substituent.

Problem 9.87 First, let's determine the molecular formula for compound **1**.

C 81.76
H <u>10.98</u>
92.74

100.00
<u>–92.74</u>
7.26 %O

C 81.76/12.011 = 6.807
H 10.98/1.008 = 10.89
O 7.26/15.999 = 0.454

C 6.807/0.454 = 14.99
H 10.89/0.454 = 23.99
O 0.454/0.454 = 1.00

Empirical formula = $C_{15}H_{24}O$

Formula weight ($C_{15}H_{24}O$) = 220 g/mol

Because the mass spectrum of compound **1** displays a molecular ion with *m*/*z* = 220, the empirical formula equals the molecular formula.

Now, how many degrees of unsaturation are present?

$\Omega = [2(15) + 2 - 24]/2 = 4$

Four degrees of unsaturation suggests the possibility of a benzene ring, which accounts for all of the degrees of unsaturation.

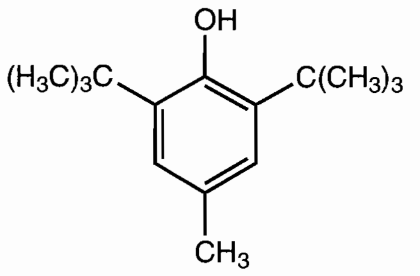
(continued)

Problem 9.87 *(continued)*

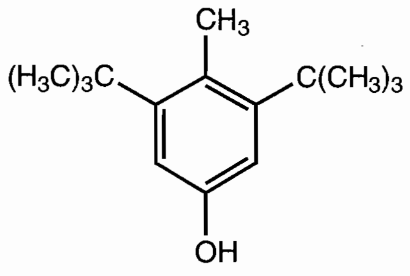
Next, examine the spectral data. The IR spectrum of compound **1** shows a sharp, medium-intensity band at 3660 cm^{-1}. The high frequency and sharpness of this absorption suggest the possibility of a "free" O—H stretch, that is, no hydrogen bonding. This information will prove to be particularly useful later on.

All 24 hydrogens are apparent in the ^1H NMR spectrum of compound **1**. However, there are only seven signals in the ^{13}C NMR spectrum, which indicates a reasonably high degree of symmetry. The 18H singlet at δ 1.43 ppm in the ^1H NMR spectrum of **1** is highly suggestive of two identical *tert*-butyl groups. This supposition is further supported by the singlet at δ 34.2 ppm and the quartet at δ 30.4 ppm in the ^{13}C NMR spectrum. The 3H singlet at δ 2.27 ppm in the ^1H NMR spectrum is indicative of a methyl group attached to the benzene ring. This methyl carbon dutifully appears as a quartet at δ 21.2 ppm in the ^{13}C NMR spectrum. The 1H singlet at δ 5.00 ppm in the ^1H NMR spectrum could be due to a phenolic hydrogen. Finally, the 2H singlet at δ 6.98 ppm in the ^1H NMR spectrum is consistent with two identical phenyl hydrogens. The doublet at δ 125.5 ppm in the ^{13}C NMR spectrum supports this assignment. It is also worth noting that there are only three other signals for the phenyl carbons, all of which are singlets. Also note the deshielded signal at δ 151.5 ppm, which corresponds to the phenyl carbon directly attached to the oxygen. Thus, compound **1** must be a tetrasubstituted benzene derivative with a high degree of symmetry.

Given the deduced structural fragments and the high degree of symmetry, there are really only two structures, **A** and **B**, that we need to consider for compound **1**.



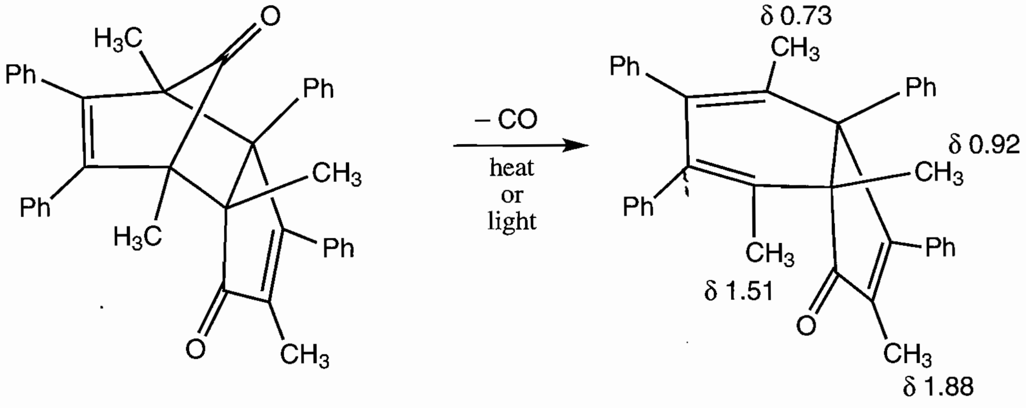
A



B

Both these structures would exhibit only seven signals in the ^{13}C NMR spectrum. Structure **A** appears to be the better candidate for at least two reasons. First of all, the phenyl hydrogens ortho to the OH group in structure **B** would be appreciably shielded in the ^1H NMR spectrum, as would the corresponding carbons in the ^{13}C NMR spectrum. (Why?) This is clearly not the case. Second, we return to the IR spectrum of compound **1**. Recall that the O—H stretch of **1** is quite sharp and appears at a very high frequency, suggesting the absence of hydrogen bonding. It is obvious that intermolecular hydrogen bonding involving the OH group would be sterically inhibited by the large *tert*-butyl groups in structure **A** but not in structure **B**. Thus, compound **1** is 2,6-di-*tert*-butyl-4-methylphenol, **A**, commonly called butylated hydroxytoluene (BHT), which is used as a stabilizer (antioxidant) at concentrations of 0.025% in solvents such as THF.

Problem 9.88 The loss of CO from compound **A** is similar to the elimination reaction we saw in Figure 8.46 (p. 359). The MS data confirm that there is loss of CO in going from **A** to **B**. Now we need to check to see if the spectral data are consistent with this proposed structure of compound **B**.



A (dimer) **B**

Ph– = C_6H_5– = phenyl–

<u>IR and NMR Spectra of Compound **B**</u> The presence of a band at 1704 cm^{-1} in the IR spectrum of compound **B** is consistent with the C═O stretch of a conjugated ketone. The ^1H NMR spectrum is also consistent with the proposed structure. For example, there are 20 aromatic hydrogens, which we expect from the four phenyl groups. There are four different methyl singlets as expected, but assigning the methyl signals is not going to be easy. Three of the methyl groups are allylic and should be about δ 1.7 ppm (see Table 9.5). The methyl group that is α to the ketone might be expected to be the furthest downfield of the four. So let's assign it as the δ 1.88 ppm. The upfield methyl ought to be the bridgehead methyl that isn't allylic. We can guess that it is at δ 0.73 or 0.92 ppm. The two remaining methyls look very similar, but one is at δ 1.51 ppm and the other at δ 0.92 or 0.73 ppm. The factor that we haven't included in our thinking is the way aromatic rings can influence signals of hydrogens that are forced to be near the center of the aromatic ring. Such hydrogens will be shifted upfield (p. 406) due to the ring current. The methyl group, pointing to the back of the structure as drawn above, is surrounded by three phenyl rings. Perhaps one of those rings is forced by steric constraints to be oriented so that the methyl group is in the center of the ring and shifted upfield. Using molecular modeling confirms that the allylic methyl is likely to be most shielded by the aromatic rings.

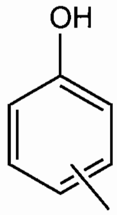
Problem 9.89 First, let's determine the molecular formula of compound **A**. From the mass spectral data, we know that compound **A** has a molecular weight of 152 g/mol. From the ^{13}C NMR spectrum, there must be a minimum of eight carbons. In addition, we know from the ^1H NMR spectrum that there are at least eight hydrogens. Any molecule of the formula C_8H_8 has a molecular weight of 104 g/mol, which leaves 48 g/mol unaccounted. The simplest fragments that could account for this missing mass are C_4 or O_3. As the IR spectrum of compound **A** suggests the presence of at least two oxygen atoms (the peak at 3205 cm^{-1} could be an O—H stretch and the peak at 1675 cm^{-1} could be a C═O stretch), let's assume that the missing fragment is O_3 and see where this leads. Therefore, the tentative molecular formula of compound **A** is $C_8H_8O_3$. Now let's work out the number of degrees of unsaturation:

$$\Omega = [2(8) + 2 - 8]/2 = 5$$

Five degrees of unsaturation suggests the possibility of a benzene ring. Compound **A** is soluble in 5% aqueous NaOH solution, but not in 5% aqueous $NaHCO_3$ solution. Carboxylic acids and phenols are strong enough acids to react with NaOH to yield water-soluble salts. However, unlike carboxylic acids, most phenols are too weakly acidic to undergo reaction with $NaHCO_3$. Thus, these solubility data suggest that compound **A** is a substituted phenol.

(continued)

Problem 9.89 *(continued)*



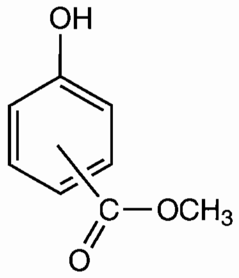
The presence of the broad peak at 3205 cm^{-1} in the IR spectrum of compound **A** is consistent with the O—H stretch of the proposed phenol. In addition, the presence of the strong band at 1675 cm^{-1} suggests the possibility of a C=O stretch, accounting for the last degree of unsaturation. The frequency of the carbonyl stretch further indicates that the carbonyl group is probably conjugated. What type of carbonyl group? An anhydride can be ruled out because of the absence of a second carbonyl stretch in the infrared; an aldehyde can be eliminated because of the absence of the C—H stretching doublet; and a carboxylic acid can be ruled out from the solubility data. These eliminations leave the possibility of either an ester or a ketone. There are several bands in the 1300–1100 cm^{-1} region of the IR spectrum that could be an ester C—O stretch. However, the ketone cannot be ruled out on this basis. (The ^{13}C NMR spectrum of compound **A** is very helpful in this regard, as we will see shortly.)

Now is a good time for an atom inventory.

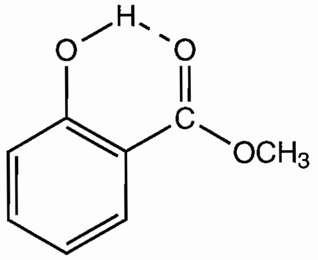
$C_8H_8O_3$	Formula
$-\ C_6$	Benzene ring
$-\ HO$	OH of phenol
$-\ C\ O$	Carbonyl group
$C\ H_7O$	Remaining

Now let's look at the proton and carbon NMR spectra of compound **A**. First of all, let's deal with the ketone versus ester problem. The carbonyl carbon of ketones (and aldehydes) has a ^{13}C NMR chemical shift in the δ 190–220 ppm range, whereas the carbonyl carbon of esters appears in the δ 150–180 ppm range. The ^{13}C NMR spectrum of compound **A** fails to show a signal for a ketone but does exhibit a singlet in the ester range (δ 170.7 or 162.0 ppm).

It is obvious from both the ^{1}H and ^{13}C NMR spectra of compound **A** that the remaining unassigned carbon (from the atom inventory) is a deshielded CH_3 group (the singlet at δ 3.92 ppm in the proton spectrum and the quartet at δ 52.1 ppm in the carbon spectrum). If we put all the structural fragments together, we obtain a methyl hydroxybenzoate; that is,

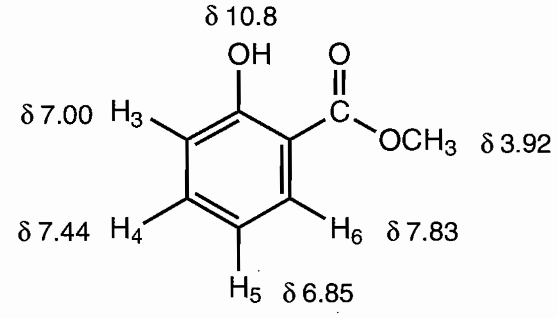


Note that this preliminary structure also accounts for the four aromatic hydrogens in the δ 6.85–7.83 ppm region of the ^{1}H NMR spectrum of compound **A**. Is compound **A** the 1,2 (ortho); 1,3 (meta); or 1,4 (para) isomer? There are several ways to approach this question; happily, all of them give the same answer. First, the IR spectrum of compound **A** shows a single aromatic C—H bending absorption at 757 cm^{-1}, which is indicative of an ortho-disubstituted benzene. Second, note that all four aromatic hydrogens in the δ 6.85–7.83 ppm region of the ^{1}H NMR spectrum show ortho coupling (J = 8 Hz). The only disubstituted isomer in which four different aromatic hydrogens all have at least one adjacent ortho proton is the ortho isomer. Finally, and more esoterically, the chemical shift of the phenolic O—H hydrogen in the ^{1}H NMR spectrum of compound **A** is very informative. The O—H hydrogen of phenols normally has a chemical shift of δ 4.0–7.5 ppm. However, an ortho carbonyl group shifts the phenolic hydrogen downfield to δ 10.0–12.0 ppm because of intramolecular hydrogen bonding. The phenolic hydrogen of compound **A** appears at δ 10.8 ppm. Thus compound **A** is methyl salicylate (methyl 2-hydroxybenzoate).



A

The ^{1}H NMR chemical shifts and coupling constants for compound **A** are summarized.

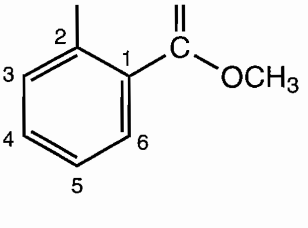


$J_{3,4} \sim J_{4,5} \sim J_{5,6} \sim 8$ Hz

A

The H(3) is shielded by the adjacent OH group and is split into a doublet by H(4). (Remember that J_{meta} and J_{para} were not observed at 300 MHz.) H(4) has a "normal" aromatic chemical shift and is split into a "triplet" by H(3) and H(5). H(5) is shielded by the para OH group and is split into a "triplet" by H(4) and H(6). Finally, H(6) is deshielded by the adjacent ester carbonyl bond and is split into a doublet by H(5).

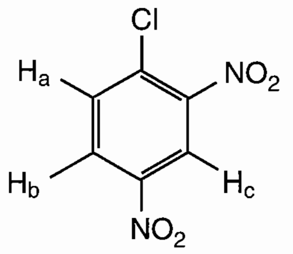
A tentative assignment of the ^{13}C NMR resonances of compound **A** is as follows:



δ 52.1(q) CH_3
112.7(s) C-1
117.7(d) C-3 (or C-5)
119.2(d) C-5 (or C-3)
130.1(d) C-6 (or C-4)
135.7(d) C-4 (or C-6)
162.0(s) C-2 (or C=O)
170.7(s) C=O (or C-2)

A

Problem 9.90

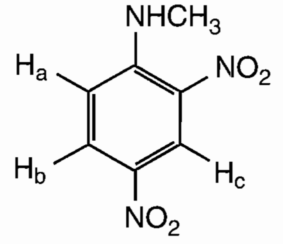


In the ^1H NMR spectrum for 1-chloro-2,4-dinitrobenzene (ignoring long-range 1,3 and 1,4 coupling),

H_a should appear around δ 7.5 ppm; it will not be strongly deshielded by the nitro groups that are 1,3 to H_a; H_a will be a doublet because there is only one vicinal hydrogen (H_b).

H_b should appear around δ 8.0 ppm because it will be deshielded by both nitro groups (resonance) and by the 1,2 nitro group (induction); H_b will be a doublet because it has only one vicinal hydrogen (H_a).

H_c should appear around δ 8.5 ppm because it will be strongly deshielded by both nitro groups as a result of resonance and induction and will be a singlet because there are no vicinal hydrogens.



In the ^1H NMR spectrum for *N*-methyl-2,4-dinitroaniline (ignoring long-range coupling),

H_a should appear around δ 7.0 ppm; it will be strongly shielded by the amine group that is 1,2. The nitro groups that are 1,3 to H_a will have little effect. H_a will be a doublet because it will "see" one vicinal hydrogen (H_b).

H_b should appear around δ 8.0 ppm because it will be deshielded by both nitro groups by resonance and by the ortho nitro group by induction. The 1,3 amino group will not have any effect; H_b will be a doublet because it "sees" one vicinal hydrogen (H_a).

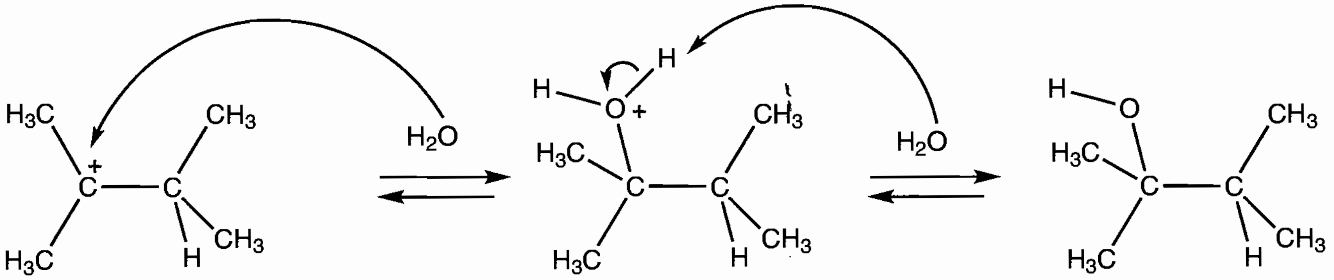
H_c should appear around δ 8.5 ppm because it will be strongly deshielded by both nitro groups as a result of resonance and induction; the 1,3 amino group will have no impact; H_c will be a singlet because there are no vicinal hydrogens.

The chemical shift for NH is difficult to predict, but adding D_2O to the NMR sample will cause the signal to be replaced by a DOH signal, which will have a different chemical shift; the NH will likely appear as a broad singlet.

NCH_3, the methyl group, will be about δ 2.5 ppm as a result of being attached to a nitrogen, and the aromatic ring will probably add to the downfield shift.

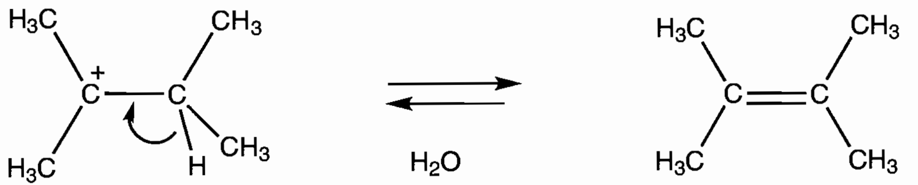
The biggest difference in the IR spectra of the starting material and the product will be the N—H stretch that will appear in the product around 3300 cm^{-1}.

Problem 9.91 The second carbocation in the reaction scheme is more stable because it is a tertiary carbocation. The reaction of that carbocation with water is shown here.



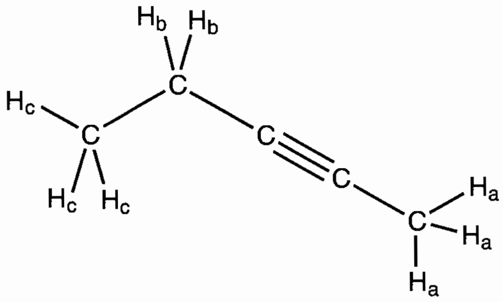
2,3-Dimethyl-2-butanol
(S_N1 product)

The major E1 product is 2,3-dimethyl-2-butene, and its ^1H NMR spectrum will be a singlet around δ 1.7 ppm. The ^1H NMR spectrum for 2,3-dimethyl-2-butanol will clearly be more complex. One could also use IR spectral data to differentiate between an alcohol and an alkene by looking for the broad band at 3400 cm^{-1} for the alcohol.



2,3-Dimethyl-2-butene
(E1 product)

Problem 9.92 Our first approximation for the ^1H NMR spectrum of 2-pentyne would be as shown in the table that follows. We can start by assuming that an alkyne will be much like an alkene. Therefore, the methyl hydrogens on C(1) would be about the same chemical shift as an allylic methyl (δ 1.7 ppm). The CH_2 group ought to be the same as an allylic methylene (δ 2.0 ppm), and the C(5) methyl might be about δ 1.0 ppm. If we limit our thinking to vicinal (three-bond) coupling, then we expect the coupling listed in our chart.



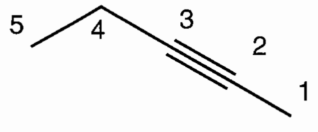
	δ	#H	coupling
a	1.7	3	s
b	2.0	2	q
c	1.0	3	t

(continued)

Problem 9.92 *(continued)*

Here are the actual ^{1}H NMR data for 2-pentyne: Ha (δ 1.77 ppm, 3H, t, J = 2.5 Hz), H_b (δ 2.13 ppm, 2H, quartet of quartets, J = 2.5, 7.3 Hz), H_c (δ 1.11 ppm, 3H, t, J = 7.3 Hz). We were close on the chemical shifts, but we missed the long-range coupling that is observed in alkynes. The five-bond coupling through an alkyne is an impressive long-range interaction. The J_{ab} varies from 2 to 3 Hz! So our H_a signal will actually be a triplet (J = 2.5 Hz) because H_a couples to the two H_b hydrogens. The H_b couples to the three H_a hydrogens (J = 2.5 Hz) and to the three H_c hydrogens (J = 7.3 Hz) so that it is a quartet of quartets.

There is much more guessing in predicting chemical shifts for the ^{13}C NMR for 2-pentyne because Table 9.6 has larger ranges and less specificity. We can guess that the methyl on the alkyne would be further downfield in the range of methyls (δ 0–30 ppm). The two alkyne carbons will be very similar, and we might as well pick the middle of the range (δ 70–90 ppm) for them. The methylene might be near the downfield limit of the methylene range (δ 15–55 ppm). The C(5) methyl will be near the starting point for a typical methyl, which is about 10 ppm. The coupling data will simply be a reflection of the number of hydrogens attached to each carbon and using the $n + 1$ rule.



	δ	coupling
1	30	q
2	80	s
3	80	s
4	50	t
5	15	q

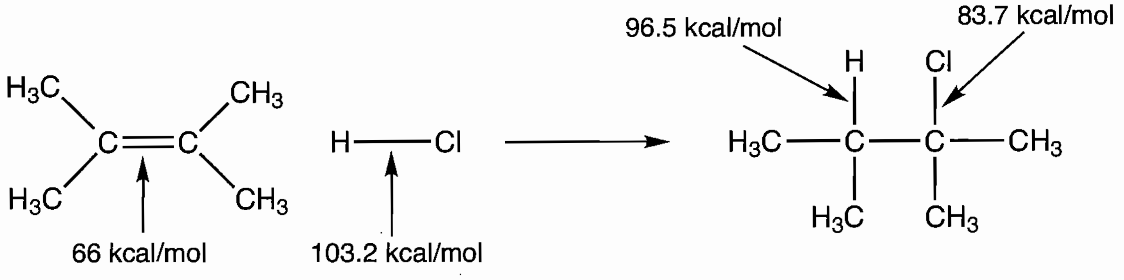
Here are the actual ^{13}C NMR data for 2-pentyne: C(1) δ 3.4 ppm, q; C(2) δ 74.8 ppm, s; C(3) δ 80.8 ppm, s; C(4) δ 12.6 ppm, t; C(5) δ 14.4 ppm, q. We were close enough on the chemical shifts, except for the C(1) and C(4). These signals must be shifted upfield because of the alkyne ring current (Fig. 9.42). The coupling was correct!

The only significant IR band would be the weak carbon–carbon triple bond stretch at ~2200 cm^{-1}. The mass spectrum would show a molecular ion at 68 because the molecular formula is C_5H_8.

10

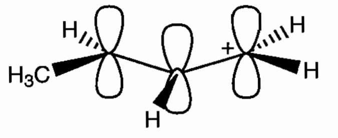
Electrophilic Additions to Alkenes

Problem 10.1 As always, our estimate of the exothermicity or endothermicity of the reaction is made by comparing the bond energies of the bonds broken and made in the reaction. In this case, the bonds broken are the π bond of the alkene and the σ bond of hydrogen chloride. The bonds made are the carbon–hydrogen and carbon–chlorine bonds in the product chloride.

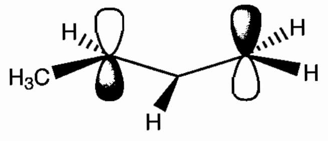


The bonds to be broken are worth 169.2 kcal/mol, but the bonds made are worth 180.2 kcal/mol. Accordingly, the reaction is exothermic by about 11 kcal/mol (180.2 – 169.2). $\Delta H \cong -11$ kcal/mol.

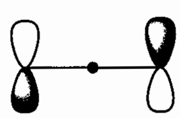
Problem 10.3 The orbital in Figure 10.12 that can accept electrons from a nucleophile is the lowest unoccupied molecular orbital (LUMO). It is the orbital shown below.



The orbitals involved in the mixing of this allylic cation



The LUMO for this molecule with all the atoms still shown

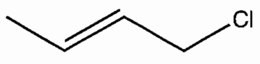


The LUMO of just the allyl system

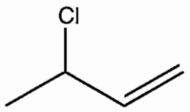
The reason the nucleophile reacts with the LUMO is that it is the most available empty orbital. The nucleophile can add to either end of the allylic system. If the nucleophile is chloride, for example, the product can be either 1-chloro-2-butene (chloride attacking the carbon on the right side of the LUMO shown above) or 3-chloro-1-butene (chloride attacking the carbon on the left side of the LUMO shown above).

(continued)

Problem 10.3 *(continued)*

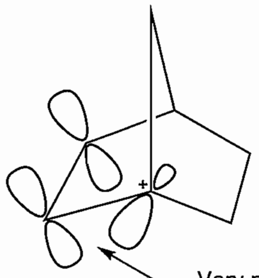


1-Chloro-2-butene



3-Chloro-1-butene

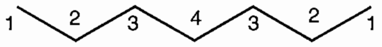
Problem 10.4 Here, *on paper*, the resonance double arrow is as correct as shown in the problem. However, geometry raises its ugly head, and there is really little or no overlap between the *p* orbitals making up this deceptive, "imitation" allylic system. Because there is no overlap, there is no real resonance.



Very poor overlap:
This is not a real allylic system

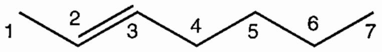
Problem 10.5

(a) ^{13}C NMR: Heptane has four unique carbons. The symmetry of heptane was covered in Chapter 2 (p. 92). There will be four signals in the ^{13}C NMR spectrum of heptane.



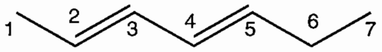
^{1}H NMR: Heptane has four hydrogen signals. The same symmetry applies to this molecule. The hydrogens on the carbons labeled 1 are equivalent. The hydrogens on the carbons labeled 2 are equivalent and different from the hydrogens on the carbons labeled 3. The methylene on carbon 4 is unique.

(b) ^{13}C NMR: (E)-2-Heptene has seven unique carbons. There will be seven signals in its ^{13}C NMR spectrum.



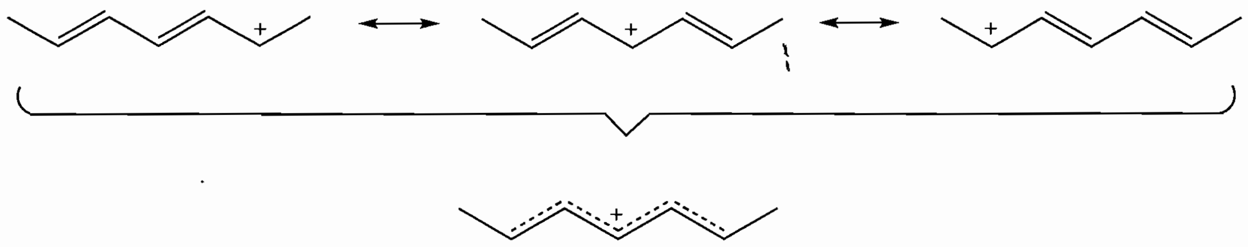
^{1}H NMR: There are seven different hydrogen signals in (E)-2-heptene. The hydrogens on each carbon are unique.

(c) ^{13}C NMR: (2E,4E)-2,4-Heptadiene has seven unique carbons. There will be seven signals in its ^{13}C NMR spectrum.



^{1}H NMR: There are seven different hydrogen signals in this molecule as well.

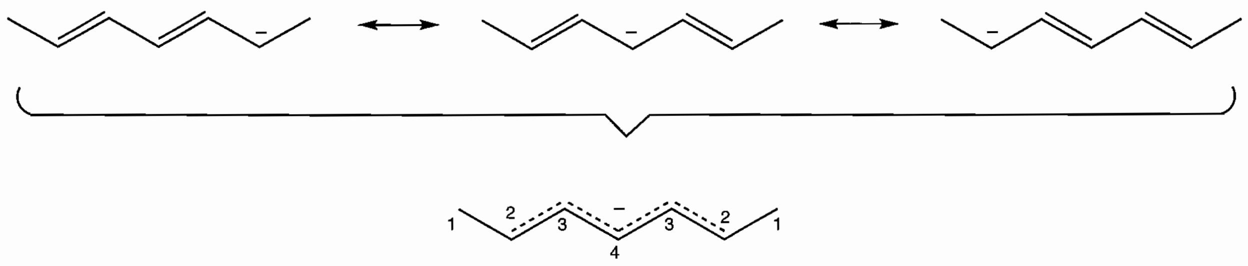
(d) ^{13}C NMR: This heptadienyl cation is a combination of three resonance structures. We can write a dotted line structure that represents all three resonance structures and allows us to see the symmetry in the molecule.



There are four unique carbons in this heptadienyl cation, therefore there will be four signals in its ^{13}C NMR spectrum.

^{1}H NMR: There will be four hydrogen signals in the ^{1}H NMR spectrum of this cation. There is a plane of symmetry through the central carbon. So the hydrogens on the left methyl group are equivalent to the hydrogens on the right methyl group. The hydrogen on the carbons numbered 2 are equivalent, as are the hydrogens on the carbons numbered 3. The hydrogen on the middle carbon is unique.

(e) ^{13}C NMR: The heptadienyl anion is also a combination of three resonance structures. We can write a dotted line structure that represents all three resonance structures and allows us to see the symmetry in the molecule. Again there are four unique carbons in this heptadienyl ion, therefore there will be four signals in its ^{13}C NMR spectrum.



^{1}H NMR: This structure also has four different hydrogens because of the symmetry in the molecule. The hydrogens on the left methyl group are equivalent to the hydrogens on the right methyl group. The hydrogen on the carbons numbered 2 are equivalent, as are the hydrogens on the carbons numbered 3. The hydrogen on the middle carbon is unique. There will be four signals in the ^{1}H NMR spectrum of this anion.

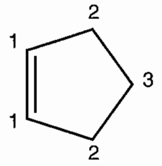
(continued)

Problem 10.5 *(continued)*

(f) ^{13}C NMR: The five carbons in cyclopentane are equivalent. There will only be one signal in its ^{13}C NMR spectrum.

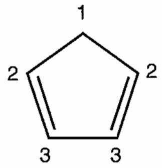
^{1}H NMR: There will only be one signal in the ^{1}H NMR spectrum of cyclopentane.

(g) ^{13}C NMR: Cyclopentene has three unique carbons. There will be three signals in its ^{13}C NMR spectrum.



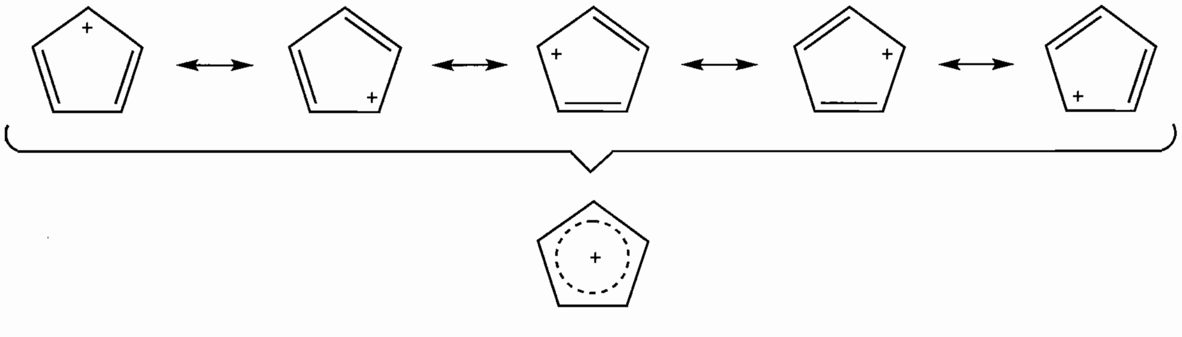
^{1}H NMR: There is a plane of symmetry in this molecule that allows us to see that the hydrogens on the double bond of cyclopentene are equivalent. The hydrogens on the carbons numbered 2 are equivalent to each other. The hydrogens on the carbon numbered 3 are unique. There are three signals in the ^{1}H NMR spectrum of cyclopentene.

(h) ^{13}C NMR: Cyclopentadiene also has three unique carbons. There will be three signals in its ^{13}C NMR spectrum.



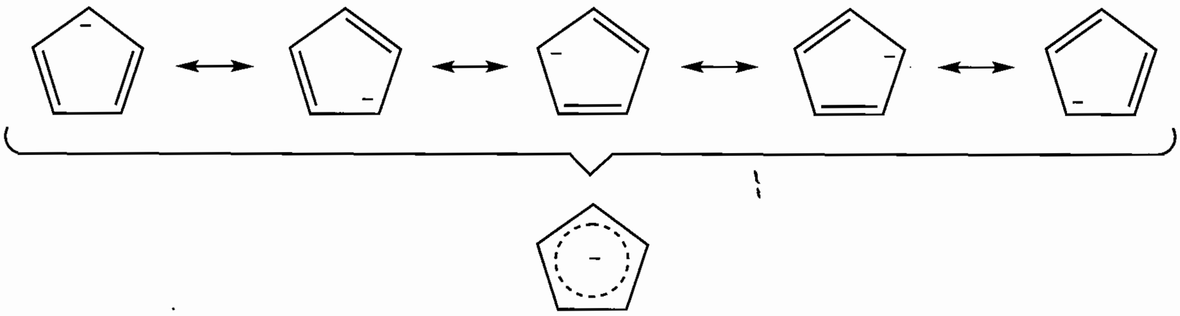
^{1}H NMR: There are also three signals in the ^{1}H NMR spectrum of cyclopentadiene.

(i) ^{13}C NMR: The cyclopentadienyl cation is very unstable, as we will see in Chapter 14. There are five resonance structures we can draw for this molecule. The composite structure shows that every carbon is equivalent in this cation. There would only be one signal in the ^{13}C NMR spectrum of the cyclopentadienyl cation.



^{1}H NMR: There would only be one signal in the ^{1}H NMR spectrum of this cation.

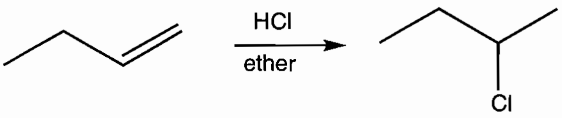
(j) ^{13}C NMR: The cyclopentadiene anion is a very stable anion, as we will see in Chapter 14. There are five resonance structures we can draw for this molecule. The composite structure shows that all five carbons are equivalent. There is only one signal in the ^{13}C NMR spectrum of the cyclopentadiene anion.



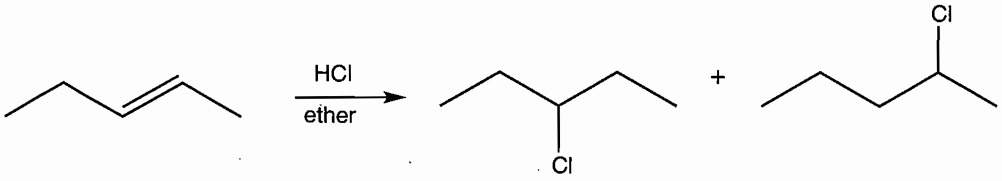
^{1}H NMR: There is only one signal in the ^{1}H NMR spectrum of the cyclopentadiene anion.

Problem 10.6 The answers for HCl are shown. The reactions will be the same with HBr, with the Br instead of the Cl in the product.

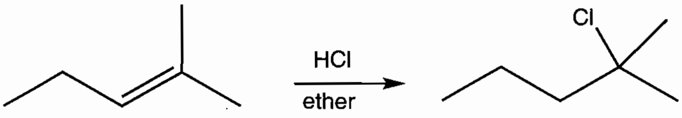
(a) The electrophile adds to the C(1) carbon, which forms the secondary carbocation. The chloride anion reacts with the cation to form 2-chlorobutane.



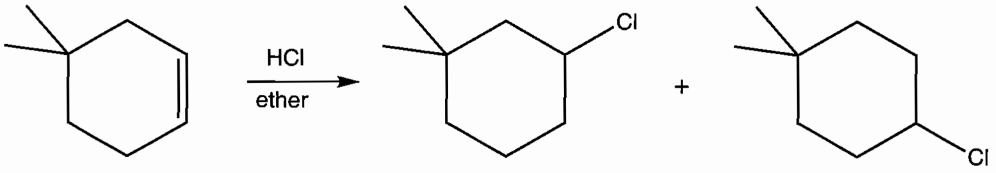
(b) The electrophile will add to either carbon of the alkene because the intermediate carbocation in both cases is a secondary carbocation. There will be no predictable preference. The chloride will capture whichever carbocation is formed and the ratio of the products will be close to 50:50.



(c) The electrophile adds to C(3) of 2-methyl-2-pentene. That forms the intermediate tertiary carbocation, which reacts with the chloride anion.



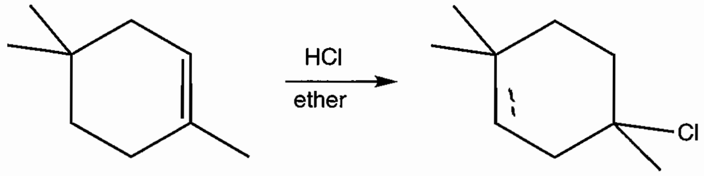
(d) Treatment of 4,4-dimethylcyclohexene with HCl could give several products. There are minor products that can arise from hydride shifts and even methyl shifts. 3-Chloro-1,1-dimethylcyclohexane and 4-chloro-1,1-dimethylcyclohexane would be the major products.



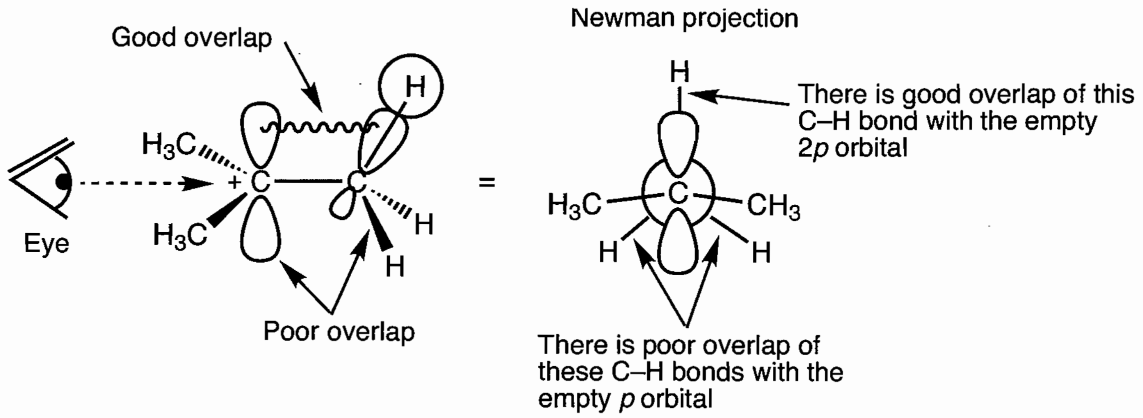
(continued)

Problem 10.6 *(continued)*

(e) 1,4,4-Trimethylcyclohexene reacts with the electrophile so that the tertiary carbocation is formed. The major product would come from chloride anion capturing the cation intermediate.



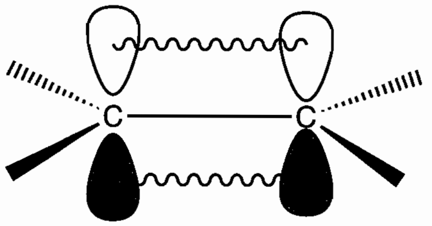
Problem 10.7 "Yes and no" might be the best answer. Certainly one can draw a resonance form for each carbon–hydrogen bond of the three methyl groups, making a total of nine. However, orbitals must overlap for there to be real delocalization. All nine carbon–hydrogen bonds cannot be properly lined up at the same time. A look at one methyl group makes the point.



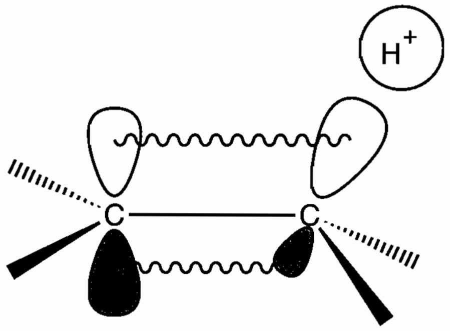
There is good overlap of this C–H bond with the empty 2*p* orbital

There is poor overlap of these C–H bonds with the empty *p* orbital

Problem 10.8 It is weaker. Overlap is less good, as the orbitals involved are not optimally lined up.

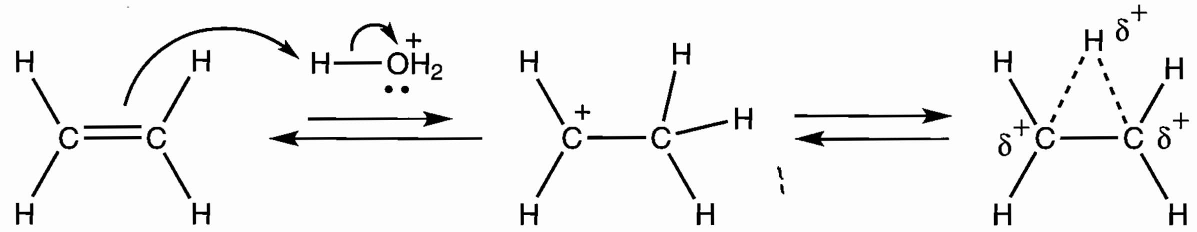


The π bond in ethylene is made up of 2*p*/2*p* overlap. The two 2*p* orbitals are parallel and overlap well



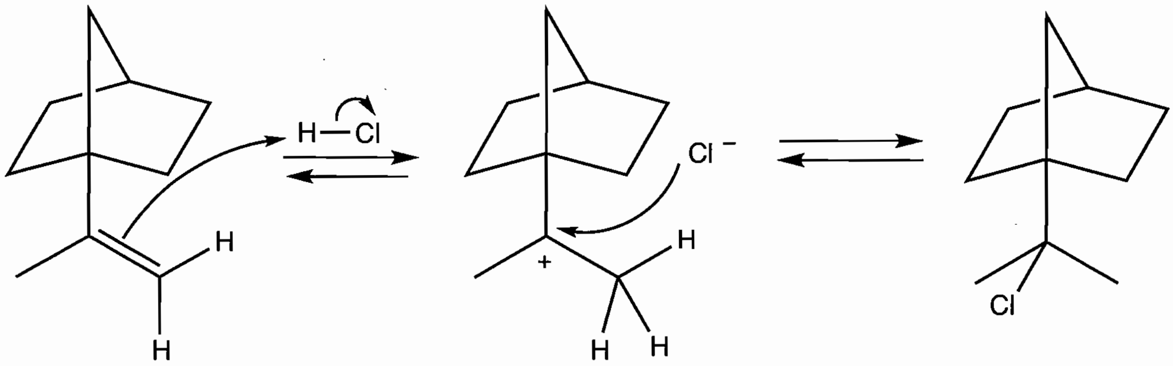
In the "hyperconjugative" resonance form for the ethyl cation, the "double" part of the double bond is not made up of 2*p*/2*p* overlap, but by 2*p*/*sp*^{3} overlap. These orbitals do not overlap as well as the two 2*p* orbitals, and the bond will be weaker

Problem 10.9 Protonation of ethylene must lead to a primary carbocation, a most unstable species. This reaction is very difficult due to the high energy of activation (recall the Hammond postulate, p. 351). In this very endothermic reaction, the transition state will resemble the product and therefore be very high in energy.

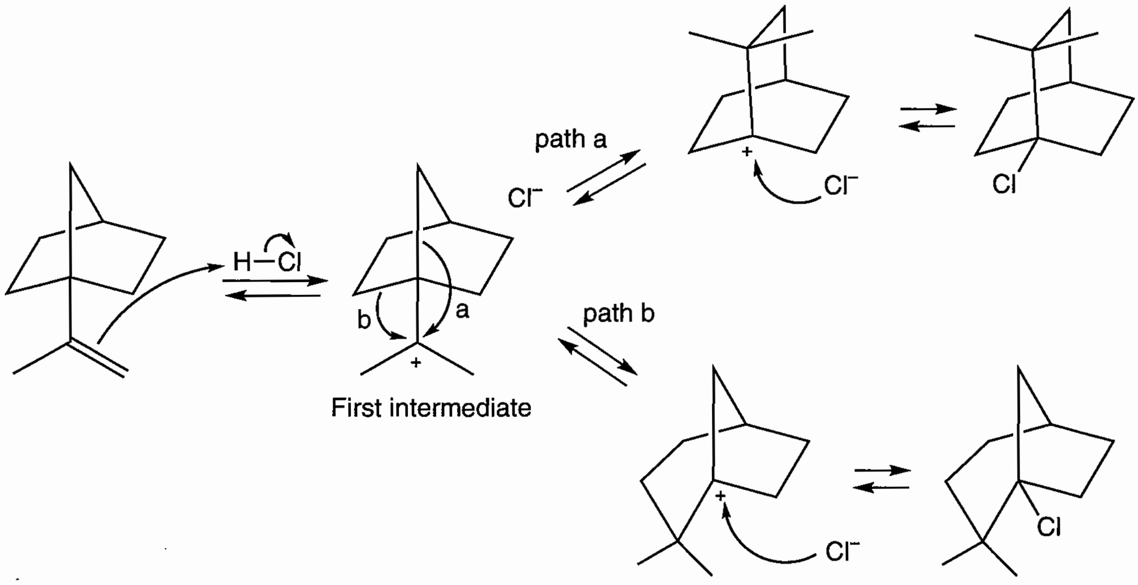


The structure that has the proton shared between the two carbons of ethylene is more stable because the positive charge is shared between three atoms.

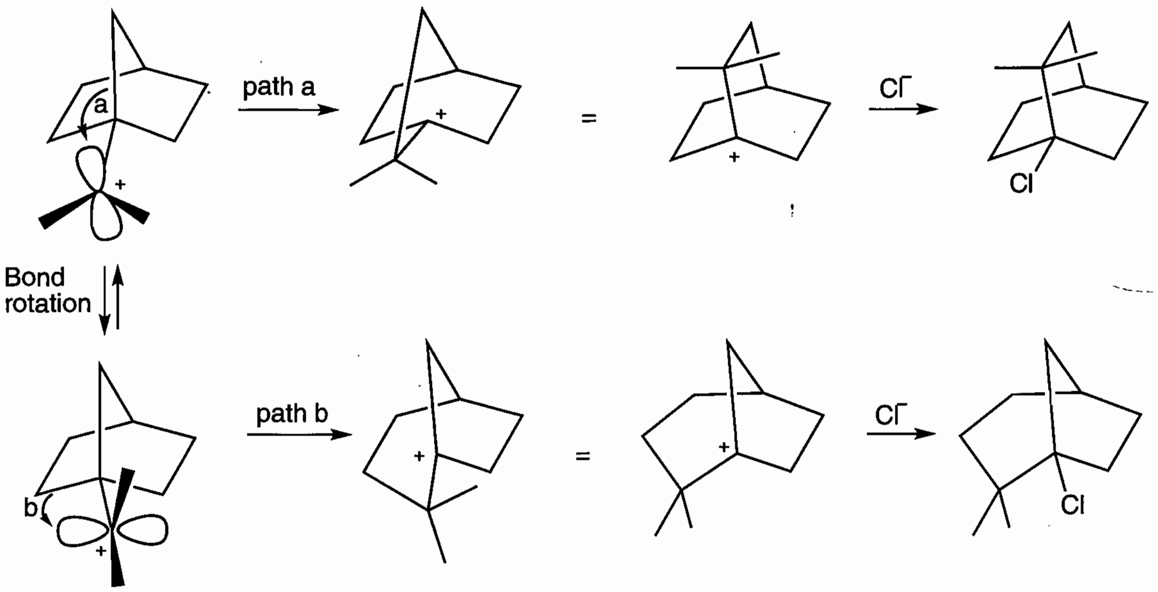
Problem 10.10 This reaction involves a carbocation intermediate. We have seen the same intermediate in Problem 8.15 (p. 355). The initial tertiary carbocation that is formed can be captured by the chloride ion to give the first product listed. The hydrogens on the alkene (vinylic hydrogens) are shown in the first step for clarity.



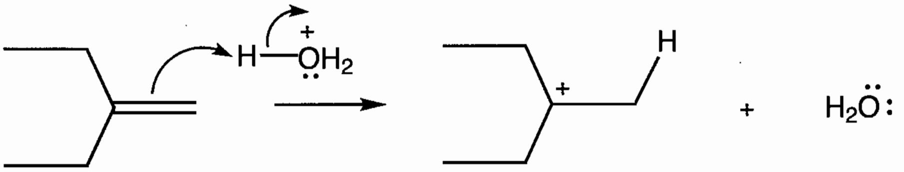
As we saw in Problem 8.15, the cation can also undergo rearrangement. Notice that there is symmetry in the first intermediate. Migration of either of the two different carbons attached to the carbon adjacent to the carbocation will result in two different tertiary carbocation intermediates. Reaction between either of those new carbocations and chloride ion will lead to the other two products listed.



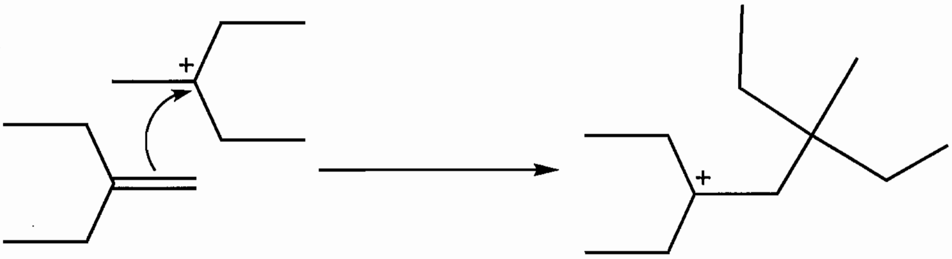
Problem 10.11 It is the orientation of the empty *p* orbital (the electrophile) that determines the product outcome. If the empty *p* orbital is aligned with the one carbon bridge (path a), the shift that occurs will give rise to the bicyclo[2.2.2]octane framework. Path b will occur if the *p* orbital is aligned with either of the two-carbon bridges. That path will give rise to the bicyclo[3.2.1]octane intermediate. These intermediate carbocations will react with the chloride nucleophile to form the products that are shown.



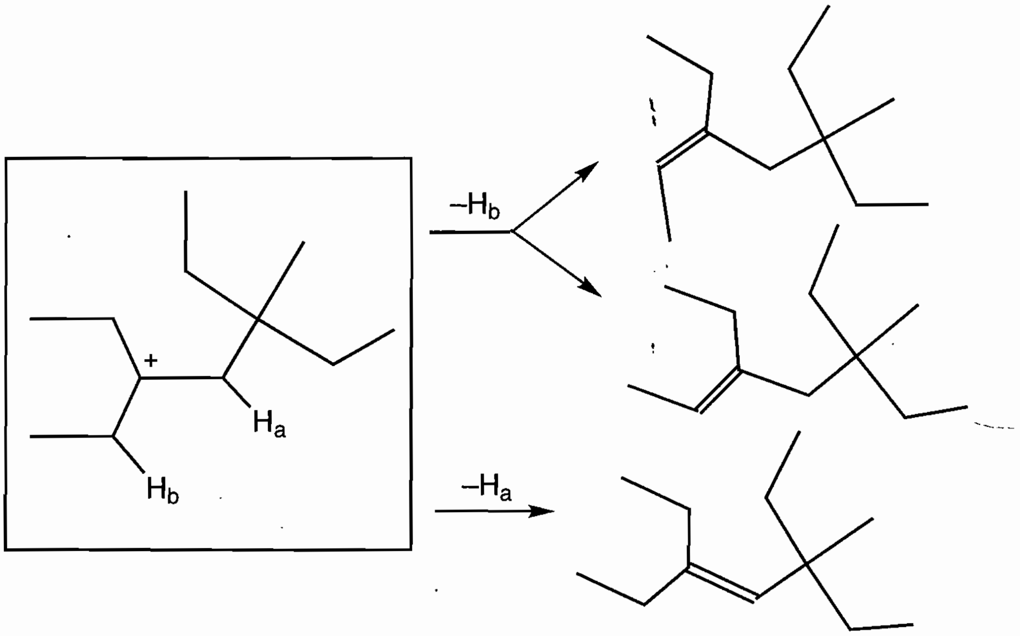
Problem 10.12 Protonation of 2-ethyl-1-butene takes place to give the more stable, tertiary carbocation rather than the less stable primary carbocation.



The tertiary carbocation can add to another alkene, again producing the more stable tertiary carbocation.

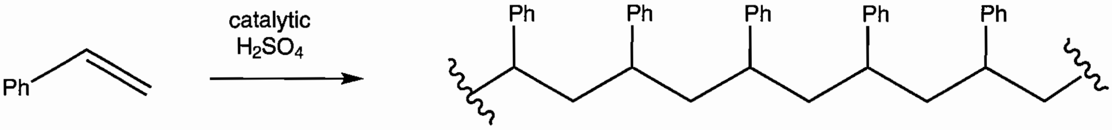


There are three different products that can be formed by loss of a proton from this new cation:

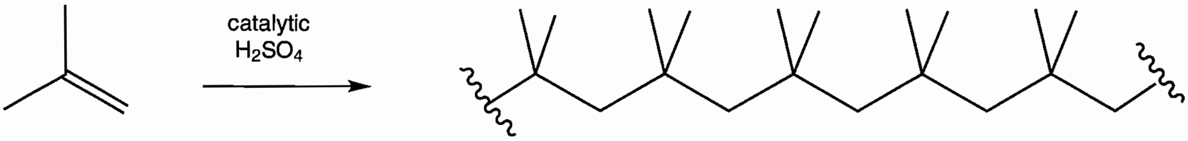


Problem 10.13

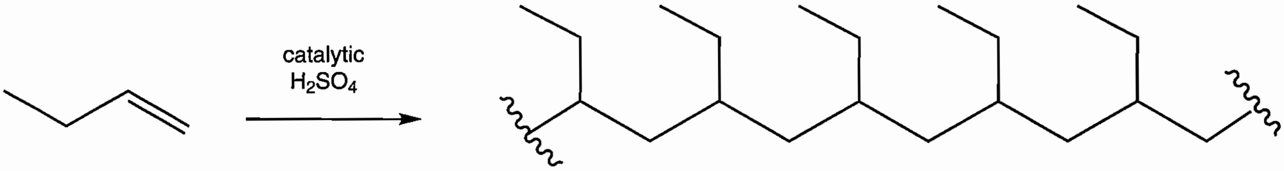
Polystyrene



Polyisobutylene



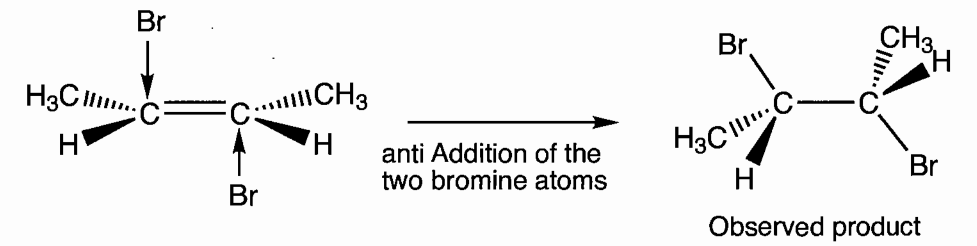
Polybutylene

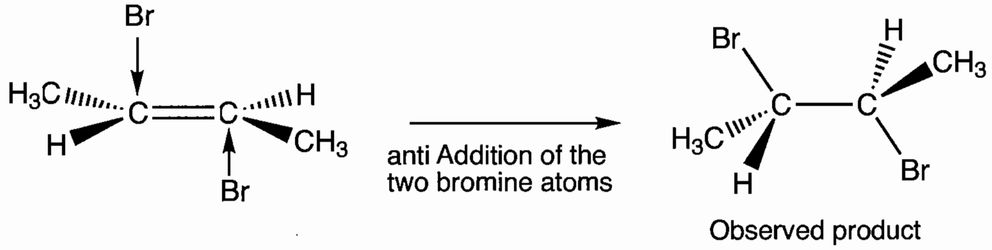


Problem 10.15 Boron has five positive charges in its nucleus. The boron in BH_3 has two electrons in its 1*s* orbital and three electrons involved in the bonds to the three separate hydrogens. Therefore, the five electrons that boron has as its own, balance the five protons in its nucleus. The boron in R—BH_3 has four electrons involved in bonds, which means the boron has six electrons that it senses as its own (two in the 1*s* orbital and four from the bonds). Therefore, the boron will have a formal charge of -1.

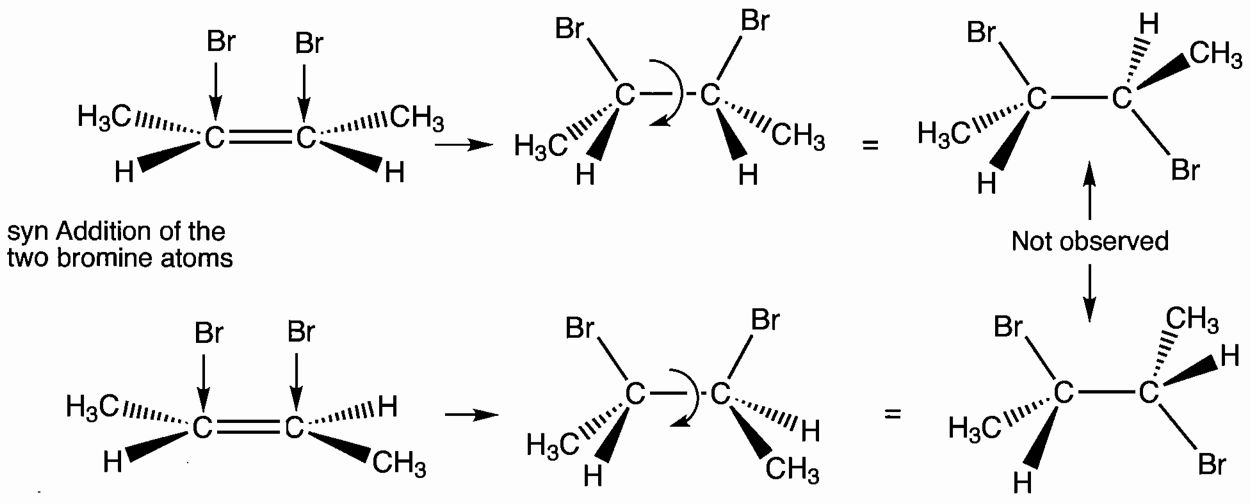
The boron in BH_3 (or BF_3) is sp^2 hybridized because it only has three bonds and no lone pairs of electrons. This hybridization is the lowest energy arrangement of orbitals for an atom with three bonds and no lone pairs. It maximizes the distance between the electrons around the central atom.

Problem 10.18 This is not a mechanistic question; it only asks from which direction (top or bottom) the two bromines attach. In this case, the structures of the products make it clear that one bromine comes from the "top" and the other from the "bottom," in what is called anti addition.

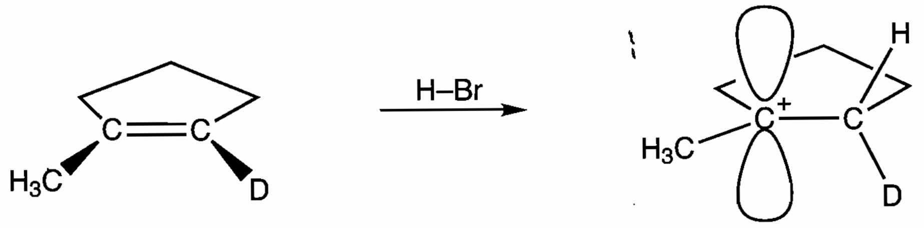




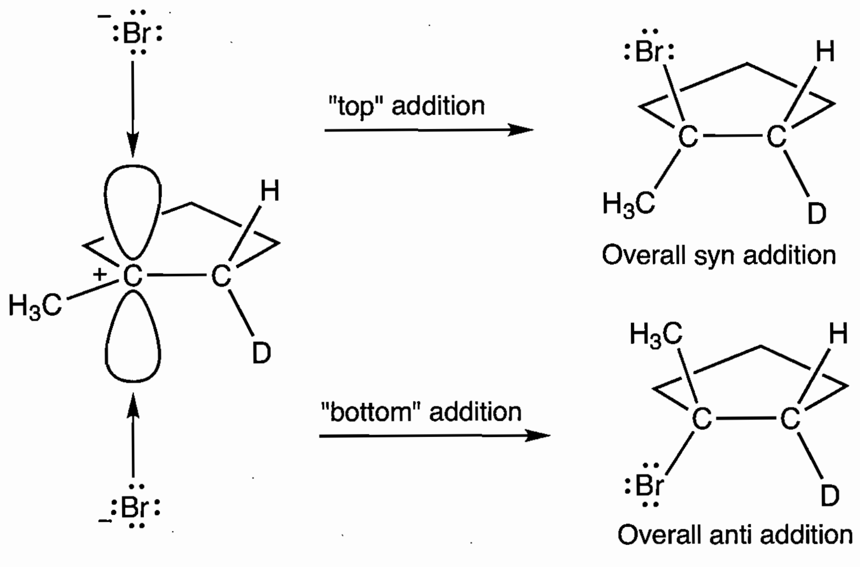
Had addition of the two bromines been from the same side, in syn fashion, just the opposite results would have been seen.



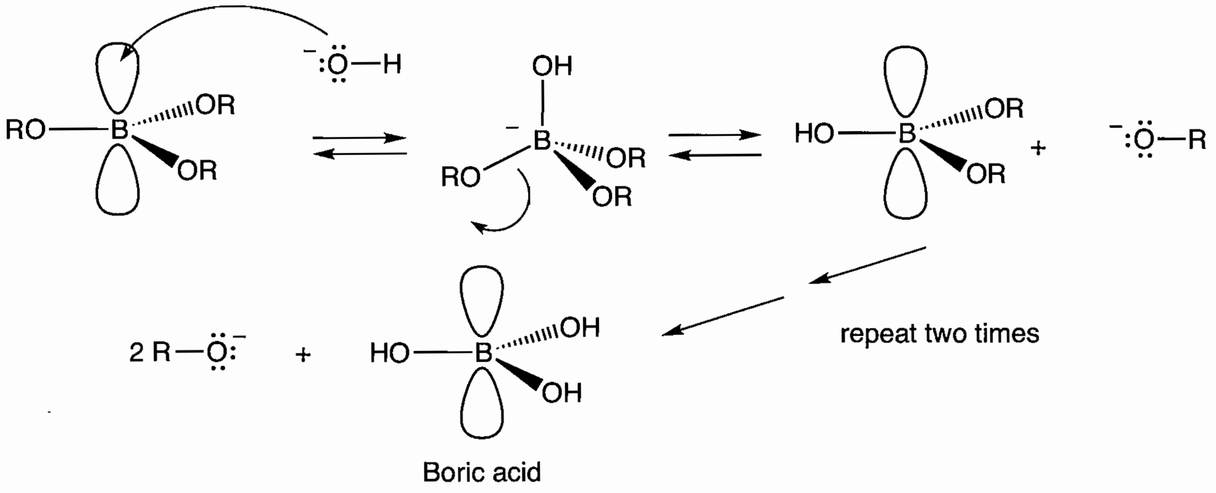
Problem 10.19 There are many possibilities, although most will require some sort of isotopic label. The question states that any appropriate starting material is available, so that's not a problem. Here's one in which a deuterated cycloalkene is used:



Addition can occur to either lobe of the $2p$ orbital to give either syn or anti addition. Both products will be formed. A careful determination of the structure of the product will allow a determination of the direction of addition.

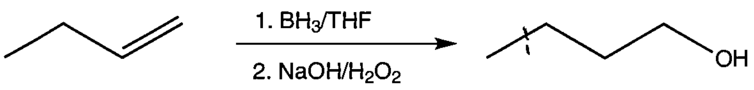


Problem 10.21 The boron atom in a boronic ester, $B(OR)_3$, remains a Lewis acid, as it still has an empty $2p$ orbital. Hydroxide is a strong nucleophile and adds to the Lewis acidic boron atom. Loss of ^{-}OR completes the first stage. Two repetitions lead to boric acid.

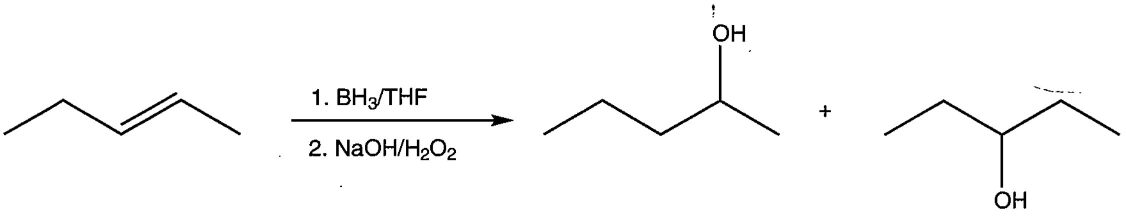


Problem 10.22

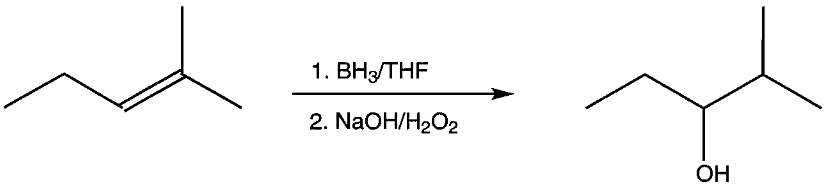
(a) 1-Butanol is the only product in this reaction.



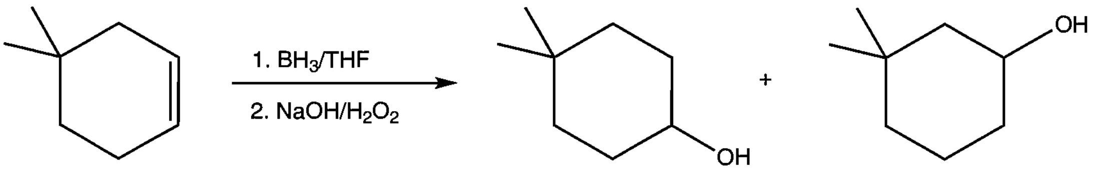
(b) The electrophile (BH_3) will add to either carbon of the 2-pentene. Oxidation leads to similar amounts of 3-pentanol and racemic 2-pentanol.



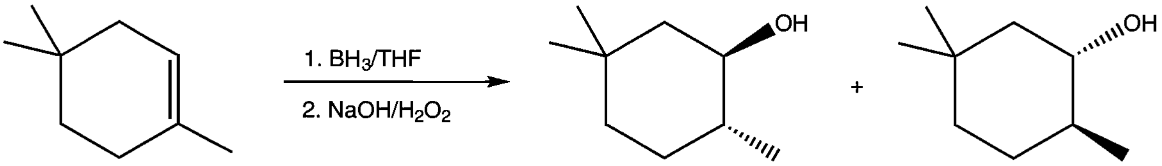
(c) The reaction of BH_3 with 2-methyl-2-pentene, followed by oxidation of the boron, gives a racemic mixture of 2-methyl-3-pentanol.



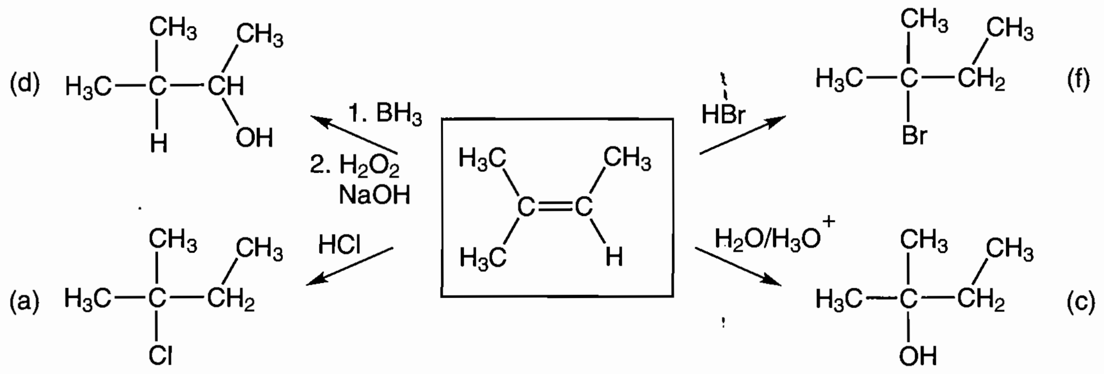
(d) Electrophilic addition of BH_3 to 4,4-dimethylcyclohexene, followed by oxidation with hydrogen peroxide, gives 4,4-dimethylcyclohexanol and a racemic mixture of 3,3-dimethylcyclohexanol.



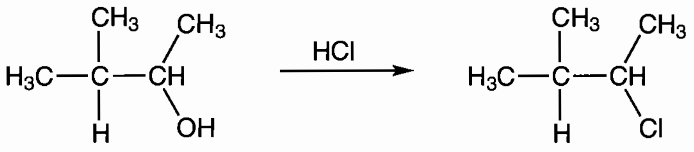
(e) The hydroboration/oxidation reaction of 1,4,4-trimethylcyclohexene gives a racemic mixture of (1*R*,2*R*)-2,5,5-trimethylcyclohexanol and (1*S*,2*S*)-2,5,5-trimethylcyclohexanol.



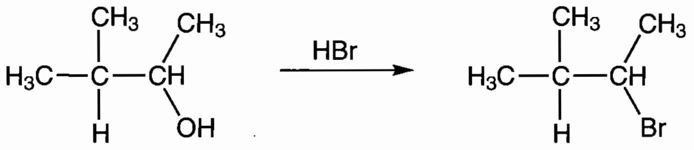
Problem 10.23 There are several straightforward parts to this problem, which only require that you remember one synthetic procedure.



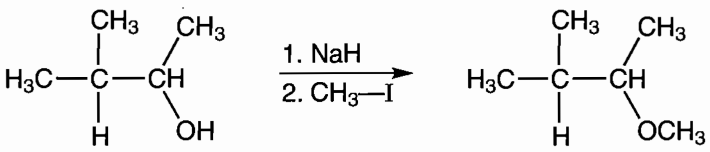
The remaining three molecules demand one more level of sophistication as they cannot be made directly but require a second transformation involving a molecule already constructed.



(b)



(e)



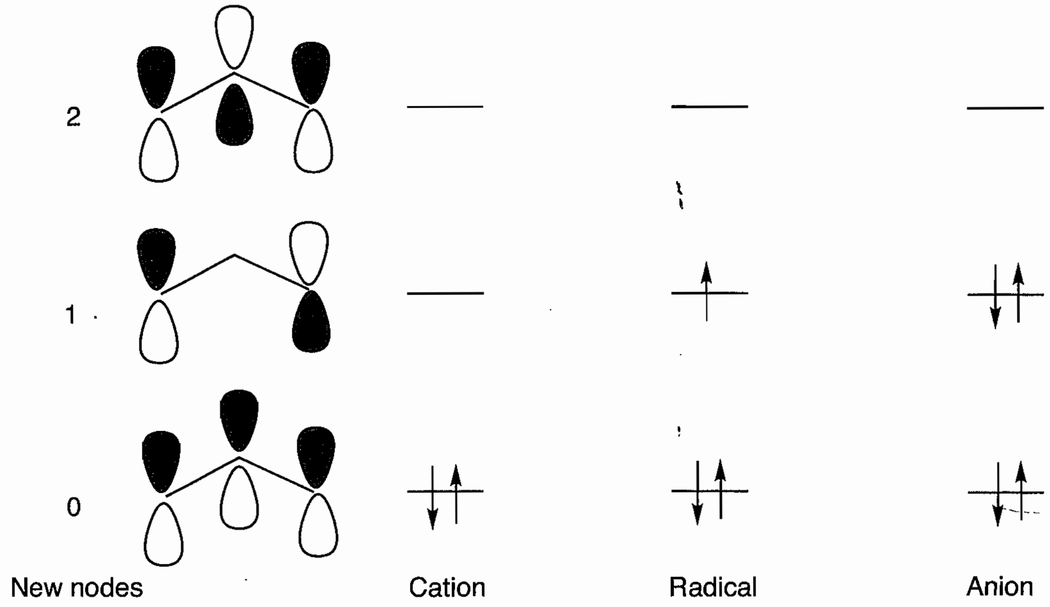
(g)

Additional Problem Answers

Problem 10.24 The π molecular orbital system for allyl consists of three orbitals. These were discussed in the chapter, and by now it should be possible to write them out without the construction process. It is especially useful to recall that the number of new nodes will increase 0 . . . 1 . . . 2. In the π system of the cation, there are only two electrons. In the neutral radical, there must be one more, and in the negatively charged anion, two more.

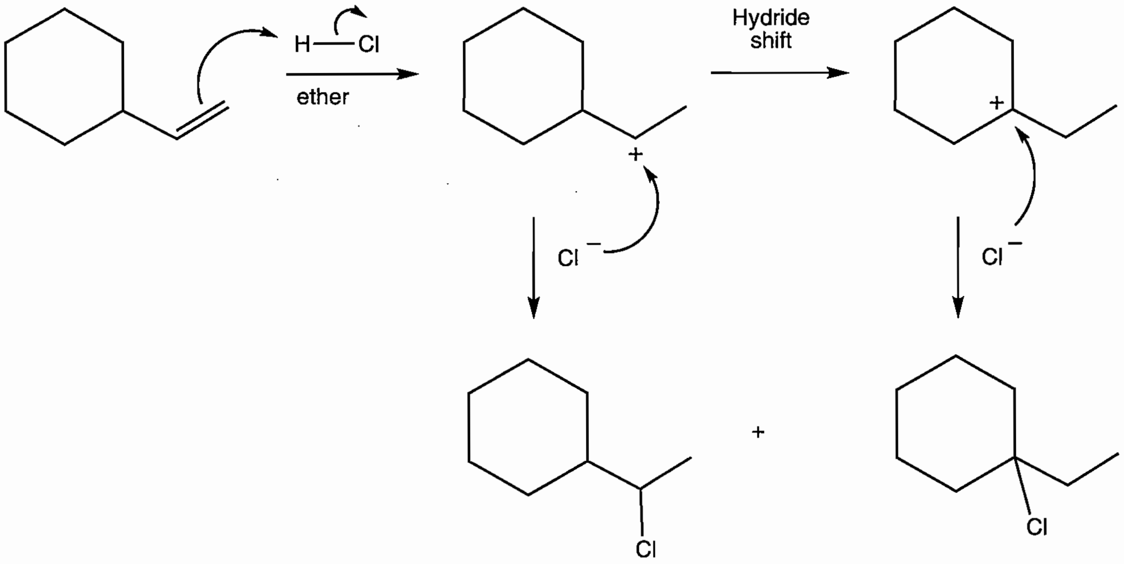
(continued)

Problem 10.24 *(continued)*

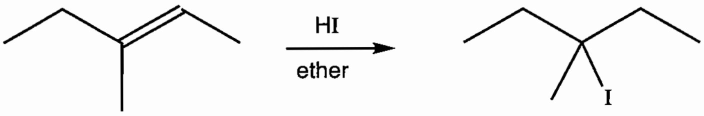


Problem 10.25

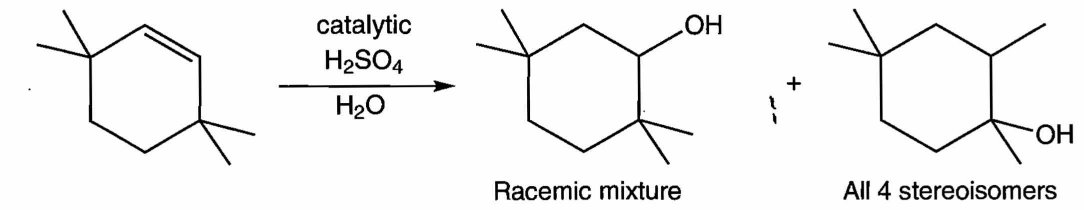
(a) Initial addition of the electrophile gives a secondary carbocation. That cation can be captured by chloride to give the first product. Hydride shift will occur to give the more stable tertiary carbocation, which results in formation of the 1-chloro-1-ethylcyclohexane as a second product.



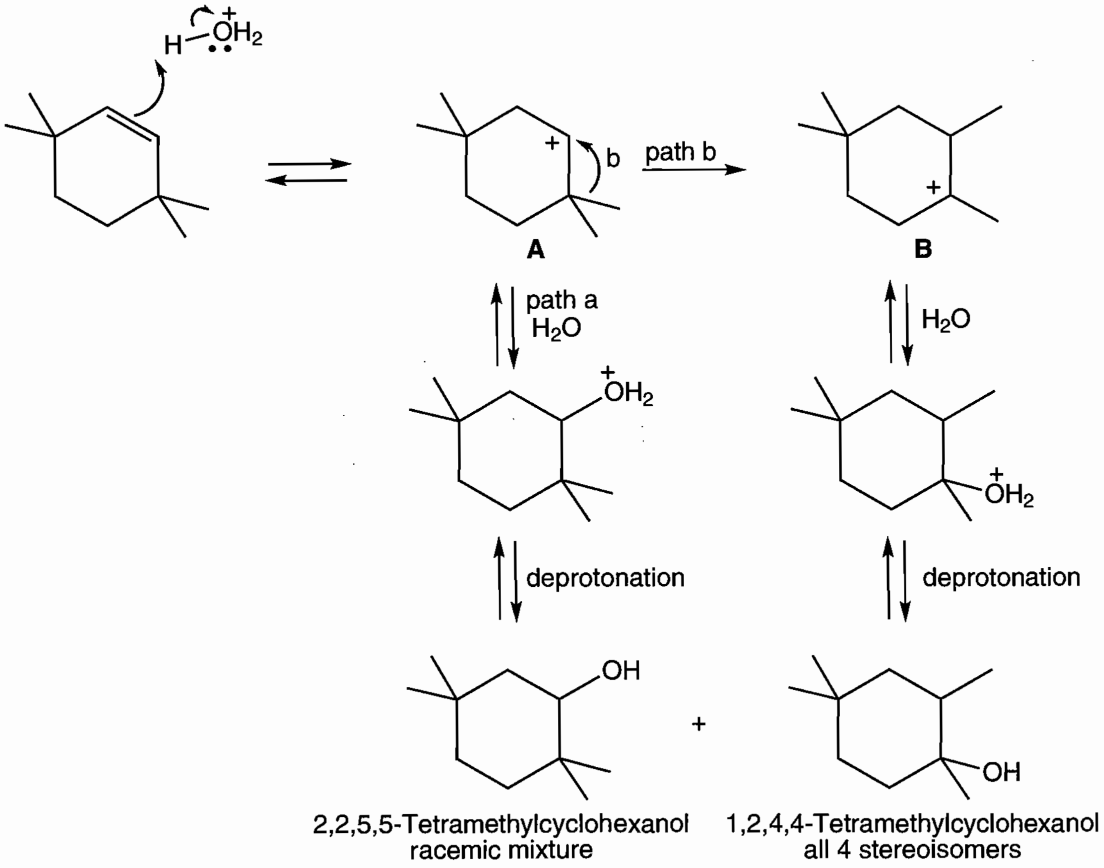
(b)



(c) The products for this reaction are shown.



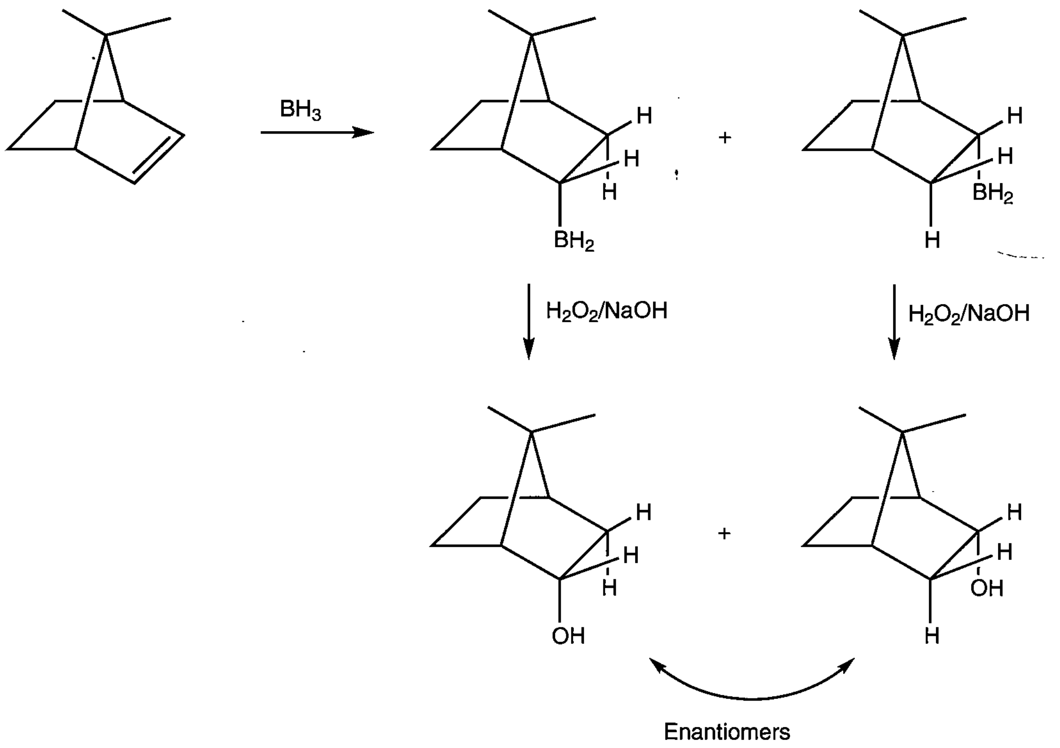
3,3,6,6-Tetramethylcyclohexene is symmetrical. Protonation of the alkene can occur on either carbon. Water will capture the resulting carbocation **A** to give a protonated alcohol (path a) that produces 2,2,5,5-tetramethylcyclohexanol after deprotonation. A methyl shift (path b) in the initial secondary carbocation (**A**) will give a tertiary carbocation (**B**). Capture of the tertiary carbocation gives a protonated alcohol, which gives the 1,2,4,4-tetramethylcyclohexanol isomers upon deprotonation. There are two stereogenic carbons in the second product. We expect the (*R*,*R*), (*R*,*S*), (*S*,*R*), and (*S*,*S*) stereoisomers to be formed.



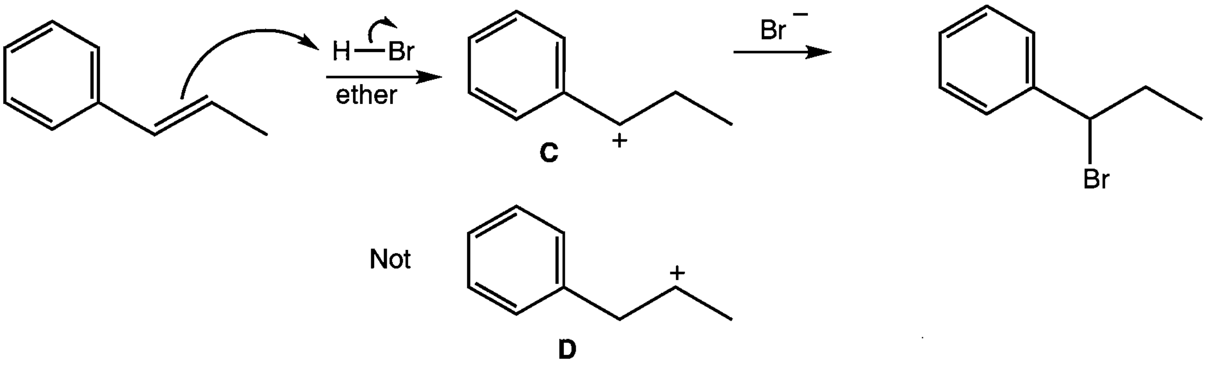
(continued)

Problem 10.25 *(continued)*

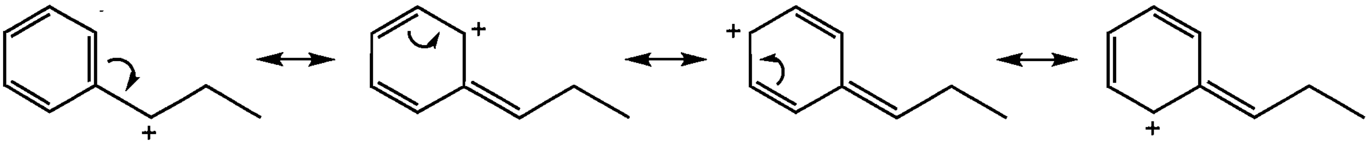
(d) The hydroboration of this alkene will occur from the less hindered side of the double bond. The carbon with two methyl groups on the top face of the alkene is very bulky. The addition of the electrophile (boron) and the hydride is a syn addition and can occur so that the boron is attached to either of two original alkene carbons. The second step of the reaction is the oxidation of the boron, which then leads to the alkyl shift from the boron to an oxygen. This reaction occurs with retention of configuration. Therefore, the oxygen remains on the less hindered face of what was the alkene. The two possible alcohol products are enantiomers.



(e) Addition of HBr to 1-phenylpropene will give a single product. To come to this conclusion, we need to consider the two carbocations (**C** and **D**) that could arise from the initial addition of the electrophile. Both carbocations are secondary, but carbocation **C** is benzylic. The benzylic cation is resonance stabilized and much more stable than the cation **D**. The only product of this reaction will be formed from capture by bromide of the intermediate carbocation **C**.

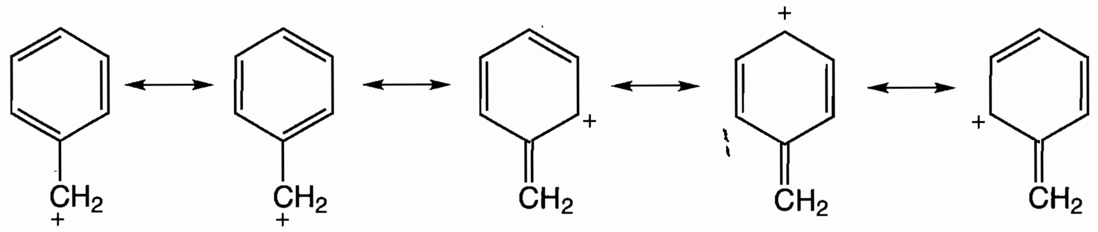


Resonance stabilization of the benzyl carbocation **C**

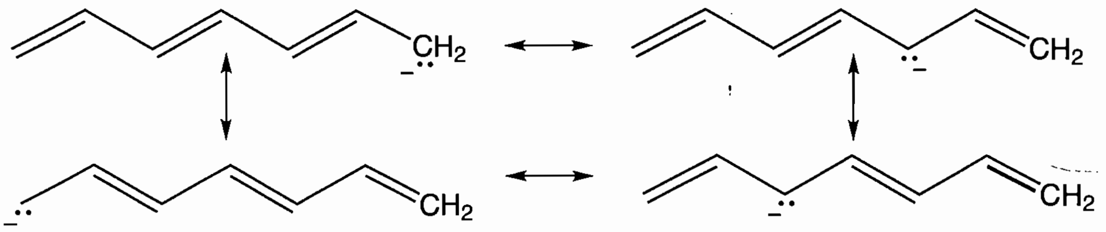


Problem 10.26

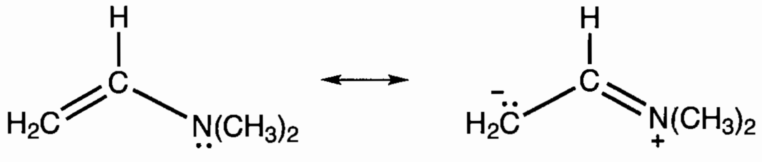
(a)



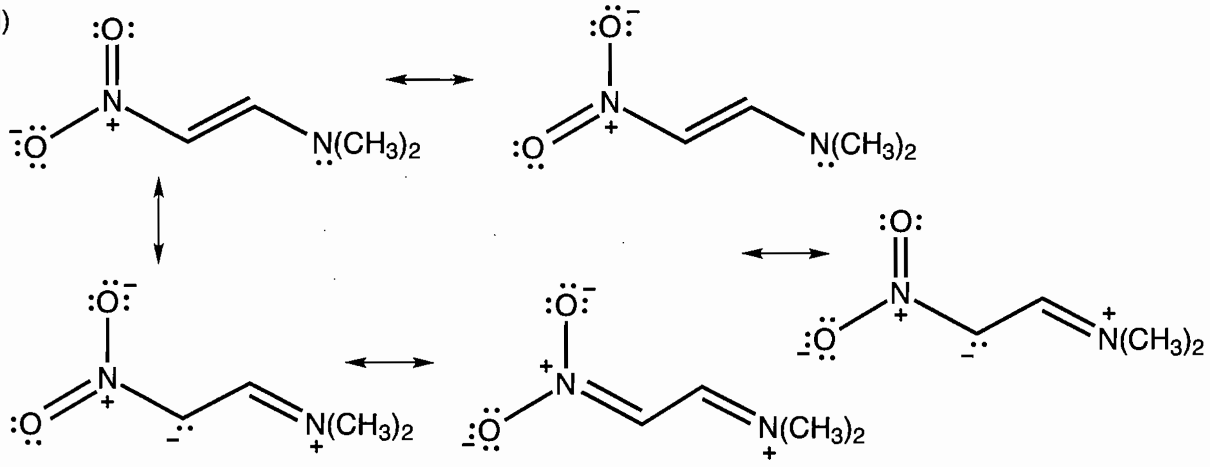
(b)



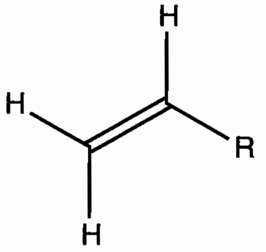
(c)



(d)



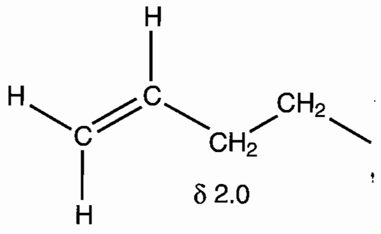
Problem 10.27 The C_5H_{10} molecule will have 1 degree of unsaturation. It will be either an alkene or a ring. We see from the ^1H NMR data that there are three hydrogens in the vinyl hydrogen region (around δ 5.5 ppm). Because there is only one double bond possible (from the degrees of unsaturation) and we have three vinyl hydrogens, we can conclude that the double bond is monosubstituted. That conclusion gives us this partial structure:



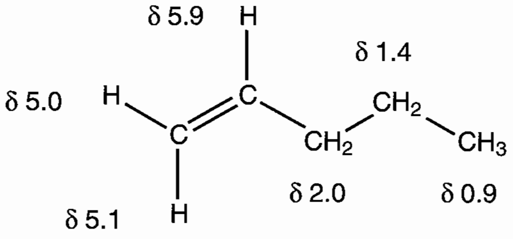
(continued)

Problem 10.27 *(continued)*

Because the double bond is the only functional group in the molecule, we expect that the allylic position should be the group most deshielded (other than the vinyl hydrogens, of course). The ^1H NMR data tell us that there is a CH_2 at δ 2.0 ppm. That chemical shift is exactly where we expect an allylic CH_2 group. It appears as a quartet, so it "sees" three hydrogens. We know it will "see" the vinyl hydrogen on the adjacent carbon in one direction, so there has to be a CH_2 in the other direction in order to "see" three hydrogens. That analysis gives us this piece:

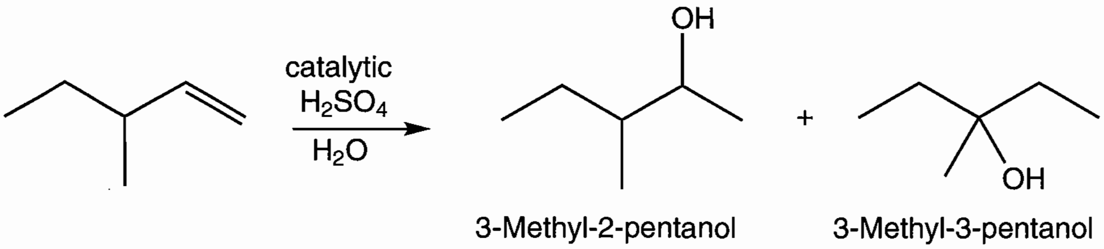


Now we have the molecule almost determined. The signal at δ 1.4 ppm that is a CH_2 sextet must "see" five hydrogens on the adjacent carbons. That means there must be a $CH_2CH_2CH_3$ in the molecule. That finishes the structure.

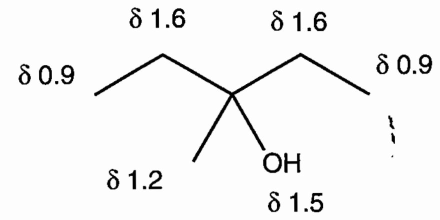


There are six unique hydrogens in the molecule, so there will be six signals in the ^1H NMR spectrum. The spectral data obtained on a 500 MHz NMR spectrometer will show the 2-bond coupling between the nonequivalent H's on C(1) and the long-range coupling between the C(1) H's and the C(3) H's, in which case the vinyl hydrogens at δ 5.0 and 5.1 ppm are multiplets.

Problem 10.28 You know that there are two products one can expect from the hydration of 3-methyl-1-pentene. They are 3-methyl-2-pentanol, which comes from normal addition of water across the double bond, and 3-methyl-3-pentanol, which involves a hydride shift in the initially formed carbocation to produce a more stable carbocation followed by addition of water.



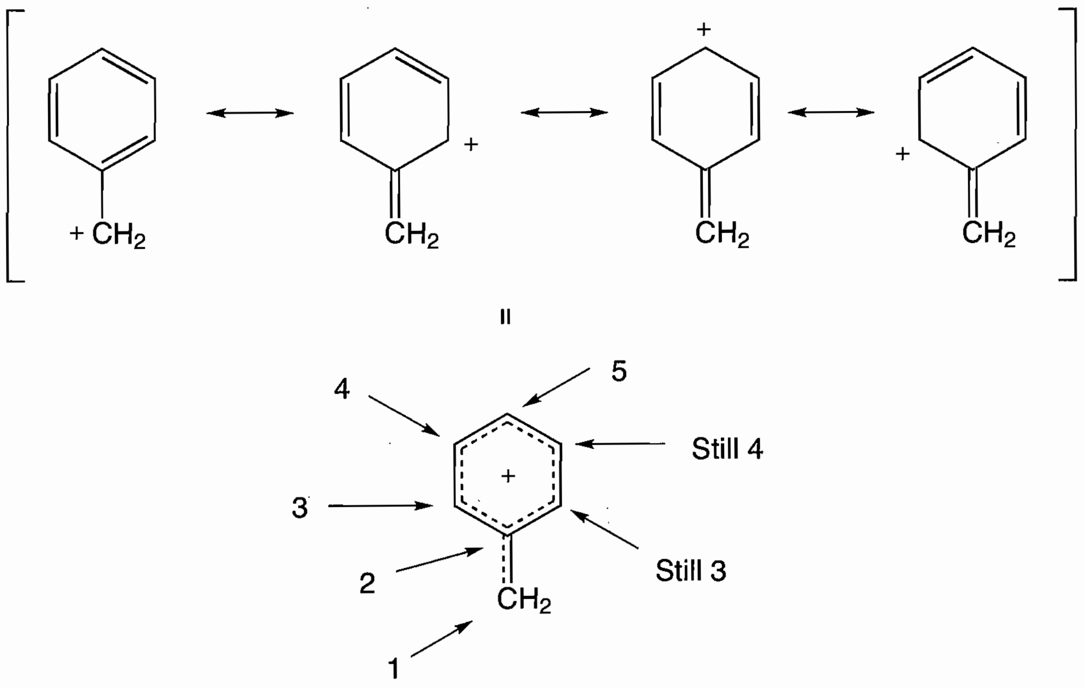
The ^1H NMR spectrum has a 6H triplet and a 3H singlet. Only 3-methyl-3-pentanol would give such signals.



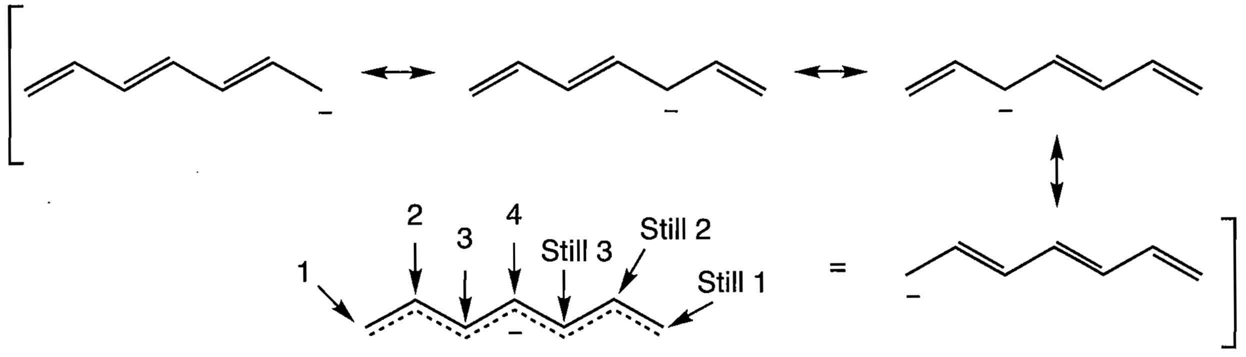
The ^1H NMR spectrum of 3-methyl-2-pentanol would be far more complex.

Problem 10.29 First, draw out the resonance forms for the two compounds, so we can see the overall symmetry.

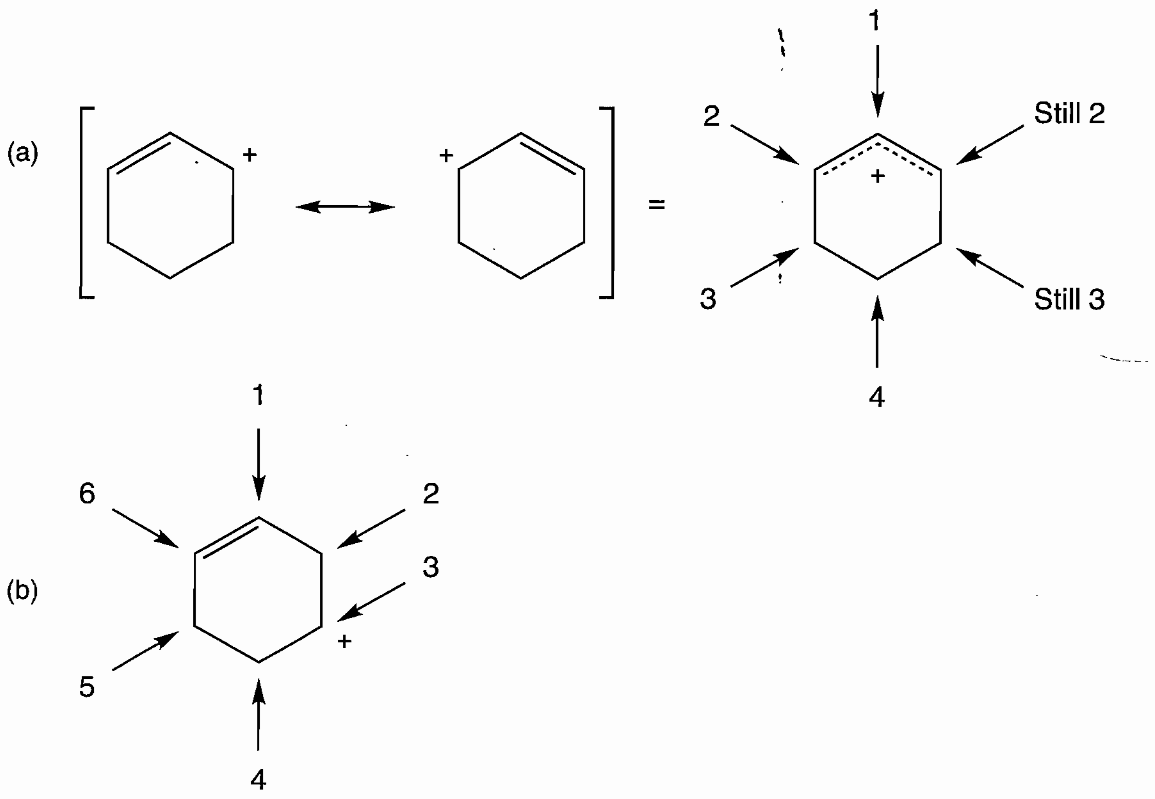
In compound (a), the charge will be delocalized to three (two different) carbons in the ring. There will be five different carbons and therefore five signals in the ^{13}C NMR spectrum.



In compound (b), there will also be delocalization to make some of the carbons equivalent. There will be four signals.



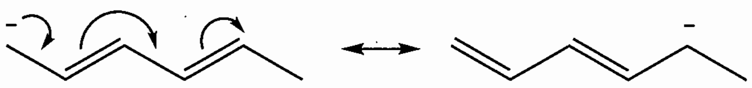
Problem 10.30 In (a) once again, resonance makes the system more symmetric than it looks at first glance. There are only four different carbons, and so only four signals appear in the ^{13}C NMR spectrum. In (b), there is no resonance stabilization (be sure you see this!) and therefore all the carbons are different. There will be six signals.



Problem 10.31

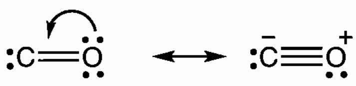
(a) These are not resonance structures. The structure on the left is an allylic carbocation. The structure on the right is not. Atoms must be moved to go from one structure to the other. Therefore they aren't resonance structures.

(b) These are resonance structures. Only electrons are moved to go from one structure to the other. The electron pushing is shown.



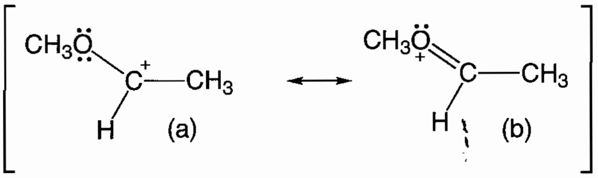
(c) These are not resonance structures. They are identical molecules. One structure need only be flipped over in order to draw the second.

(d) These are resonance structures. Only electrons have been moved.



(e) These two molecules are not resonance structures. A vinyl hydrogen has been moved in the structure on the left. It shows up in the isopropyl group of the structure on the right.

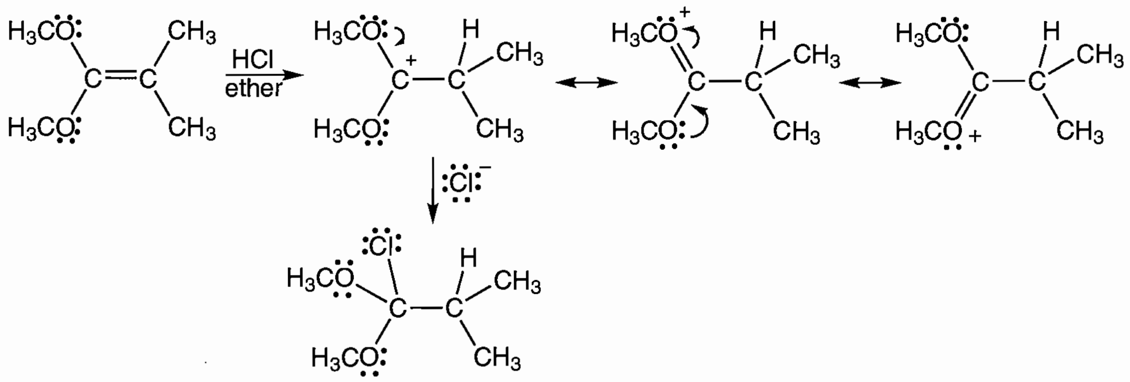
Problem 10.32 First, draw good Lewis structures for this pair.



This problem is tougher than it first appears to be. At first glance, one might assume that resonance form (a) would be the more important one because (b) has a positive charge on oxygen, a more electronegative atom than carbon. However, form (b) has one more bond than (a), and in (a) the carbon atom does not have a filled octet and is electron deficient. In (b) both the oxygen and carbon have complete octets of electrons, making this structure the more important resonance form.

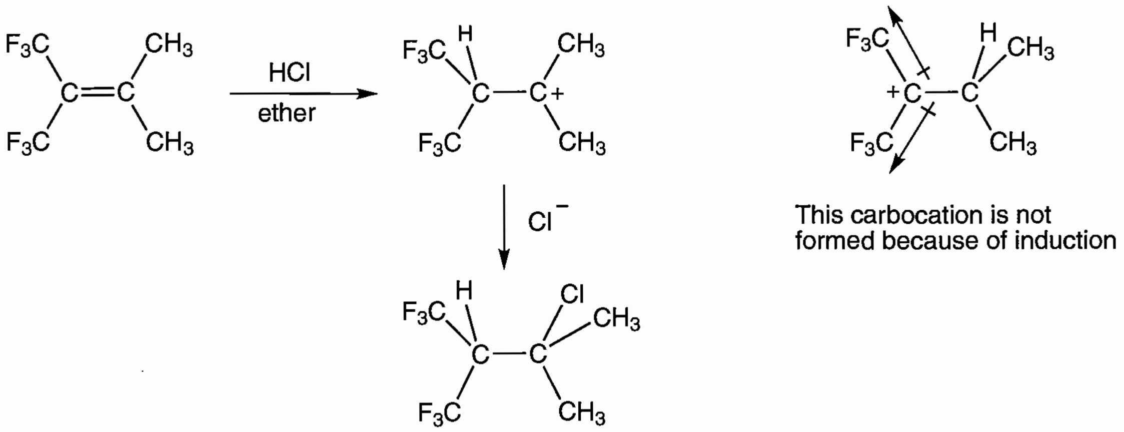
Problem 10.33

(a) Addition of the electrophile to the dimethyl-substituted carbon gives a carbocation that is resonance stabilized, as shown. This intermediate is relatively stable. It will be captured by the chloride to give 1-chloro-1,1-dimethoxy-2-methylpropane.



1-Chloro-1,1-dimethoxy-2-methylpropane

(b) The regioselectivity of this reaction is controlled by induction. The alkene will react with the electrophile to protonate one carbon or the other. Protonation will occur on the carbon attached to two trifluoromethyl groups producing the tertiary carbocation shown. Protonation on the carbon with two methyl groups would lead to a much higher energy carbocation over a prohibitively high transition state.

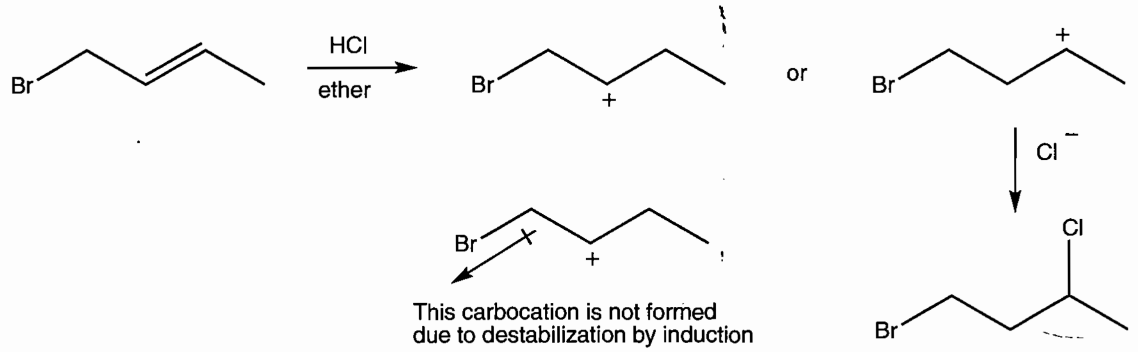


This carbocation is not formed because of induction

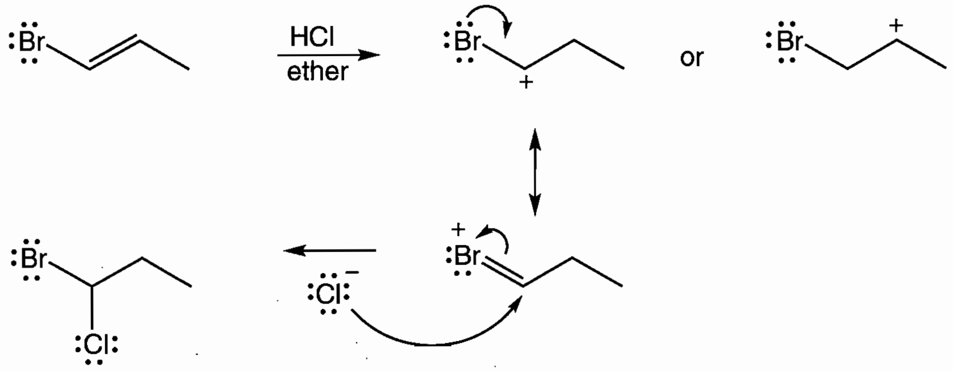
(continued)

Problem 10.33 *(continued)*

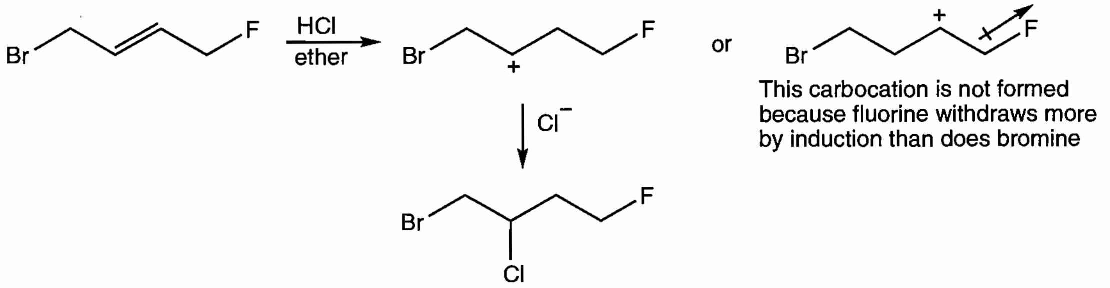
(c) The outcome of this reaction is also controlled by induction. The two possible carbocations for the first step of the reaction are shown. The bromine is electronegative and it will destabilize the carbocation that is closer, which means the transition state will be higher. As a result, it is the carbocation that is more distant from the bromo group that is formed as the first intermediate. Capture by chloride gives 1-bromo-3-chlorobutane.



(d) In this case it is resonance that controls the reaction. We first draw the two possible carbocations and then we decide if one is more stable than the other. In this case, one of the carbocations is resonance stabilized. The preferred path will include the more stable cation, and the major product will be 1-bromo-1-chloropropane.



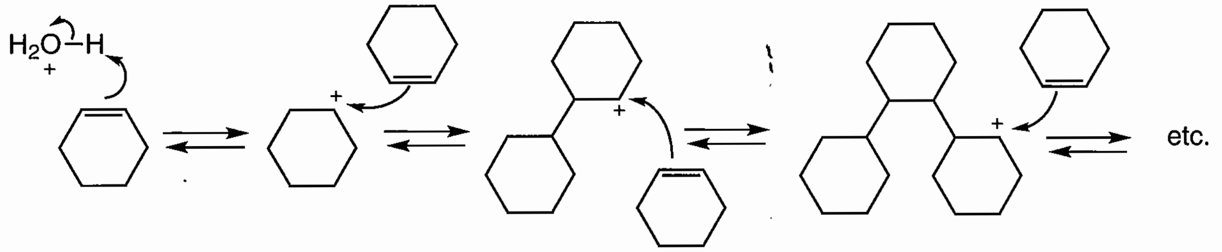
(e) Protonation of 1-bromo-4-fluoro-2-butene will form one of two carbocations. The carbocation that is closer to the fluorine will be more destabilized as a result of induction, since fluorine is more electronegative than bromine. Therefore, the transition state leading to the carbocation that is closer to the bromine will be lower and lead to the major product, 1-bromo-2-chloro-4-fluorobutane.



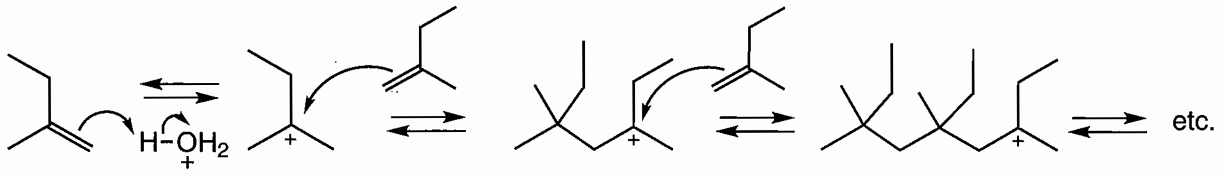
This carbocation is not formed because fluorine withdraws more by induction than does bromine

Problem 10.34

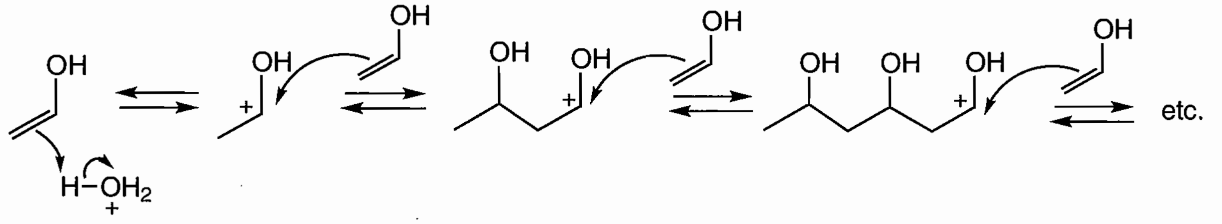
(a) Cyclohexene can make polycyclohexene.



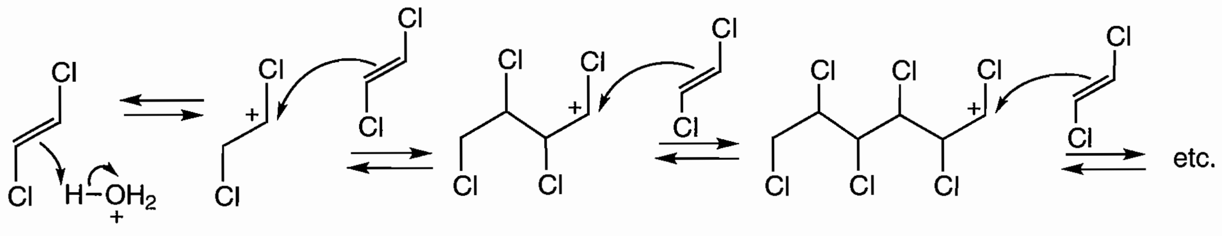
(b) Polyisopentylene comes from polymerization of 2-methyl-1-butene.



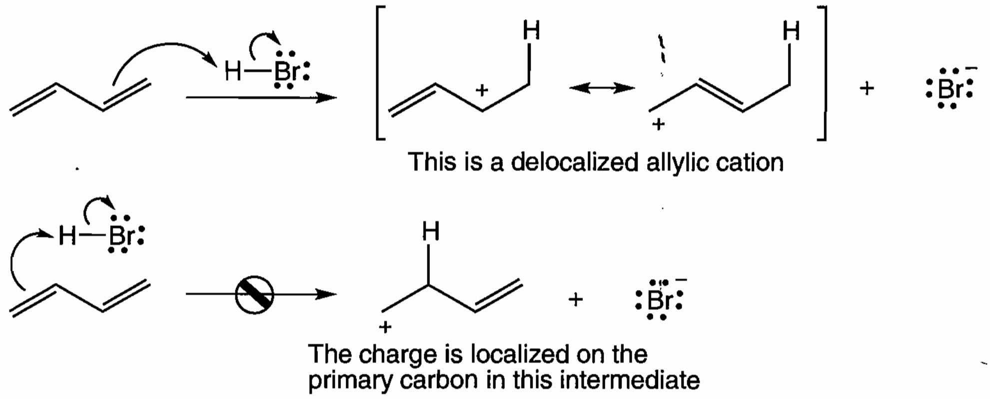
(c) Vinyl alcohol polymerizes to give polyvinyl alcohol.



(d) One could make this polydichloroethylene from (*E*)- or (*Z*)-1,2-dichloroethylene.



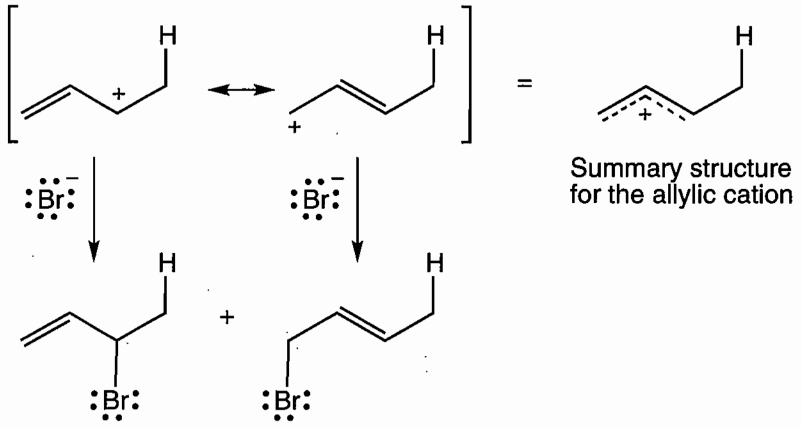
Problem 10.35 The first problem is to decide in which direction butadiene will protonate. There really is no choice; one protonation leads to a resonance-stabilized carbocation, the other to a simple localized primary carbocation.



This is a delocalized allylic cation

The charge is localized on the primary carbon in this intermediate

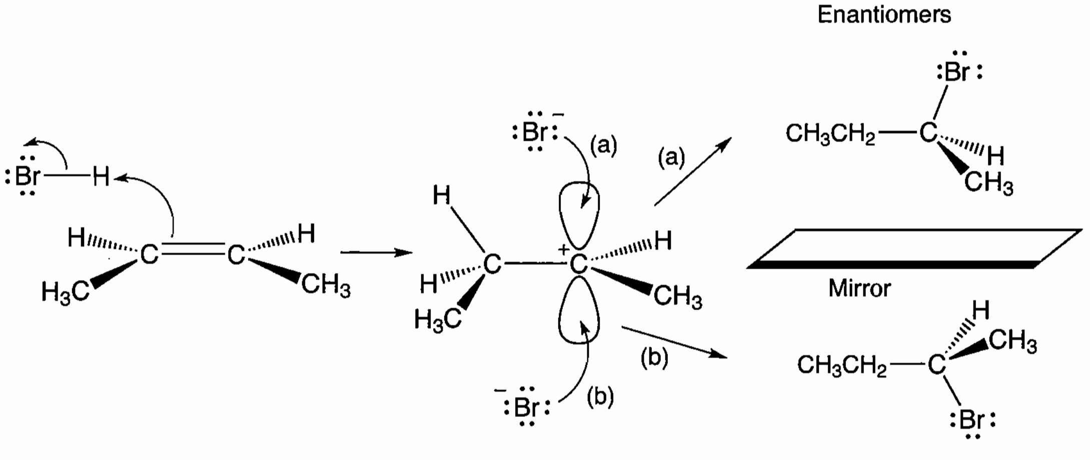
Two carbons share the positive charge in the resonance-stabilized, allyl cation. Be careful in the drawing below not to fall into the trap of thinking of the two resonance forms as separate entities. Two carbons share the charge in a *single* structure, summarized at the right of the figure with the "dashed bond" structure.



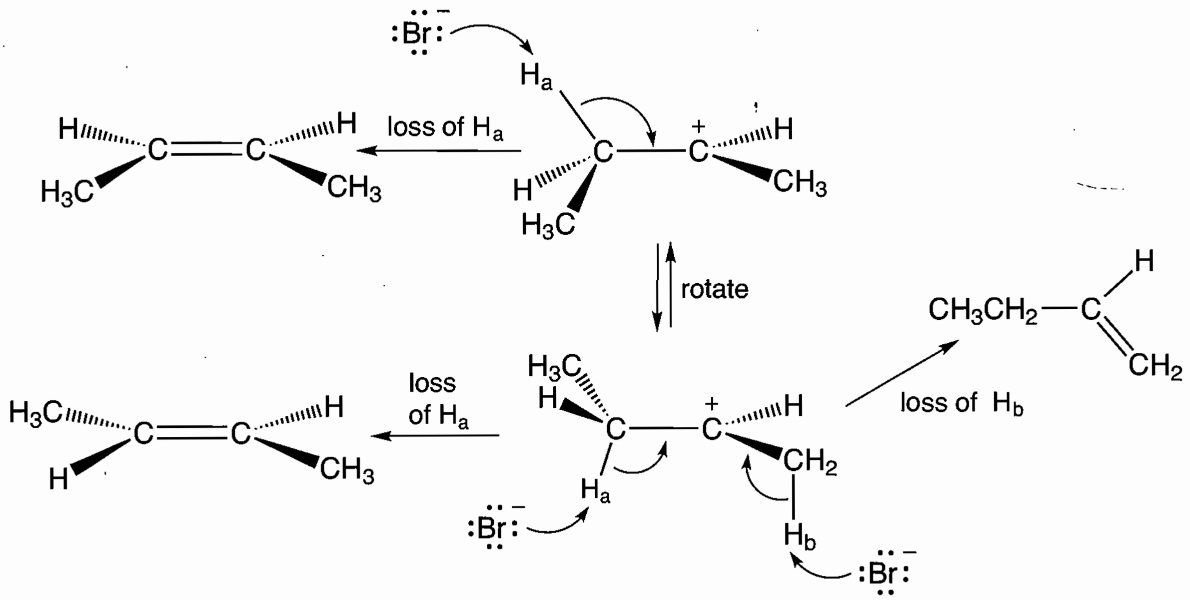
Summary structure for the allylic cation

Problem 10.36

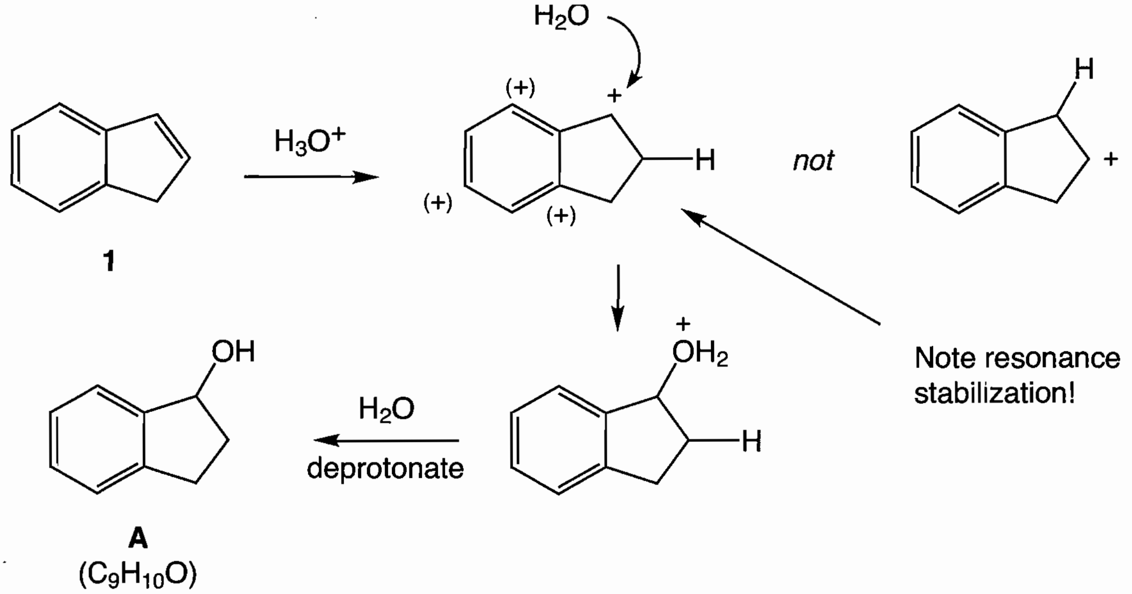
(a) Protonation gives a planar, secondary carbocation. Addition of bromide ion from the top of the cation gives one enantiomer; addition from the bottom gives the other. As these two pathways are equivalent, the two products must be formed in equal amounts. This reaction gives a racemic mixture.



(b) There is something else that the carbocation can do besides react with the bromide ion. Like all other cations, it can lose a proton to give an alkene, if there is a proton attached to an adjacent carbon atom. In this case there are two such protons, H_a and H_b. H_a can be lost from two rotational isomers of the carbocation to give the starting alkene, *cis*-2-butene and its diastereomer, *trans*-2-butene. Alternatively, H_b can be lost to give 1-butene. Any base in the reaction can assist in proton removal. The figure shows bromide acting as the base.



Problem 10.37 Compound **A** is formed by a straightforward hydration in Markovnikov fashion:

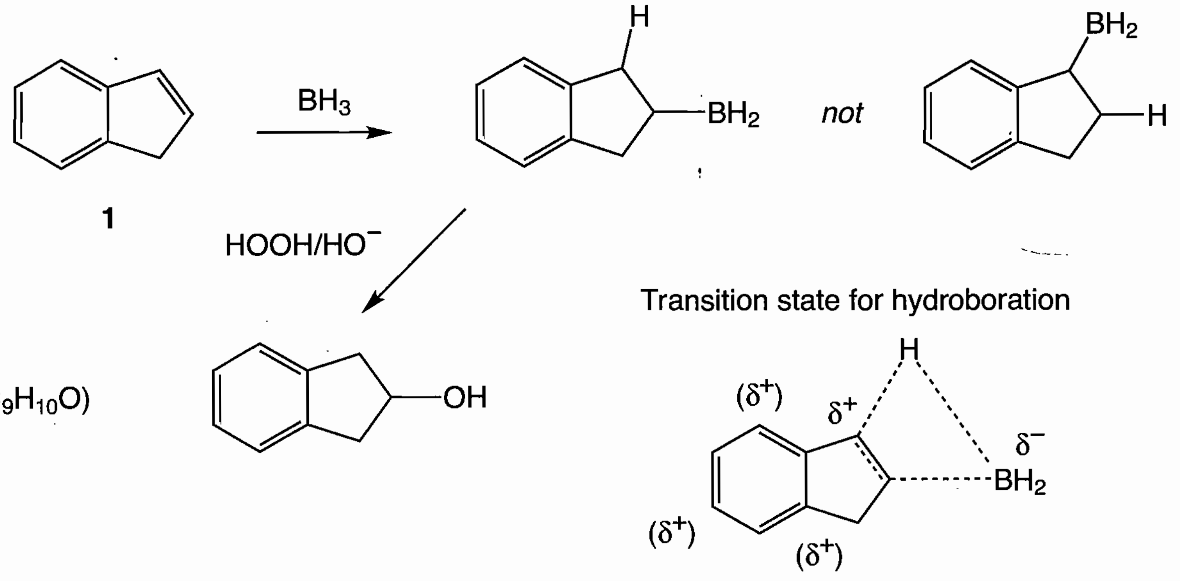


(continued)

Problem 10.37 *(continued)*

All nine carbons in **A** are different, so the ^{13}C NMR spectrum will show nine signals, and this must be the first route.

The second route uses hydroboration/oxidation conditions and therefore must give anti-Markovnikov addition. Here is how it works.

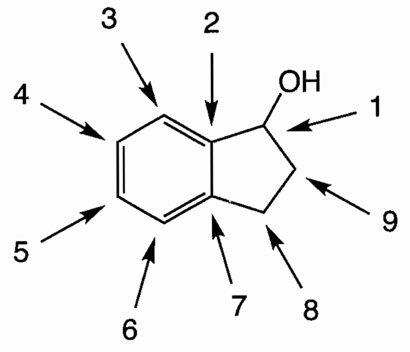


Transition state for hydroboration

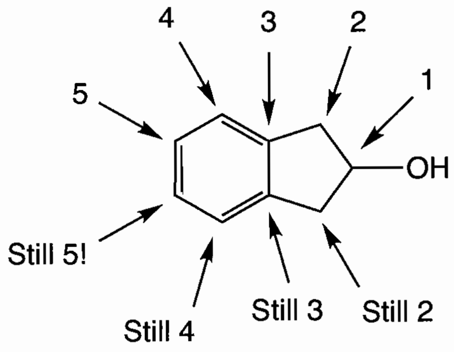
Note resonance stabilization

Compound **B** has a plane of symmery and thus only five different carbons. Its ^{13}C NMR spectrum will contain only five signals, in contrast to the nine of compound **A**.

A ($C_9H_{10}O$)

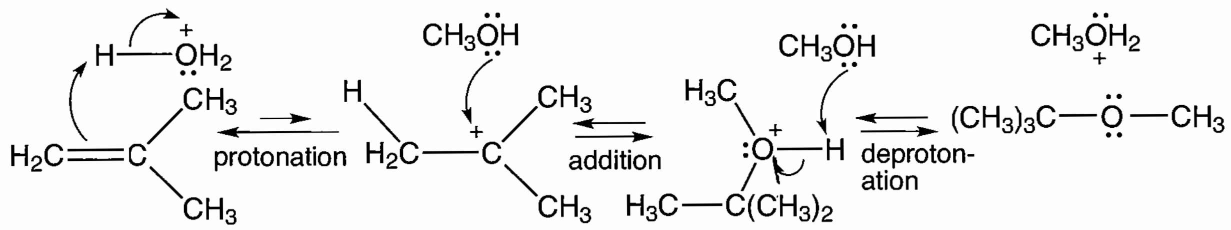


B ($C_9H_{10}O$)

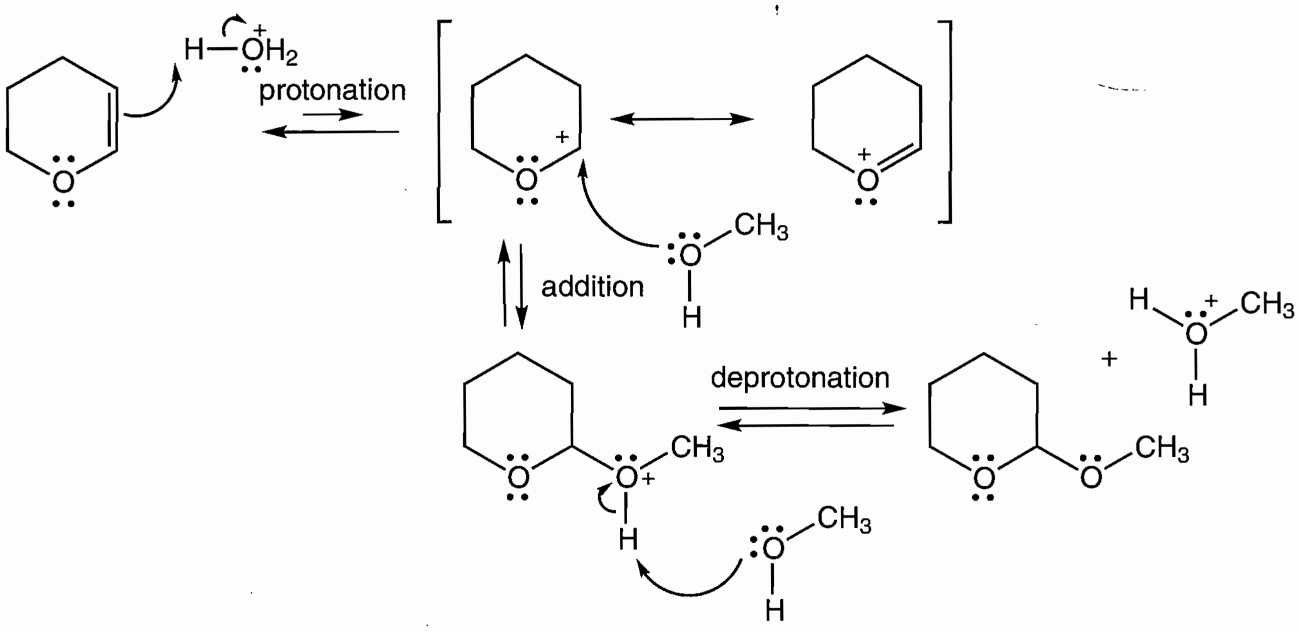


Problem 10.38

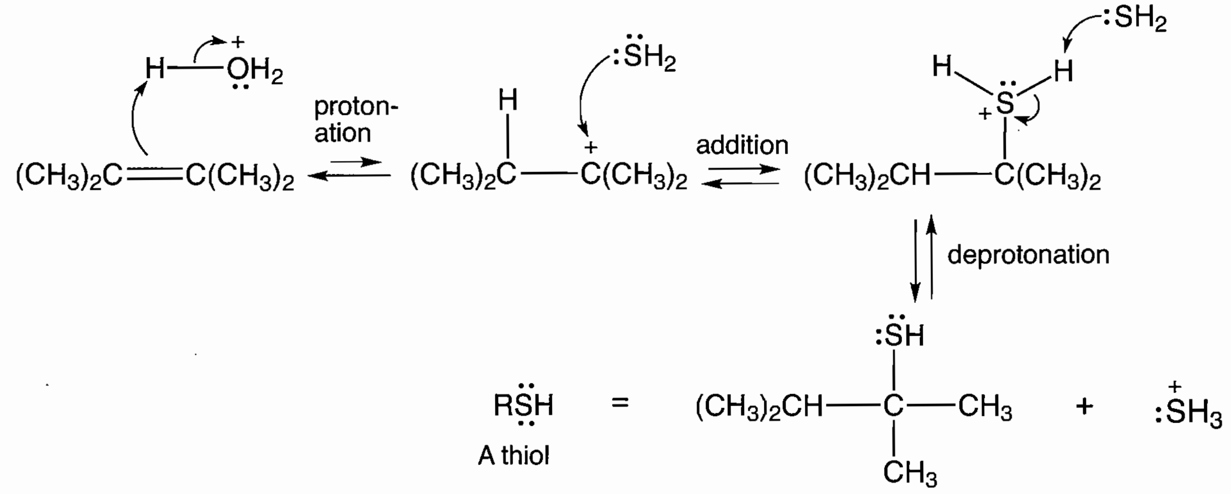
(a) This reaction is closely related to hydration. Alcohol replaces water, but the mechanistic process is the same. Protonation by either H_3O^+ or $CH_3O^+H_2$ leads to a tertiary carbocation (not the less stable primary carbocation) that is captured by alcohol. A final deprotonation gives the product.



(b) This problem is just a common example of (a), the acid-catalyzed addition of an alcohol to an alkene. In this case, protonation occurs to give the resonance-stabilized carbocation, not the localized secondary carbocation.



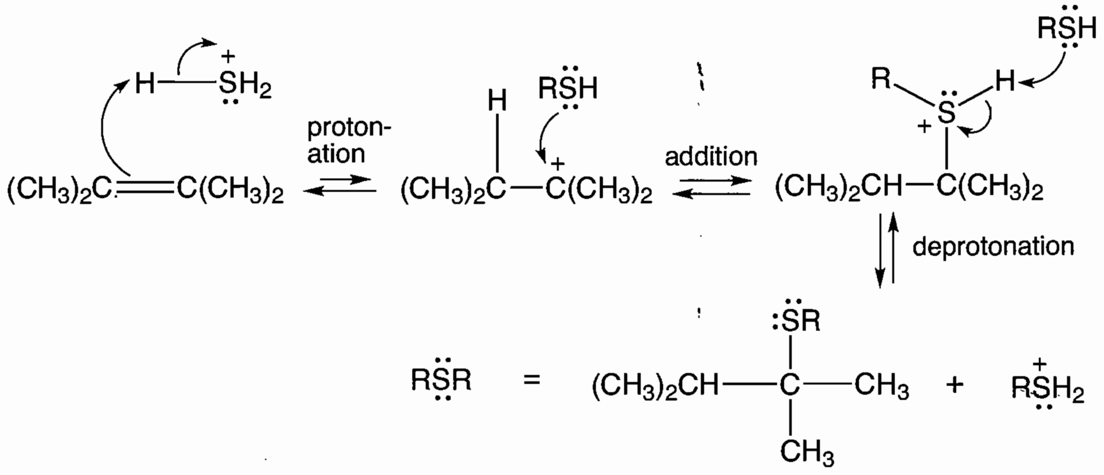
Problem 10.39 The first part of this reaction is exactly like hydration except that hydrogen sulfide (H_2S) plays the part of water. The product is a thiol (RSH). Notice the pattern of three steps: protonation, addition, and deprotonation, which is present in many addition reactions.



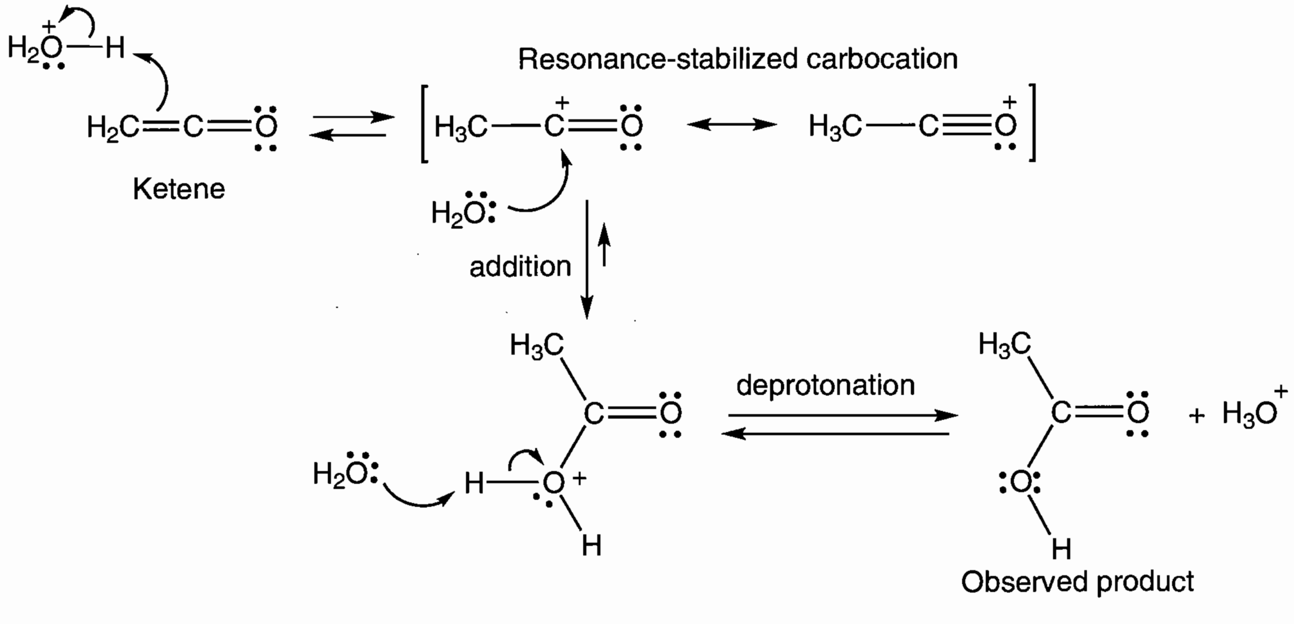
(continued)

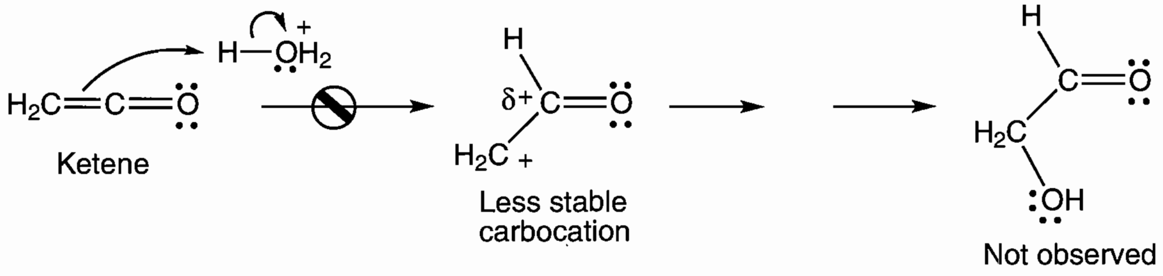
Problem 10.39 *(continued)*

As this product, RSH, builds up, it can begin to compete with H_2S for the carbocation. The product of this reaction is the thioether (RSR), the other product shown in the problem.



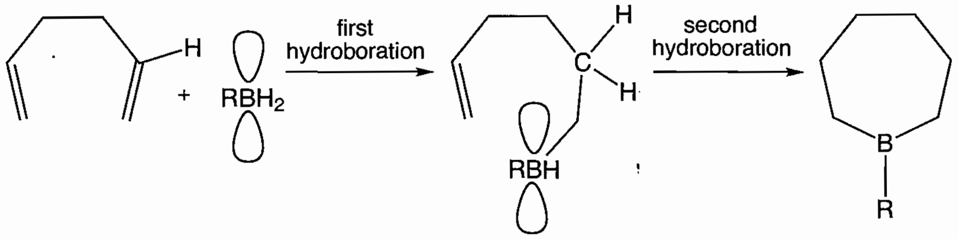
Problem 10.40 There are two possibilities for protonation of the carbon–carbon double bond in this molecule, called a "ketene." The more favorable one leads to a resonance-stabilized carbocation. Capture of this ion by water leads to the observed product. Capture of the less stable carbocation by water would give the compound that is not observed in the reaction.



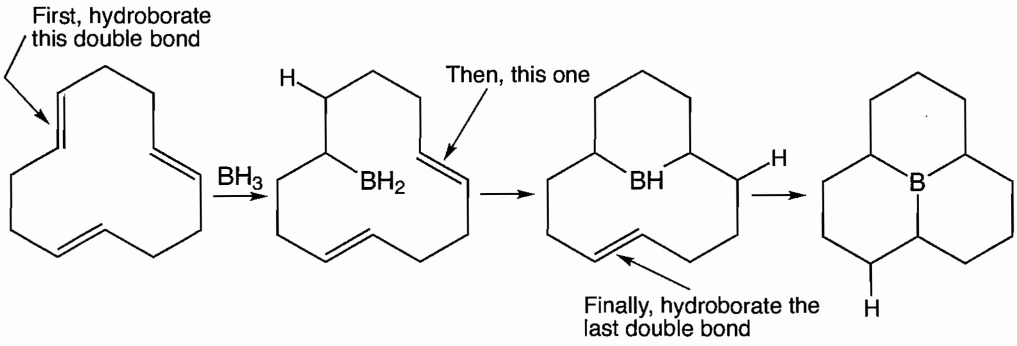


Problem 10.41 Both of these reactions involve multiple hydroborations, one or more of which are intramolecular.

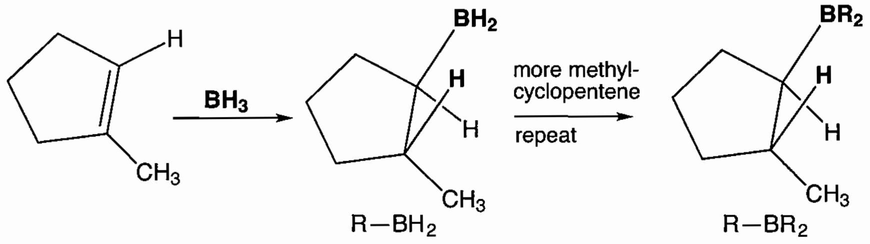
(a) Let R = $(CH_3)_2CHC(CH_3)_2$, and draw the molecule in a suggestive way. In doing this, we are only taking advantage of the free rotations about carbon–carbon single bonds.



(b)



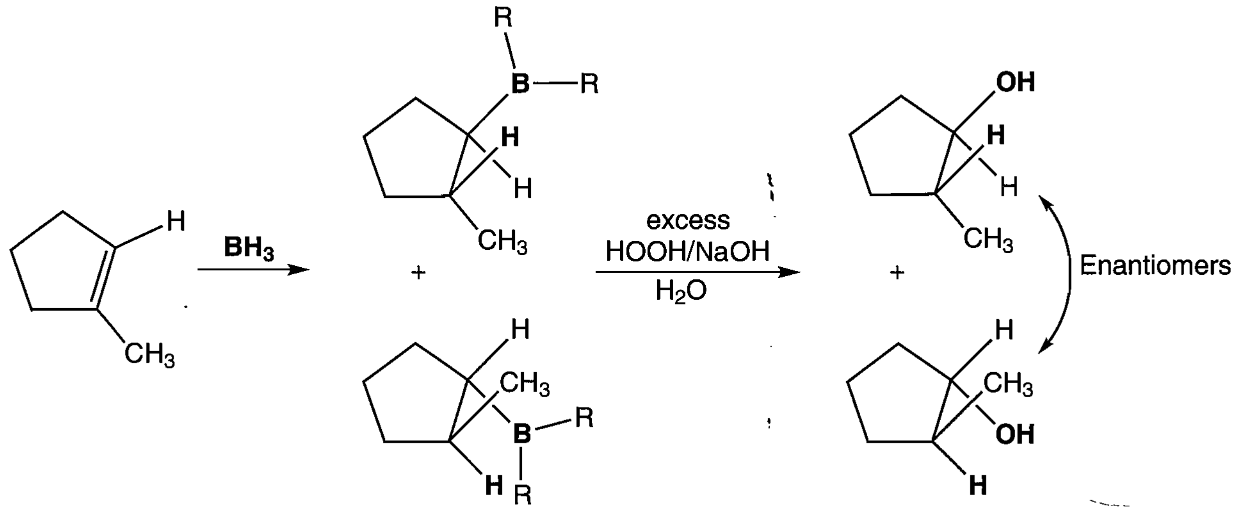
Problem 10.42 We know that the original hydroboration occurs in a syn fashion.



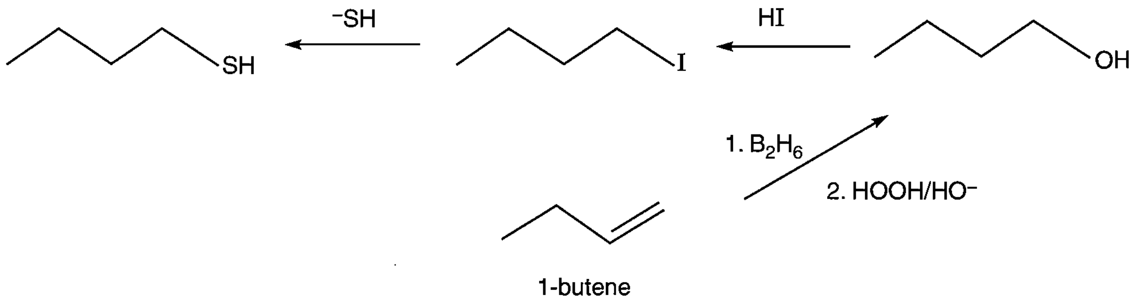
As the product alcohol has the same stereochemistry as the original borane, the overall replacement of BR_2 with OH must occur with retention, whatever the mechanism.

(continued)

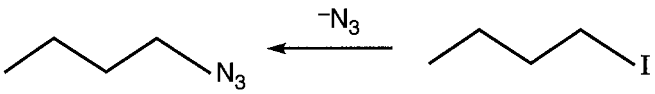
Problem 10.42 *(continued)*



Problem 10.43 Remember: Always do synthesis problems backward. So, here the question to ask is, How would I make the target molecule from anything in a single step; that is, what might be the *immediate* precursor(s) of the target molecule? In this case, displacement of a good leaving group by the excellent nucleophile ^-SH seems a good idea. This process yields another target. Apply the same process repeatedly and you will eventually get to the starting material. Here is an outline of one possible route:

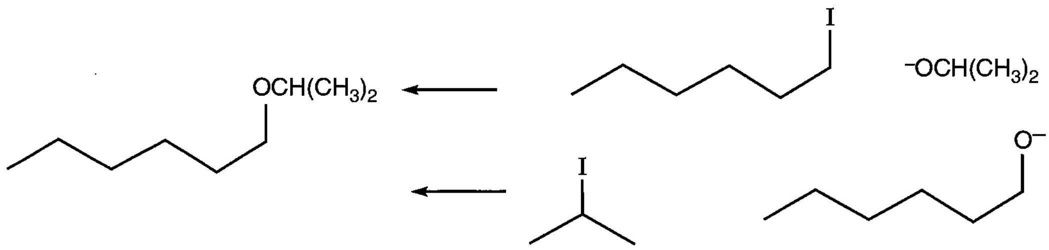


Problem 10.44 See the admonition to work backward in Problem 10.43. Here, we can use the same route to the iodide and then displace it with the excellent nucleophile azide.



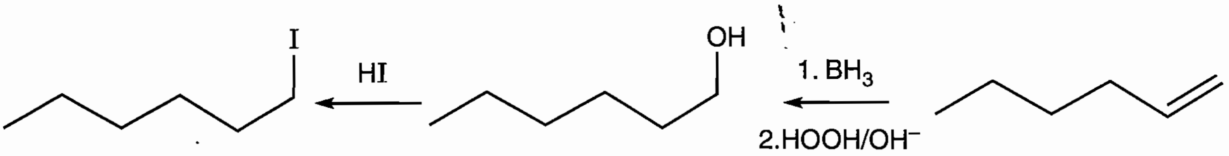
Problem 10.45 The target here is an ether (R–O–R′), so there are two possible routes:

$RO^- + R'–LG$, or $R'O^- + R–LG$. In this case the first of the two routes shown in the drawing is far better than the other. Why? The second will lead to lots of E2 elimination from the secondary iodide. We could also use different good leaving groups such as tosylates, but as we started with iodides above, we'll stick with them.

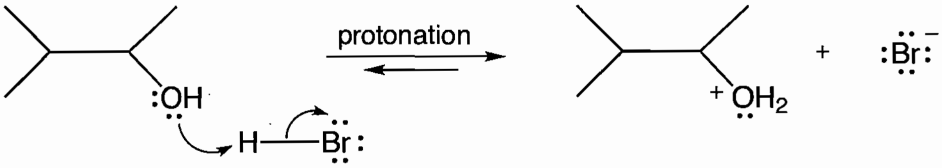


Now we need to make our reagents, isopropoxide and 1-iodohexane:

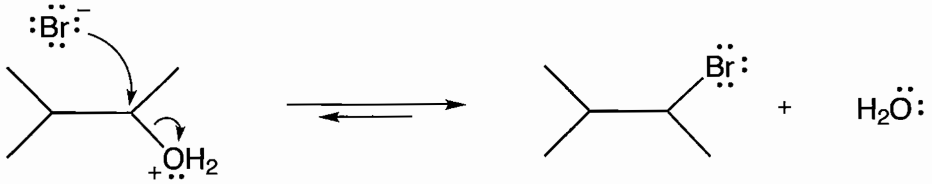
$$^{-}OCH(CH_3)_2 \xleftarrow{\text{NaH}} HOCH(CH_3)_2$$



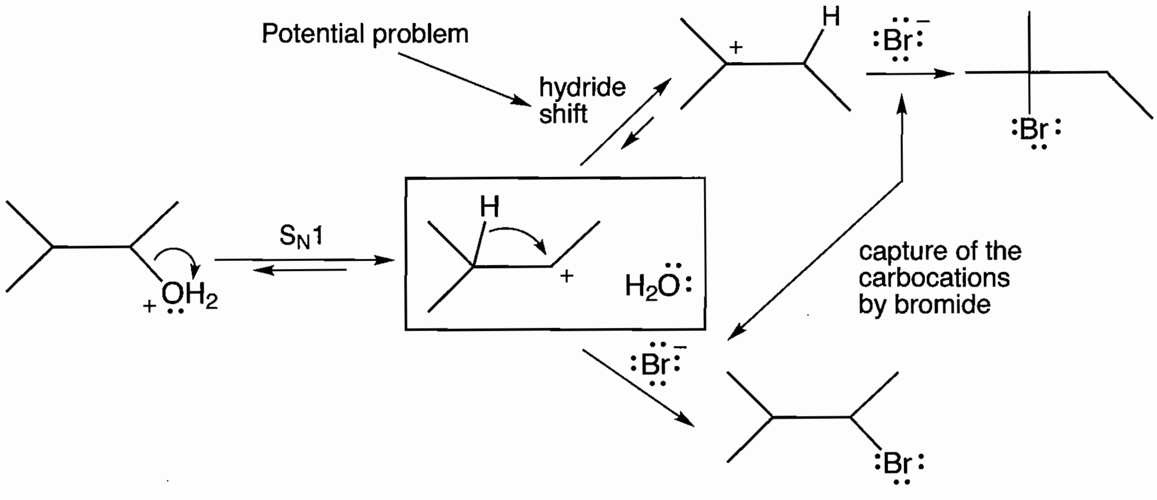
Problem 10.46 3-Methyl-2-butanol is a secondary alcohol, and it could react with hydrogen bromide and hydrogen chloride by either an S_N1 or S_N2 process (or both). In any case, the first step is protonation of the alcohol.



If the leaving group water is displaced by halide ion (shown here as bromide) in an S_N2 process, there should be no problem. (We might well expect this to be a relatively slow S_N2 reaction—Why?)

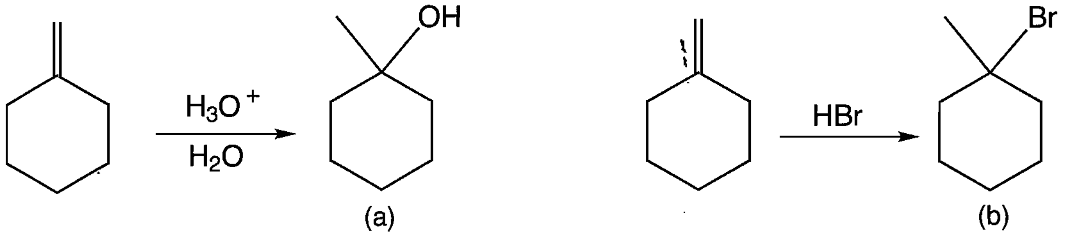


It is also possible that water could leave the protonated alcohol in an S_N1 reaction to give a secondary carbocation. If this cation is captured by halide ion, there is no problem. However, the secondary carbocation could also rearrange to the more stable tertiary carbocation through a hydride shift. If this happens, capture by halide will give 2-halo-2-methylbutanes.

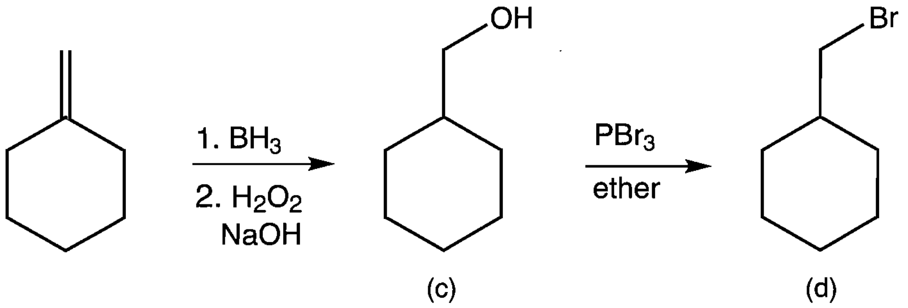


So, depending on the extent of the S_N1 component of these reactions, the desired 2-halo-3-methylbutanes could be contaminated with the isomeric 2-halo-2-methylbutanes.

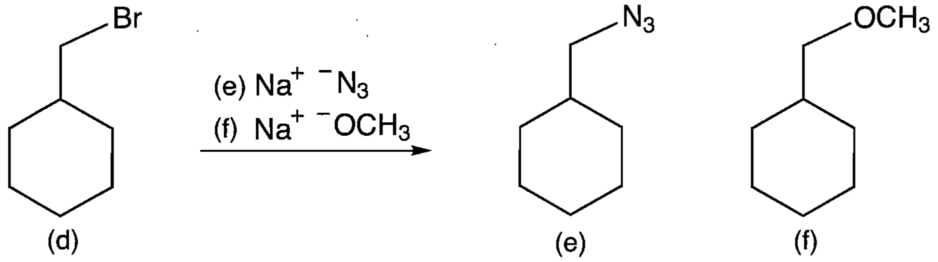
Problem 10.47 Two parts of this problem are extremely easy and require only that you remember a pair of simple Markovnikov addition reactions.



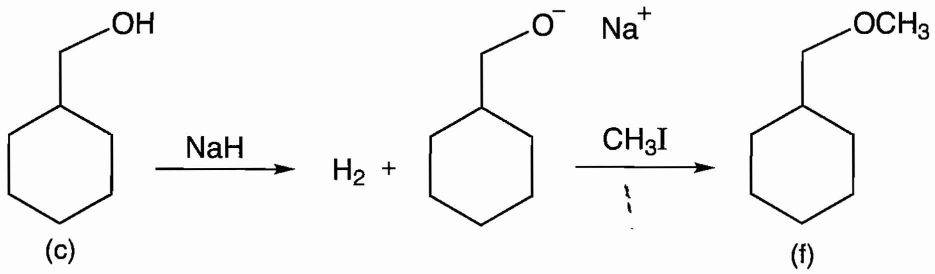
Another part, (c), involves hydroboration/oxidation to give anti-Markovnikov addition. As yet, you have no way of adding hydrogen bromide directly in an anti-Markovnikov sense, so the synthesis of (d) requires a further reaction of (c):



Similarly, (d) can be used to make (e) and (f) through S_N2 reactions.

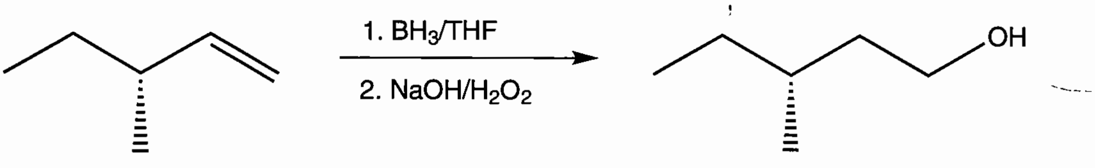


Sodium methoxide can be made from methyl alcohol by treatment with sodium hydride (NaH) or another strong base. There could be much E2 elimination in this process, however, as methoxide is a strong base. An alternative synthesis of (f) involves use of the alkoxide related to (c) as the displacing agent in an S_N2 reaction. This synthesis is a better route to (f).



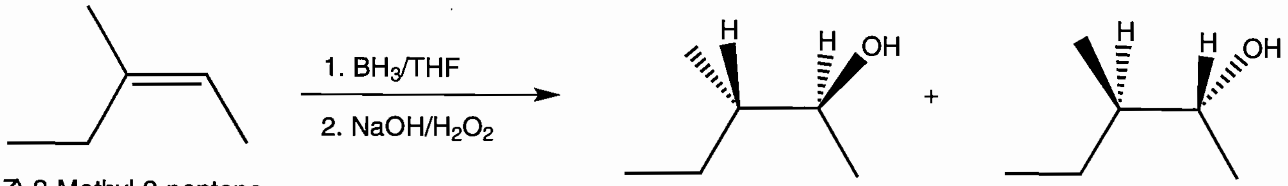
Problem 10.48

(a)



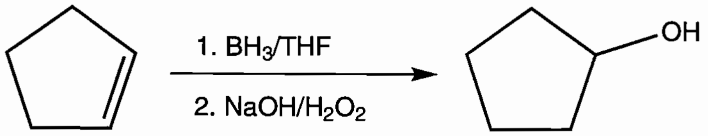
(*R*)-3-Methyl-1-pentene (*R*)-3-Methyl-1-pentanol

(b) Because the borohydride reaction occurs by syn addition, the reaction gives only (2*S*,3*S*)-3-methyl-2-pentanol and its enantiomer, (2*R*,3*R*)-3-methyl-2-pentanol.

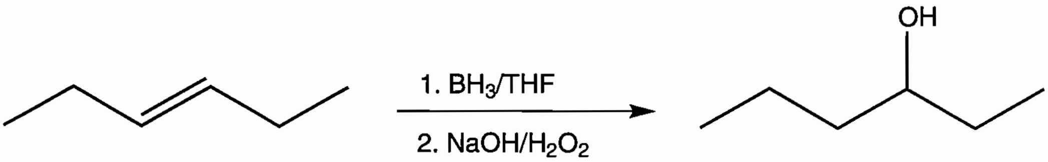


(*Z*)-3-Methyl-2-pentene

(c)



(d)



Problem 10.49

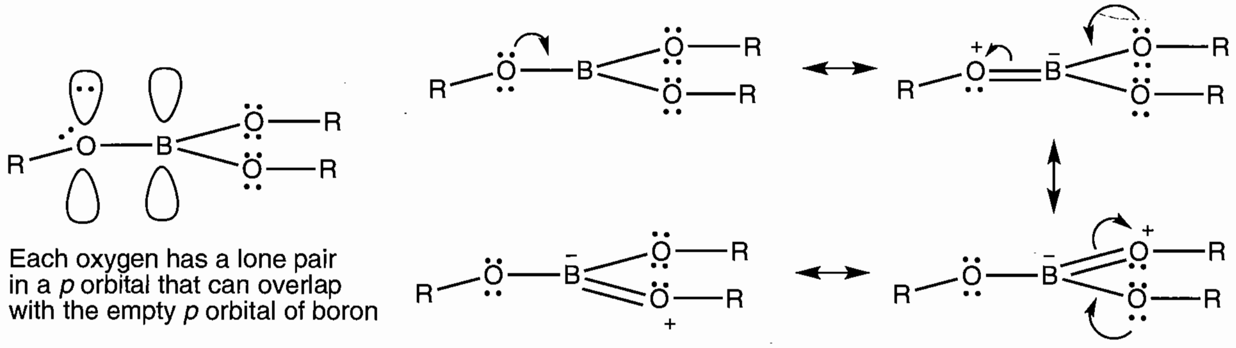
(a) (*R*)-3-Methyl-1-pentanol is chiral. The starting material, (*R*)-3-methyl-1-pentene, is also chiral. The product is formed as a single enantiomer because the starting material is a single enantiomer.

(b) The (2*S*,3*S*)-3-methyl-2-pentanol and (2*R*,3*R*)-3-methyl-2-pentanol products are chiral. The reaction gives a racemic mixture.

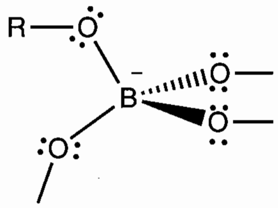
(c) Cyclopentanol is achiral.

(d) The product, 3-hexanol, is chiral. It is formed as a racemic mixture of both the (*R*) and the (*S*) enantiomers.

Problem 10.50 The boron–oxygen bond in $B(OR)_3$ has double bond character because of the resonance that is available between the empty *p* orbital of the boron and one lone pair from each of the oxygens.

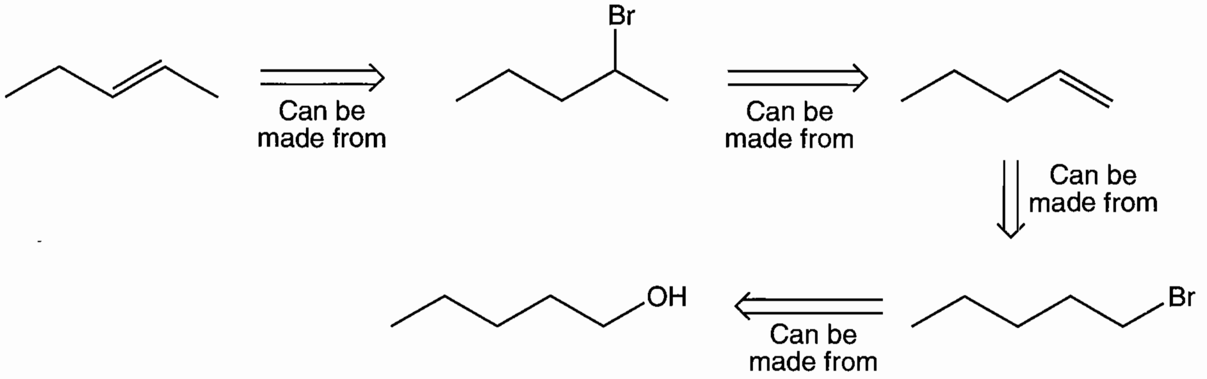


The $B(OR)_4^-$ is not able to delocalize its electrons because there is no empty *p* orbital on boron.

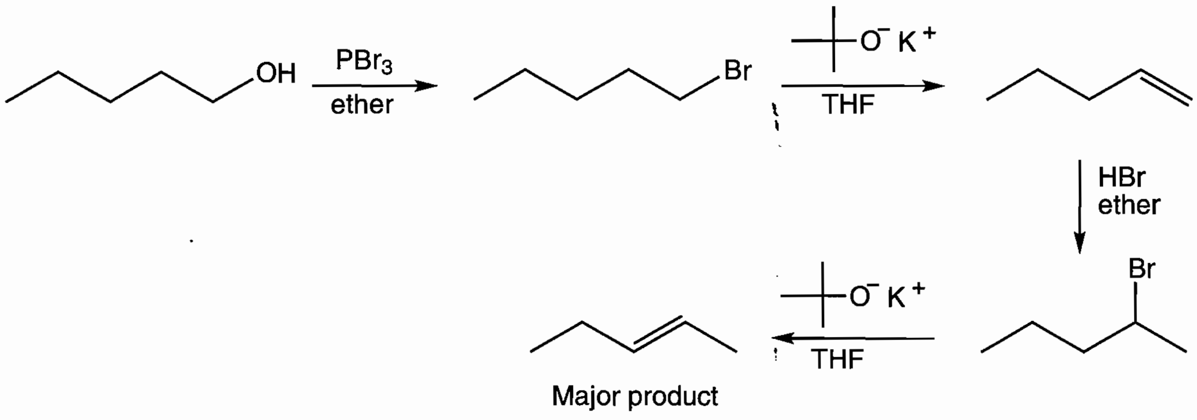


Problem 10.51 Formation of (*E*)-2-pentene could be done from 2-bromopentane using an E2 reaction, which would probably give the best yield of the desired product. An E1 reaction would certainly give a mixture of alkenes and S_N1 products. We can obtain the 2-bromopentane from 1-pentene. Although we could dehydrate 1-pentanol to obtain 1-pentene, the dehydration reactions are often accompanied by rearrangement. It would be better to make the 1-pentene from a controlled reaction such as an E2 pathway. That means we want to make 1-pentene from 1-bromopentane. We can make the 1-bromopentane from 1-pentanol using S_N2 chemistry to avoid carbocations.

Here is our analysis using arrows that tell us where each compound comes from.

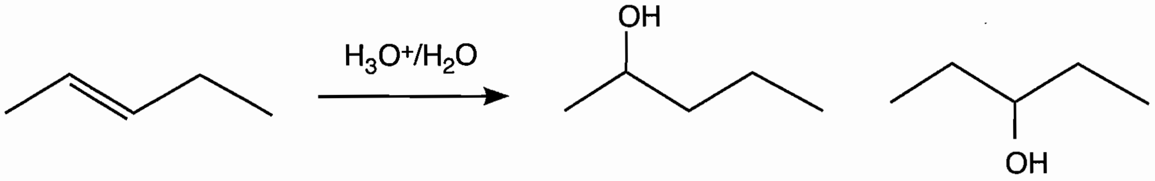


Putting it all together in a forward sense, we have:

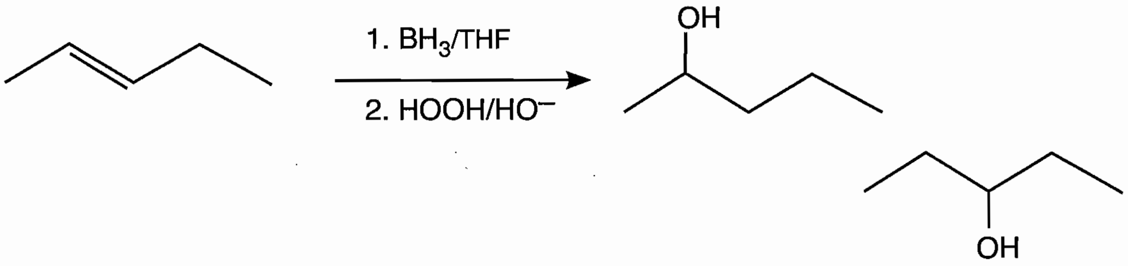


Problem 10.52 The selectivity for each of these reactions is poor because the carbocation intermediates would have a similar likelihood of formation.

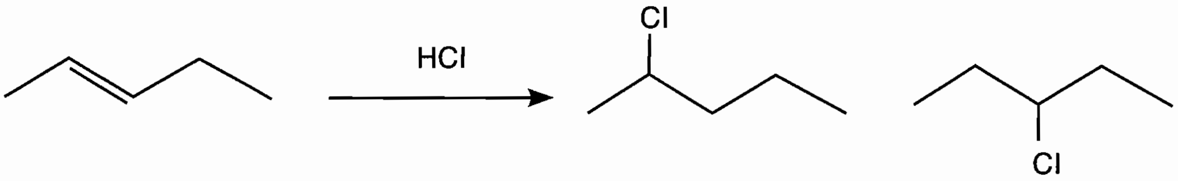
(a)



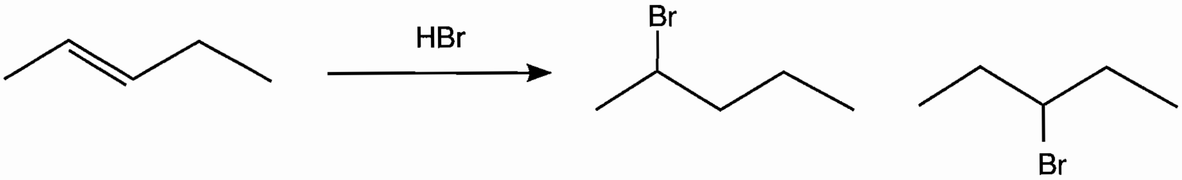
(b)



(c)



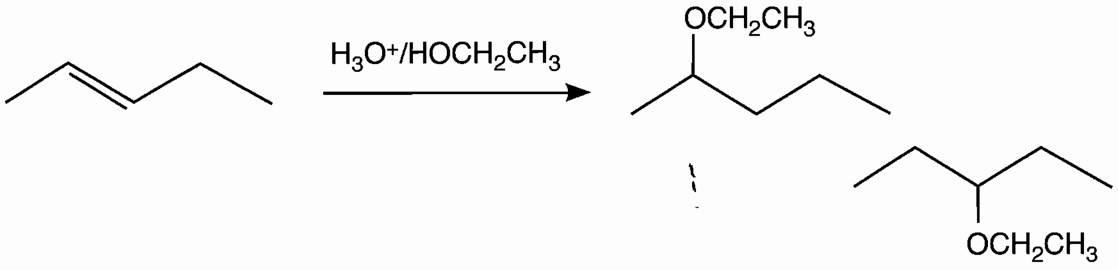
(d)



(continued)

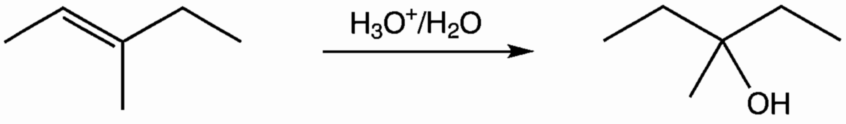
Problem 10.52 *(continued)*

(e)

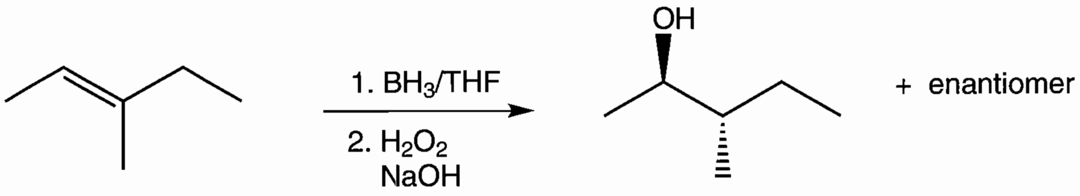


Problem 10.53

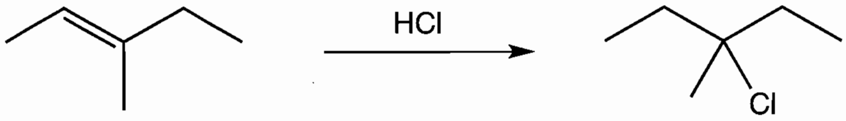
(a)



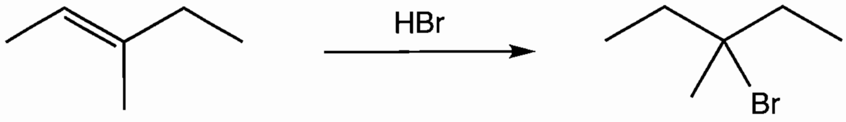
(b)



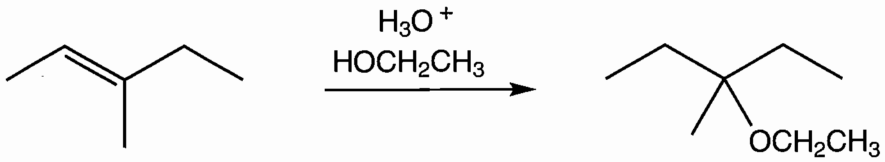
(c)



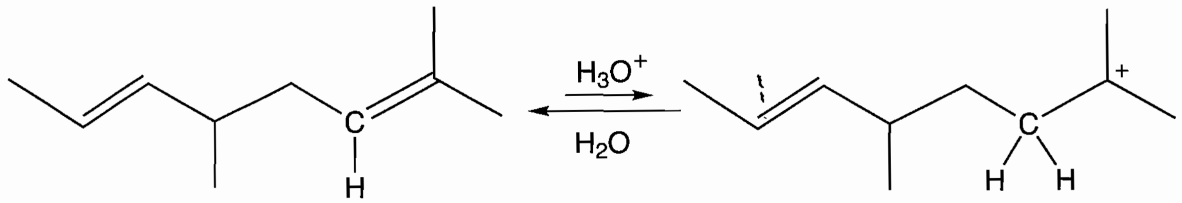
(d)



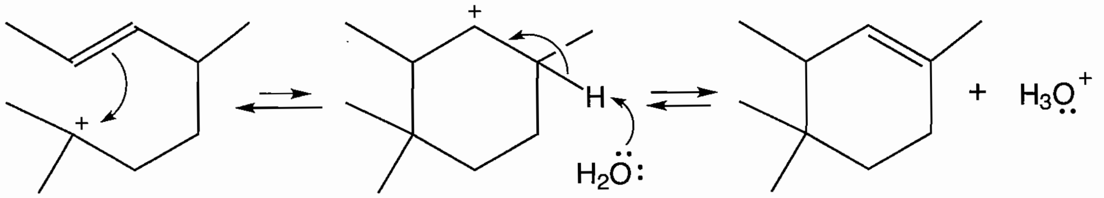
(e)



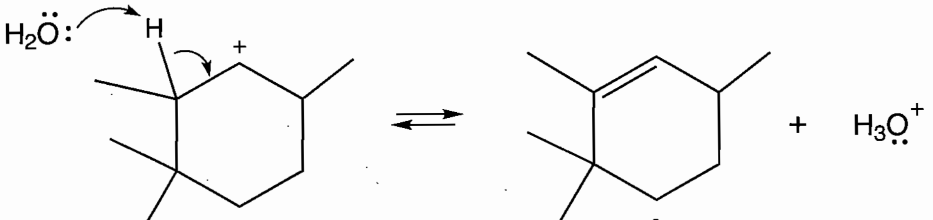
Problem 10.54 The best first step is protonation of the right-hand double bond so as to give the tertiary carbocation, the most stable carbocation possible in this system.



The product is a cyclic molecule, so clearly a ring must be closed. In this case, the carbocation (Lewis acid) adds to the internal double bond (Lewis base) to form a new carbon–carbon bond and close a six-membered ring. Don't be offended at the simplicity of this analysis; "the starting material is acyclic, but the product is cyclic; therefore a ring must be closed." It is extraordinarily important to think this way when doing problems.



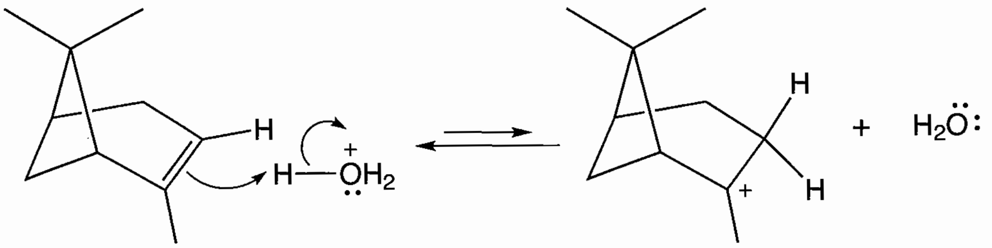
Here an important and vexing point arises. In the last step, there is another possible proton loss to give **A**, a molecule not formed in the reaction.



A

How is one to know which one to choose? The answer to this kind of question is frustrating, because sometimes the only answer is, Because of the structure of the product. There is no obvious (to us, anyway) reason that the final deprotonation goes the way it does. Can one just say, Because the product formed is more stable than the one that isn't formed? Well, you can say that, but it doesn't add anything, at least unless you can explain *why* the product shown is more stable. We are left to reason backward. Another way of putting this is to point out that it is not a fair question to ask which alkene would be formed from the cyclized carbocation. It is fair to show the product and ask how it is formed.

Problem 10.55 Once again, start by protonating to give the most stable possible carbocation.



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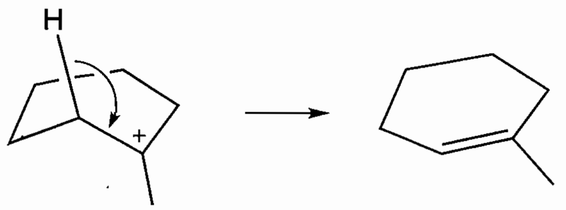
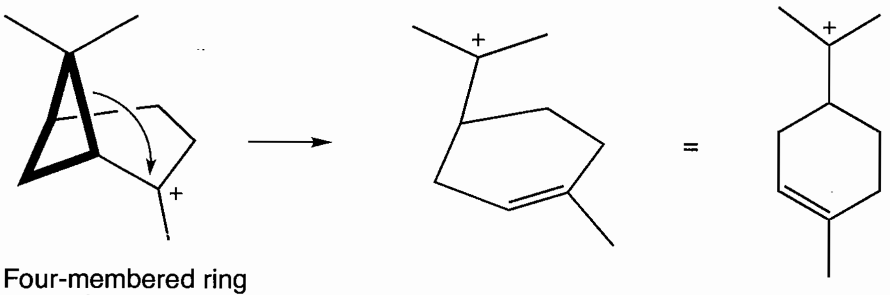
Problem 10.55 *(continued)*

Now look at the products. Clearly a ring has been opened. And it is not difficult to see why. The starting material contains a four-membered ring, and the strain of that ring is eliminated (no pun) if the ring opens. Just as a carbon–hydrogen bond adjacent to a carbocation can break, so can a carbon–carbon bond. That is what happens here. Notice that the carbocation produced is still tertiary.



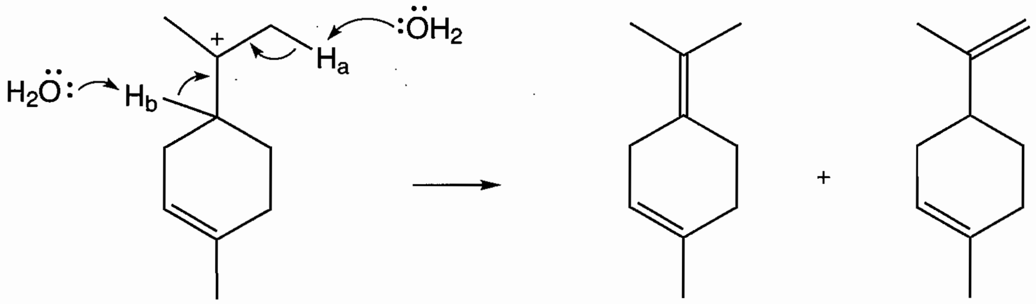
A familiar deprotonation

A less familiar, but closely related, carbon–carbon bond breaking

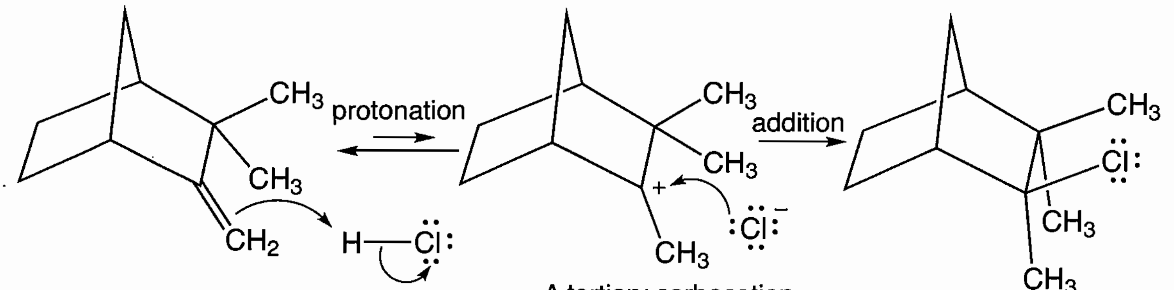


Four-membered ring in boldface

Now what? There are two possible proton losses (H_a and H_b), and they lead to the two observed products.

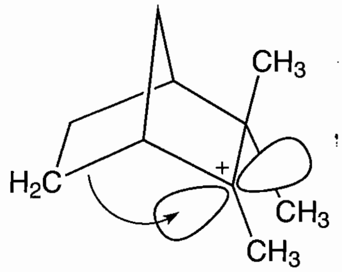


Problem 10.56 For the third time, the first step is protonation to give the tertiary carbocation. The "easy" product is formed by capture of this ion by chloride ion.

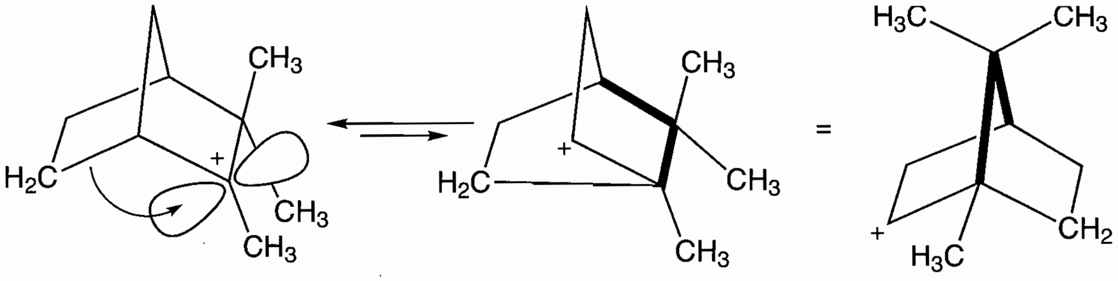


A tertiary carbocation

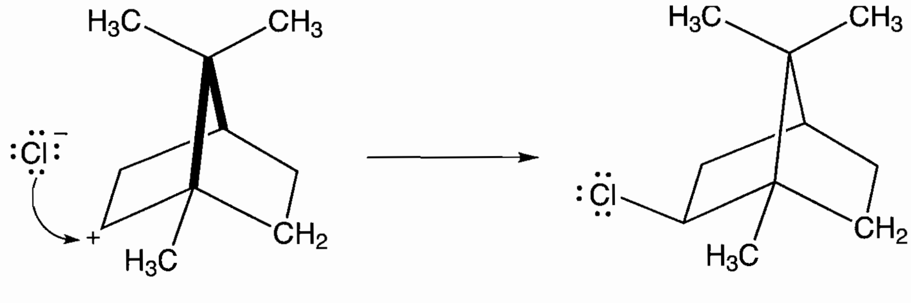
Finding the mechanism for the "hard" product is really difficult at this point. Here's how. First of all, recognize that something really strange has gone on. Apparently methyl groups have been wandering all over the place. Let's try to find another mechanism because these wholesale migrations are surely unlikely. Remember that carbons can migrate in carbocationic reactions (Wagner–Meerwein rearrangement). In the first-formed carbocation, there is a carbon atom beautifully poised for migration. The figure shows the lineup between the empty orbital of the carbocation and the carbon–carbon bond.



Migration of carbon does the trick, but it takes some spatial reorganizing to see it. Some labels are left in the drawing to show the relationship between the two pictures of the new cation.

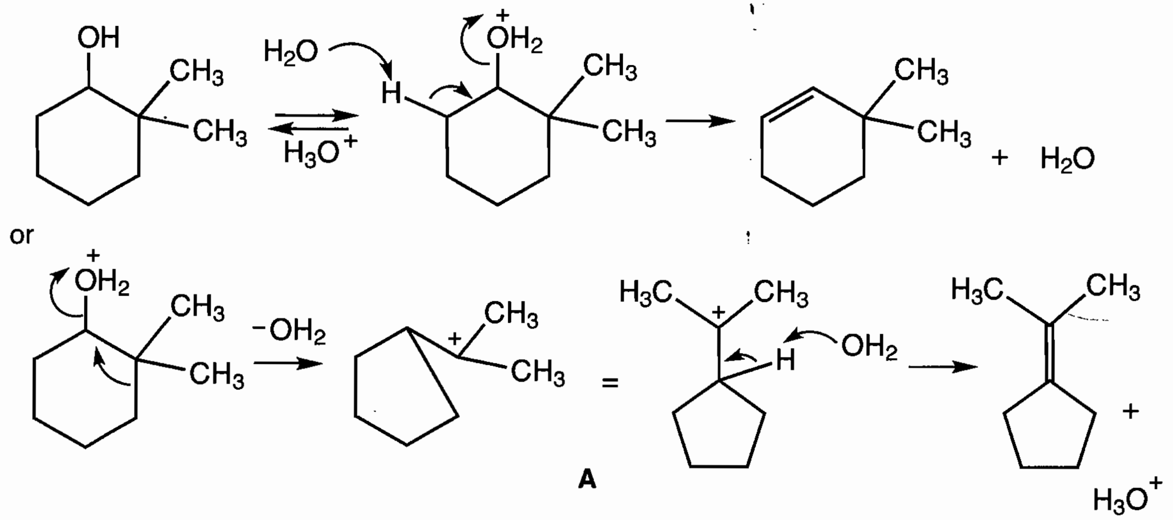


Capture by chloride gives the product.

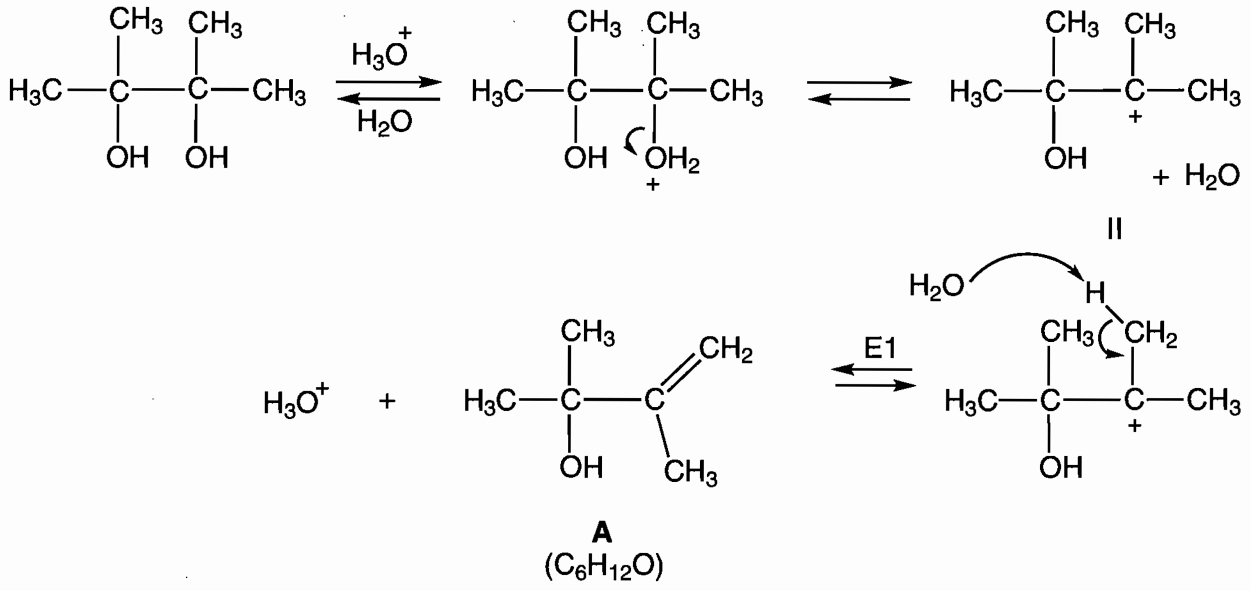


Why give a problem this hard? First, it "looks forward" to Chapter 24, where we shall see that the situation is even more complicated than it seems here. Second, it is not *that* hard, and it provides useful practice in spatial manipulation. Finally, and probably most important, problems like this are fun and mimic quite well what "real" chemists have to think about. When we find a strange compound in a reaction, we must seek a reasonable route for its formation, and sometimes that involves new chemistry that's hard for anyone to see at first. There is no reason to deny you this pleasure.

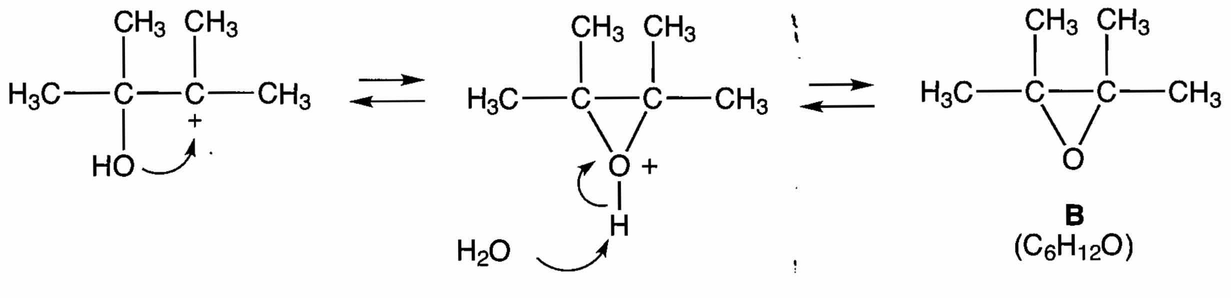
Problem 10.57 This problem begins with protonation of the alcohol. There is only one possible elimination, and this process generates one of the two products. The only difficulty in this problem is the second structure. Migration of a carbon–carbon bond gives a tertiary carbocation **A**, and now a proton can be removed to give the ring-contracted product.



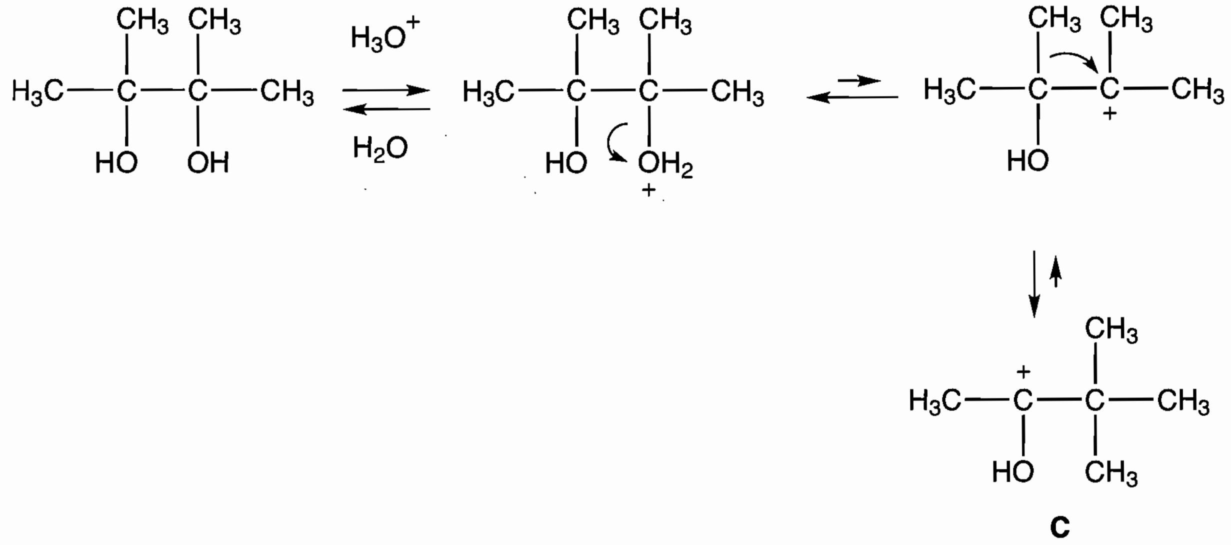
Problem 10.58 Surely the first step in the treatment of a diol in acid must be protonation of one OH. Loss of the good leaving group water (just the beginning of an $S_N1/E1$ sequence) leads to a tertiary carbocation. Loss of water seems to be a good step. Why? Look at the formula of the products, $C_6H_{12}O$. One oxygen atom has been lost from the starting material. The question now is, What further reactions are possible? If water re-adds, completing the S_N1 sequence, we simply regenerate starting material. The E1, however, is more promising as it does lead to a compound of the proper formula. The alkene **A** must be one of the "products" we are supposed to find.



Another possibility is capture of the carbocation, not by the external nucleophile, water, but by the internal nucleophile, the internal OH. This process leads to a protonated epoxide, and subsequent deprotonation gives the epoxide itself, **B**, another $C_6H_{12}O$.



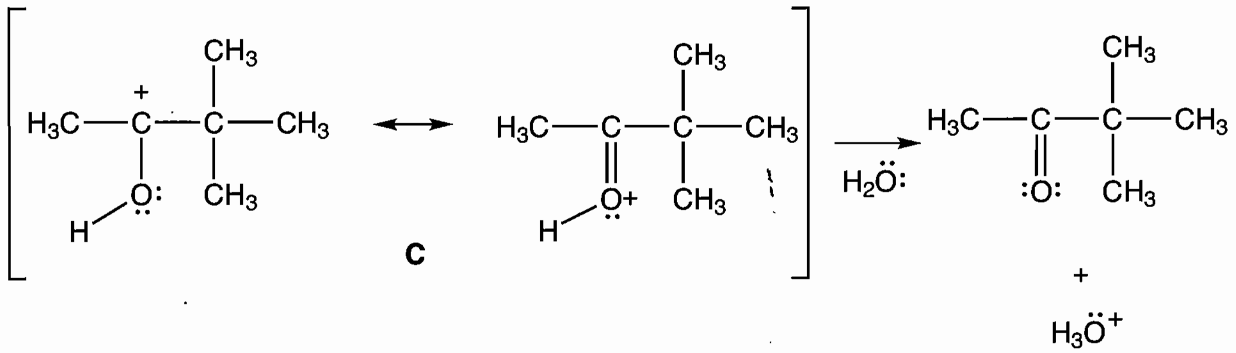
The mechanism of the pinacolone formation must have protonation and dehydration as the first two steps—there just isn't much else possible. Whenever you see a carbocation, and especially when the unexpected has happened, you are well advised to consider the possibility of rearrangement. We have seen this kind of reaction many times in carbocation chemistry. In fact, it appears whenever it is possible to migrate a group to give a more stable cation. In this molecule, there is only one possible migrating group, one of the adjacent methyl groups. The thing to do now is to write the product of this rearranged ion **C** and try to see if it looks more or less stable than the starting carbocation. We might suspect that we are on the right track because we have generated the appropriate carbon skeleton of pinacolone.



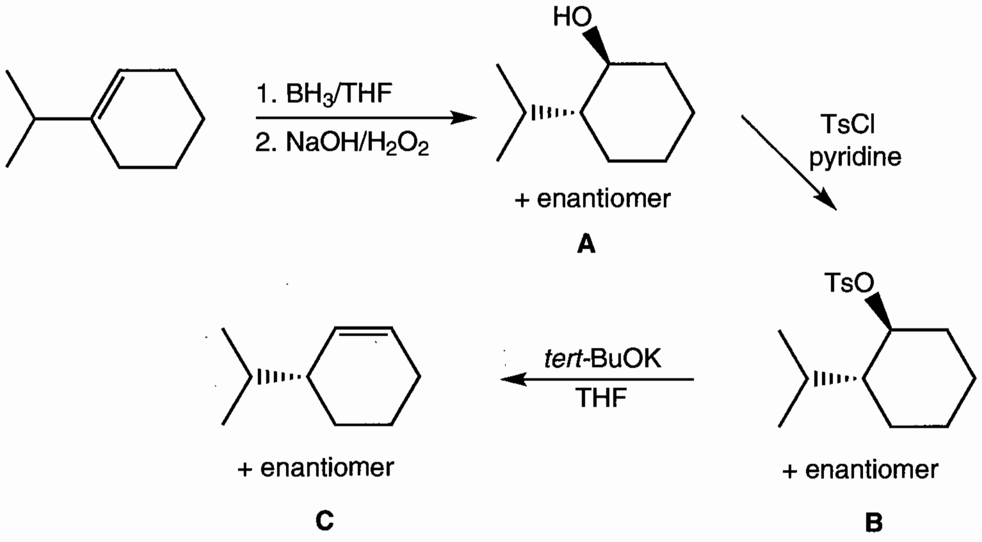
Cations flanked by heteroatoms bearing pairs of electrons are resonance stabilized, and it is this factor that makes the rearranged ion more stable than the starting cation. Deprotonation of the rearranged ion **C** by water gives the final product. This reaction, called the pinacol rearrangement, takes its name from the trivial name of the diol used in this example, pinacol, and is common whenever a 1,2-diol is treated with acid.

(continued)

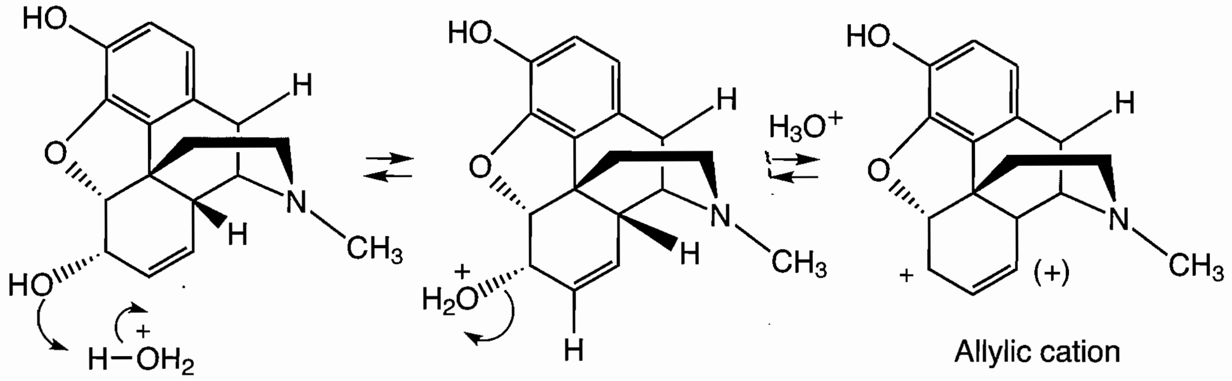
Problem 10.58 *(continued)*



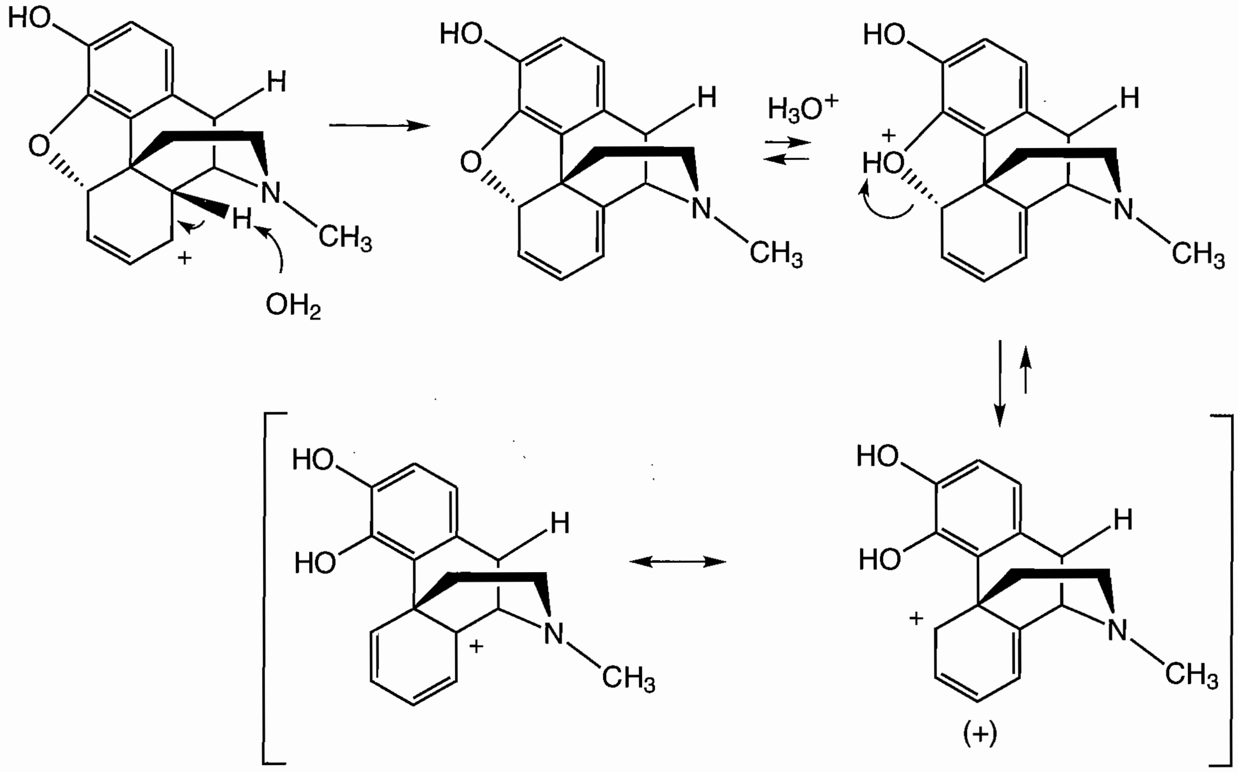
Problem 10.59 The first step of this sequence is the hydroboration/oxidation. Remember that this is a syn addition with the alcohol ending up on the less substituted carbon (anti-Markovnikov). The tosyl chloride reagent converts the alcohol into the tosylate, which is an excellent leaving group. In the last step, the E2 elimination will require an anti-periplanar β-hydrogen. This results in selective formation of product **C**. The only available anti-periplanar β-hydrogen is on the carbon to the right of the carbon bearing the tosylate, as drawn below.



Problem 10.60 This answer comes to you courtesy of Professor Grant Krow of Temple University and replaces our earlier, less good version. This problem is tough because there is a large number of "small" steps. Some of the basic outlines should be clear, however. The ether oxygen will become the second OH of the top benzene ring. The allylic OH will probably be lost in an elimination reaction that helps build the lower left ring in apomorphine. Somehow the bridge in morphine must become the new azacyclohexane ring. The real trick in this problem is to see how to do that transformation. What can happen in acid? Protonation of the alcohol, that's what. Loss of water leads to an allylic cation, nicely resonance stabilized.



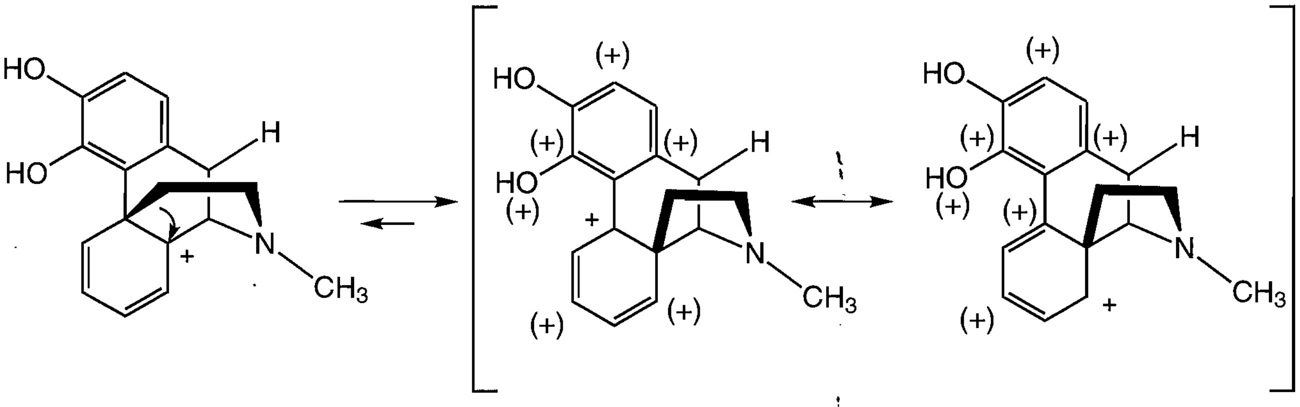
Deprotonation completes what is nothing more than an E1 elimination. Next, we protonate the ether oxygen and break a bond to make another resonance-stabilized cation.



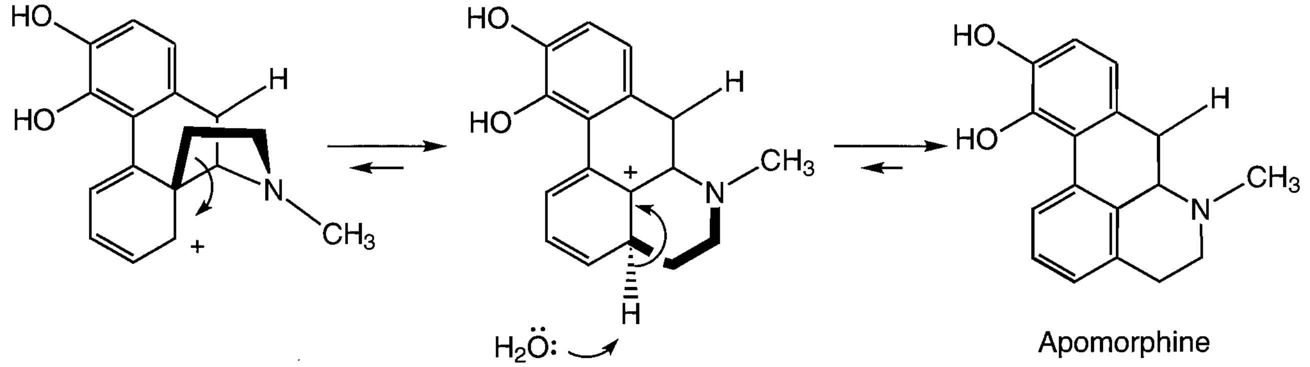
The bridge is now set to do its first migration to yield yet another beautifully resonance-stabilized cation. Look at all those atoms sharing the positive charge!

(continued)

Problem 10.60 *(continued)*



A second migration of the bridge establishes the final skeleton of the product; indeed in this rather economical mechanism (at least compared to our first effort!), we are now only a deprotonation away from the end:



Apomorphine

Problem 10.61 Here are the top views of allyl and pentadienyl:

Allyl	Pentadienyl
+ − +	+ − + − +
	+ − 0 + −
+ 0 −	+ 0 − 0 +
	+ + 0 − −
+ + +	+ + + + +

What generalizations can you make? Some things you know already. For example, you know that the number of molecular orbitals must match the number of atomic orbitals being combined. You also know that the number of nodes must increase monotonically (one more node each time) starting from the lowest molecular orbital with no nodes other than the node present in any orbital made from 2*p* orbitals.

Here are some generalizations:

(1) As long as you start at the left of the orbital with (+), the right-hand ends of the orbitals alternate sign, (+), (–), (+), (–), and so on. Presumably, if nature is a kind, symmetrical creature, this observation will always be true.

(2) The highest molecular orbital is always alternating (+) and (–). You already know the lowest energy molecular orbital is "all +." So, you can specify the lowest and highest molecular orbitals with no trouble.

(3) The middle molecular orbital is always (+), (0), (–), (0), (+), and so on.

(4) The pattern of zeros (atoms at which the sign of the wave function is zero) is symmetrical, and the number of zeros increases by one to the middle molecular orbital, then decreases by one.

Perhaps you can find other "rules." These observations, together with some faith that nature is symmetrical at this level, allow us to write molecular orbitals for acyclic, "linear" fully conjugated systems quite easily. But don't extend this business too far! These rules won't work for systems containing even numbers of carbons or cyclic molecules. For such systems, you will need other observations.

Problem 10.62 Let's apply the observations from Problem 10.61. First, there will be seven molecular orbitals and the nodes will increase monotonically. Next, the bottom (lowest energy) and top (highest energy) molecular orbitals must be as in drawing (a). We can next add the middle molecular orbital as in (b). Next, add the ends of all the molecular orbitals (c), and fill in the orbital second lowest in energy. It has only a single node and is always easy to draw (d). Now the work begins. The next-to-highest molecular orbital will have a zero in the same place as the next-to-lowest, and the two other molecular orbitals will each have two "zeros." Given that information, it is not so hard to fill the rest in (e). At the end, check to see that the proper nodal pattern (0...1...2...3...) appears.

+ − + − + − +	+ − + − + − +	+ − + − + − +	+ − + − + − +	+ − + − + − +	6
		+ −	+ −	+ − + 0 − + −	5
		+ +	+ +	+ − 0 + 0 − +	4
	+ 0 − 0 + 0 −	+ 0 − 0 + 0 −	+ 0 − 0 + 0 −	+ 0 − 0 + 0 −	3
		+ +	+ +	+ + 0 − 0 + +	2
		+ −	+ + + 0 − − −	+ + + 0 − − −	1
+ + + + + + +	+ + + + + + +	+ + + + + + +	+ + + + + + +	+ + + + + + +	0
(a)	(b)	(c)	(d)	(e)	Nodes

Problem 10.63 The central carbon is sp^2 hybridized in the intermediate. The intermediate is planar and the central carbon is attached to three other carbons.

The calculated lowest unoccupied molecular orbital shows that there is considerable sharing of the positive charge throughout the molecule, particularly with the carbon–hydrogen bonds that are parallel to the empty *p* orbital.

An approaching nucleophile can attack the empty *p* orbital from above or below (S_N1 reaction). It might also deprotonate one of the acidic hydrogens, those that have so much of the LUMO density. Remember that the LUMO is where the positive charge resides, and the hydrogens that have positive charge are by definition acidic.

Problem 10.64 There needs to be a high concentration of alkene. An alkene needs to collide with the carbocation before any other nucleophile (such as water) does.

The number of monomers needed to make a polymer is not a fixed value. Most useful polymers are of the order several thousand monomers long. This value (the number of monomers in the polymer) is referred to as the *degree of polymerization*.

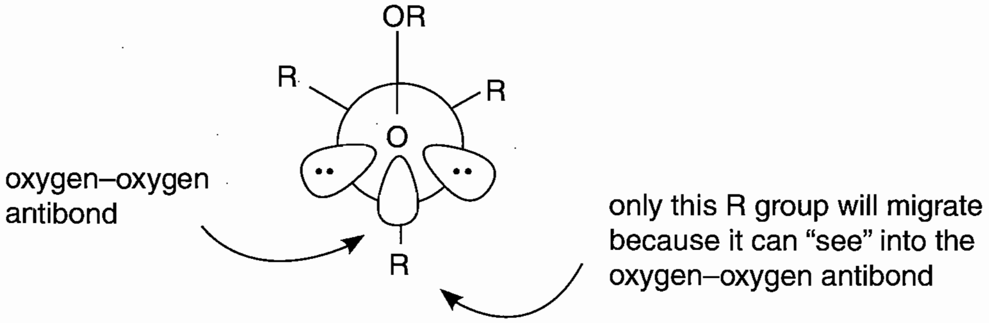
Problem 10.65 Carbocations are unstable. It isn't possible for a carbocation to just hang around. Therefore, a polymer is most unlikely to be charged.

One of the properties of milk jugs is that they don't react with the milk. Milk is mostly water. If the polymer had carbocations, then these charged carbons would react with the water in the milk.

A final step that you likely thought of is elimination. In the absence of more alkene to make a longer polymer, the carbocation probably eliminates. There might also be traces of water present in the polymer-forming process, and, as noted above, the carbocation would react with those water molecules.

Problem 10.66 The main difficulty is not knowing what the reacting borane species actually is. We know the borane is highly solvated by the tetrahydrofuran (THF), but at what point does the alkene displace the THF? We don't know how strong the borane complex with THF is in the presence of the alkene.

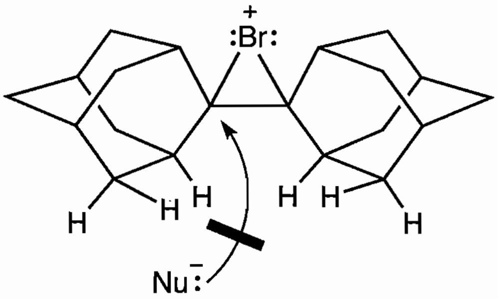
The alkyl group that shifts is the alkyl group that is anti to the oxygen–oxygen bond. The σ bond of the migrating alkyl group overlaps with the σ^* antibond of the weak oxygen–oxygen bond (hyperconjugation again). It is only the group in the anticonformation that can overlap efficiently with the antibond. The Newman projection looking down the oxygen–boron bond (boron in the back) might help you see this relationship.



11

More Additions to π Bonds

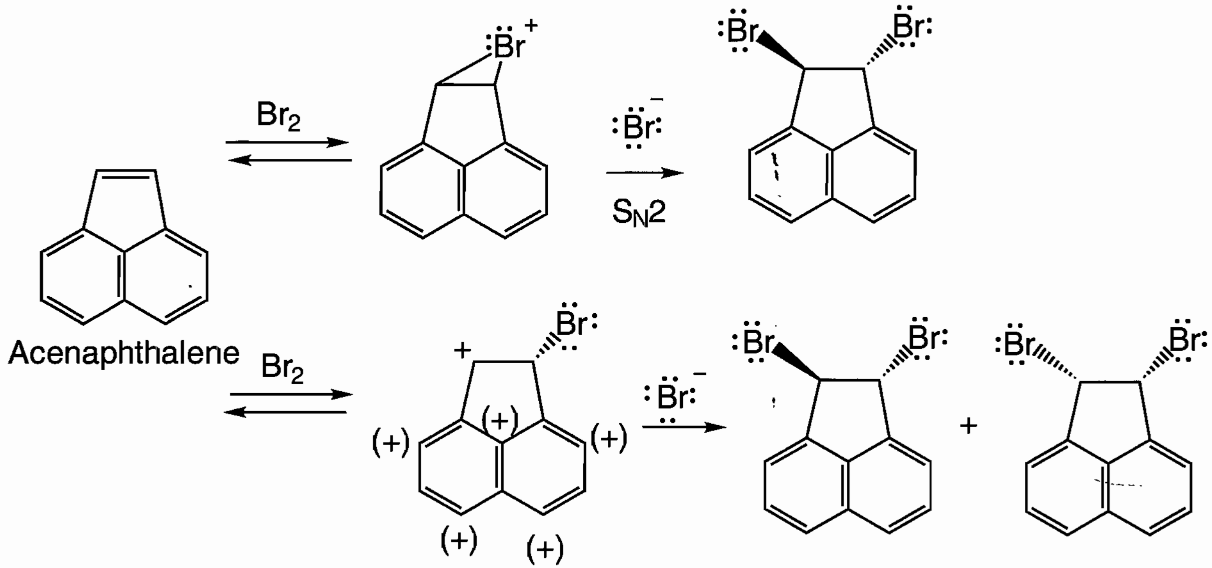
Problem 11.2 Another easy one, possibly even too easy for you to trust your answer. The bulky adamantyl groups simply shield the rear of the carbon–bromine bonds in the bromonium ion, making S_N2 attack difficult.



Problem 11.3 In this case, formation of the open carbocation competes favorably with formation of the bromonium ion. The reason is that the open cation is exceptionally well stabilized by resonance. The open cation can lead to both cis and trans products, whereas the bromonium ion is destined to give only trans dibromide. Note again the convention we use in which a charge in parentheses is used to show the various atoms sharing the charge. If it is not obvious that the charge is delocalized to these positions, draw out the resonance forms.

(continued)

Problem 11.3 *(continued)*



Open cation, well stabilized by resonance

Both cis and trans products, from addition to both sides of the planar carbocation

Problem 11.4

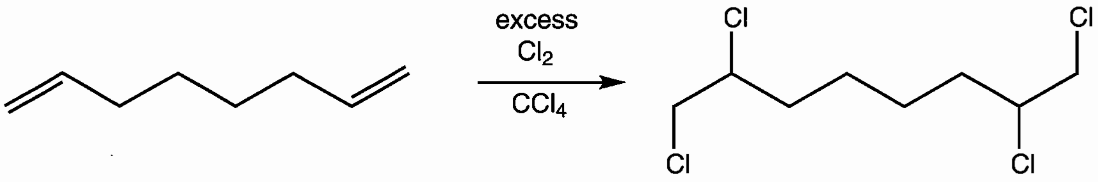
(a) The bromination of an alkene results in addition of Br to each of the alkene carbons. Presumably the addition is anti, but we are unable to know in this case.

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2 \xrightarrow[THF]{Br_2} CH_3{-}CH_2{-}CH_2{-}CH_2{-}CHBr{-}CH_2Br$$

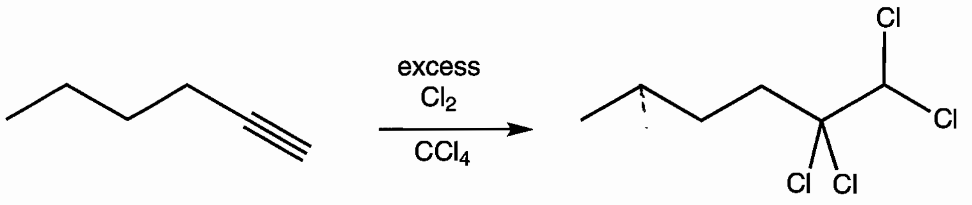
(b) We do not know if the initial 3-hexene in this problem is the (*Z*) or (*E*) isomer. Therefore, we cannot specify the stereochemistry of the dibromide product. But we predict that the bromination occurred via anti addition.

$$CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3 \xrightarrow[THF]{Br_2} CH_3{-}CH_2{-}CHBr{-}CHBr{-}CH_2{-}CH_3$$

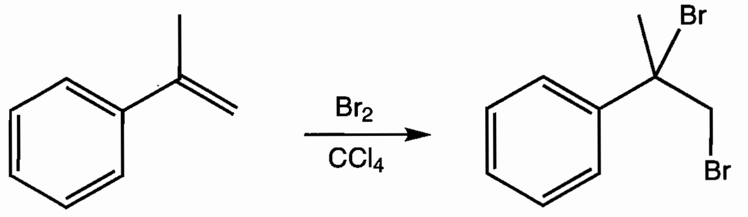
(c) Chlorination results in addition of Cl to each of the alkene carbons. We assume the addition is anti, but we have no way to know when halogenating a terminal alkene.



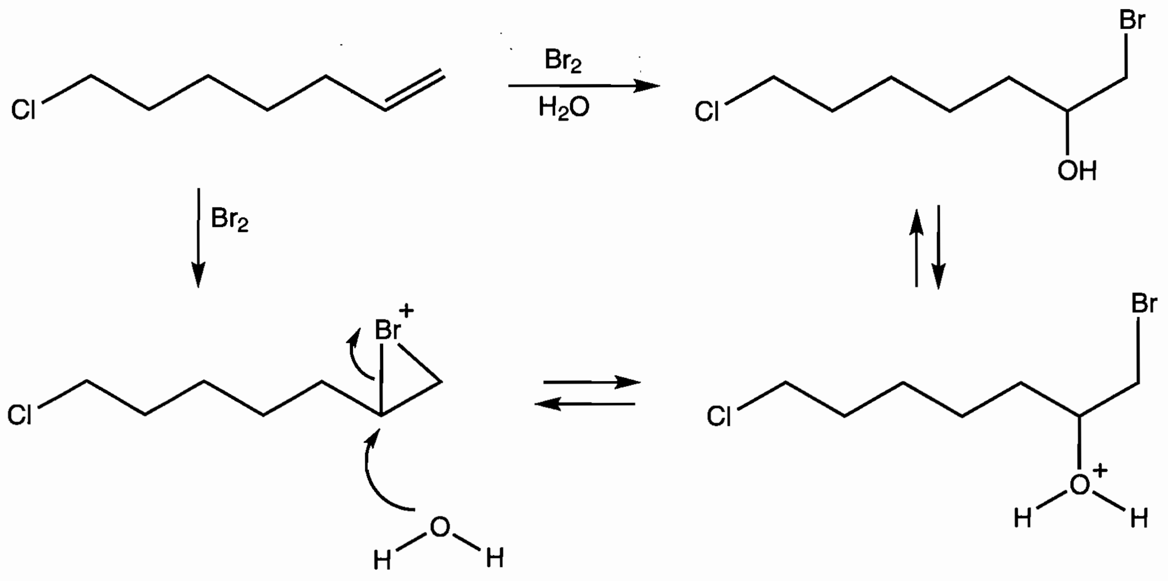
(d) An alkyne adds Cl_2 across the two π bonds to give the tetrachloride. Although we are unable to verify the stereochemistry of addition, we expect each Cl_2 adds anti.



(e) The π bonds of an aromatic ring are not as reactive with electrophiles as an alkene. So the bromination occurs only on the propene carbons. Even in excess Br_2, the reaction will give only 1,2-dibromo-2-phenylpropane.

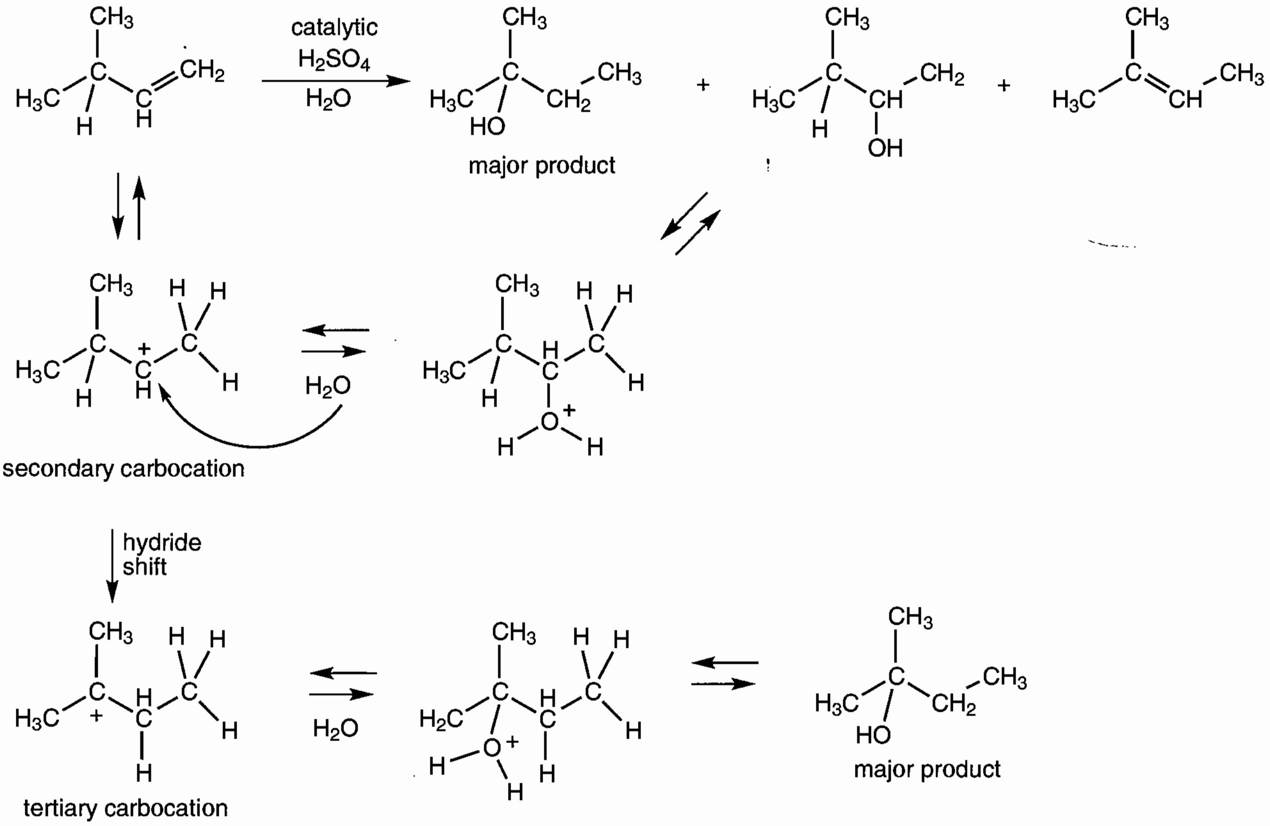


(f) The Br_2 electrophile adds to the alkene to form a bromonium ion. Water will react with the bromonium ion by adding from the backside of the weaker bond of the bromonium ion intermediate. The result is addition of water at the more substituted carbon. After deprotonation, the halohydrin is formed. Notice that the alkyl chloride is unaffected by the reaction.

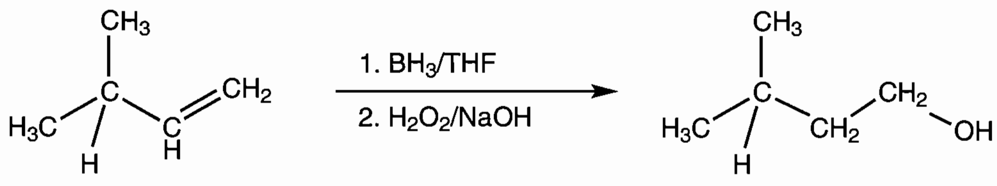


Problem 11.6

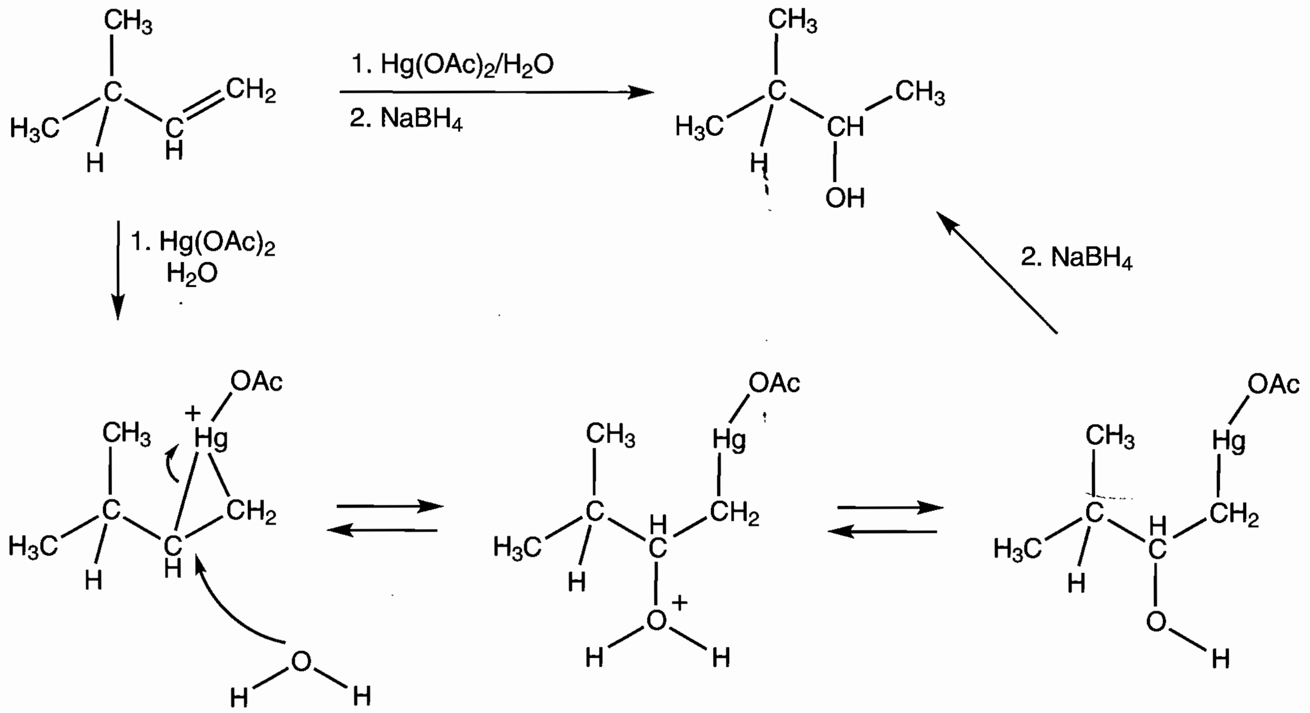
(a) The first step of the acid-catalyzed hydration of 3-methyl-1-butene forms a secondary carbocation, which will rearrange to form the more stable tertiary carbocation. It is the more stable carbocation that will be captured by the water to form 2-methyl-2-butanol. We also know that water can react with the secondary cation to give 3-methyl-2-butanol. The E1 product can also be formed.



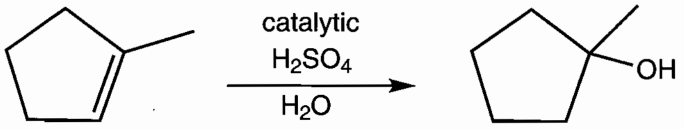
(b) The hydroboration/oxidation reaction does not involve a free carbocation. So there will not be any rearrangement. The product is a result of addition of boron and hydride across the alkene, presumably via syn addition. The boron is the electrophile. The oxidation step results in replacement of the boron by the OH group.



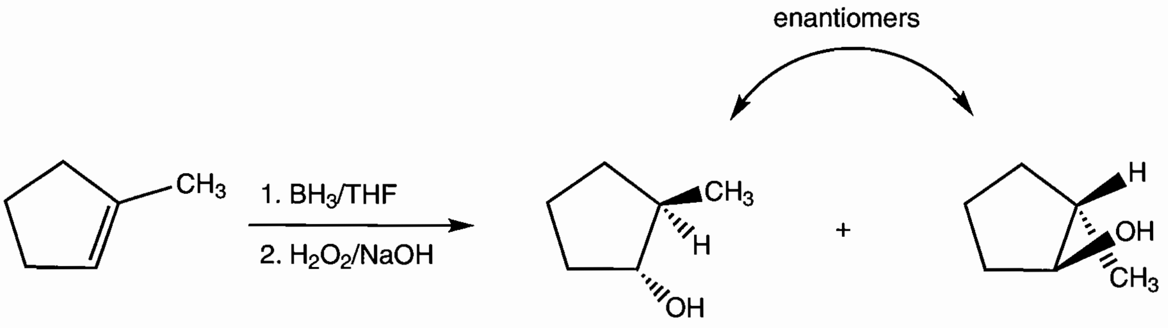
(c) The oxymercuration reaction does not involve a free carbocation. The initial mercurinium ion is opened by water attacking the more substituted carbon. The product is a result of anti addition of an OH group and mercury to the carbons of the alkene. The demercuration step replaces the mercury with hydrogen.



(d) No rearrangement is predicted in this reaction. The intermediate tertiary carbocation is relatively stable.



(e) The syn addition results in a racemic mixture of *trans*-2-methylcyclopentanol. Syn addition means that the groups that are added are adding to the same face (top or bottom) of the alkene. In this case, the groups that add to the alkene are boron and hydrogen. The boron is replaced by an OH in the second step of the reaction. The H and the OH have been added to the same face of the alkene in both products, giving the two enantiomers shown.

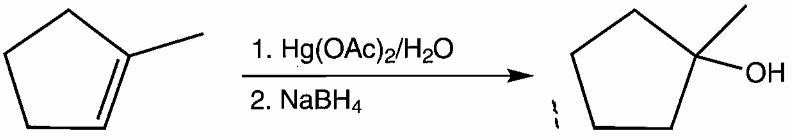


(1*R*,2*R*)-2-methylcyclopentanol (1*S*,2*S*)-2-methylcyclopentanol

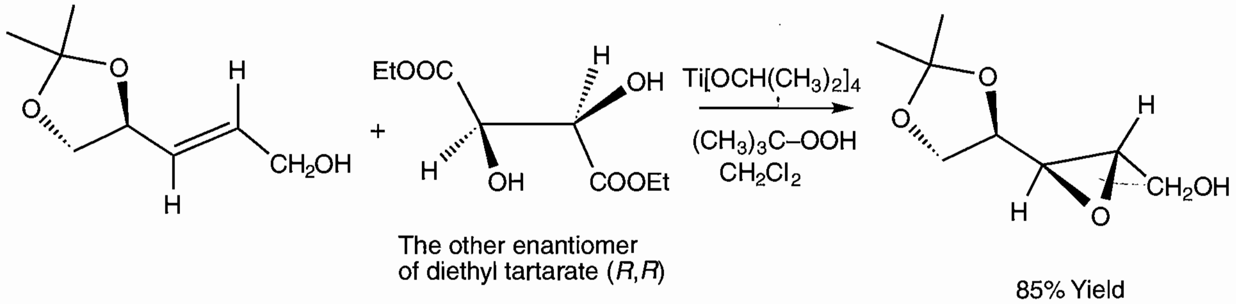
(continued)

Problem 11.6 *(continued)*

(f)

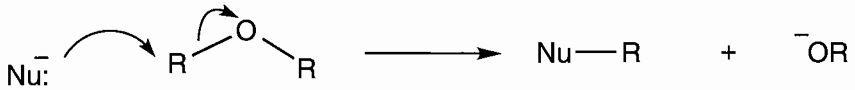


Problem 11.7 The new oxygen atom will be delivered to the other side of the double bond. So, the product, formed in 85% yield, is:

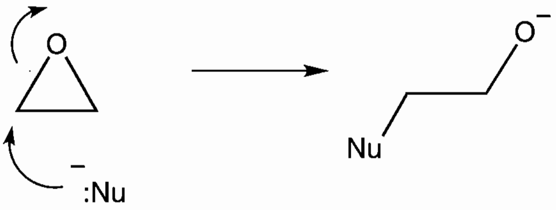


Problem 11.8 The difference appears because of the strain energy of the three-membered ring. The energy of the starting material is raised, and therefore the activation energy for reaction declines. Cyclopropane is strained by some 27 kcal/mol, and an oxirane cannot be very different. Both of these species will be more reactive than their unstrained counterparts, and ring openings of epoxides by nucleophiles are common.

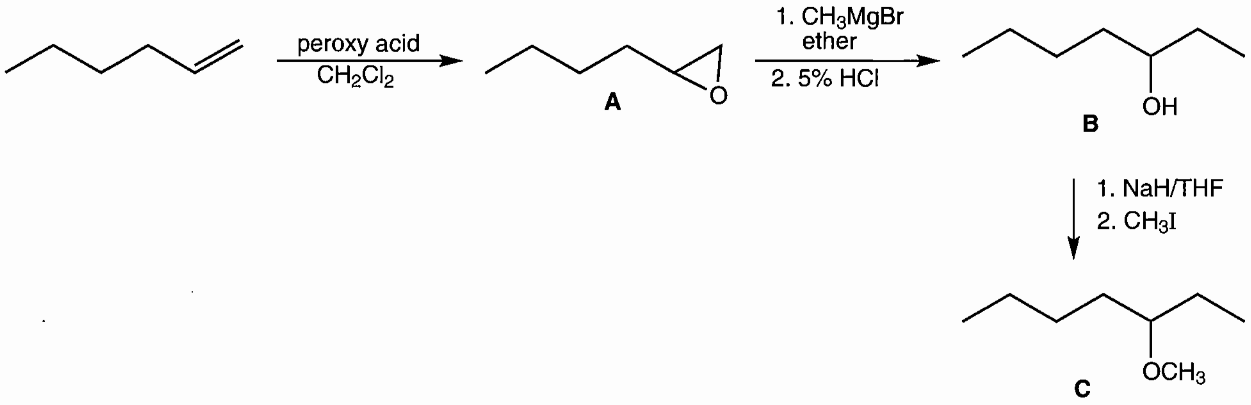
A very rare reaction; alkoxide is a poor leaving group



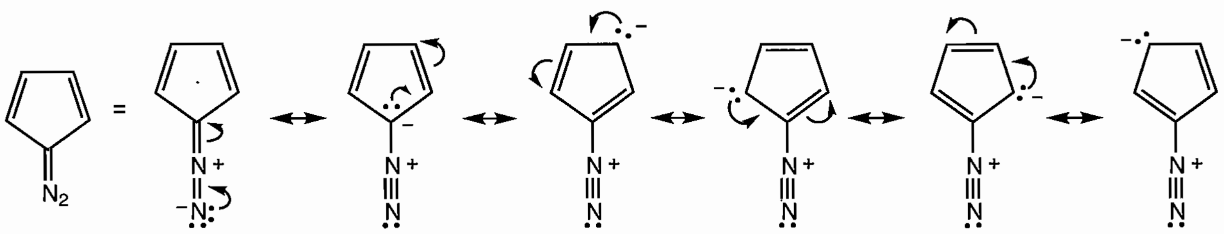
The strain in the three-membered ring raises the energy of the starting material and makes this ring opening possible



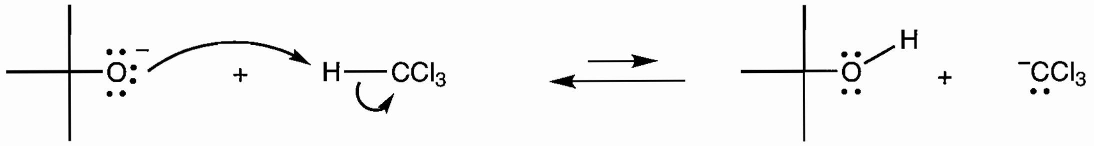
Problem 11.9 In the second step of this sequence, the Grignard reagent adds to the less substituted carbon of the epoxide.



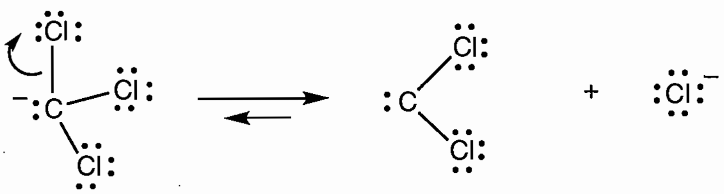
Problem 11.10 There are many resonance structures that can be drawn for diazocyclopentadiene. The first task is to draw the full structure of the diazo compound itself. The five resonance structures that we can draw by moving the anion around the five-membered ring are structures that contribute most for reasons we will see in Chapter 14.



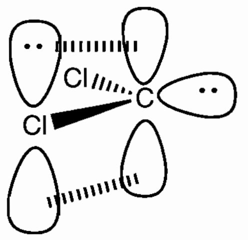
Problem 11.11 Although chloroform is not a strong acid, it can be deprotonated in strong bases such as potassium *tert*-butoxide (or sodium hydroxide).



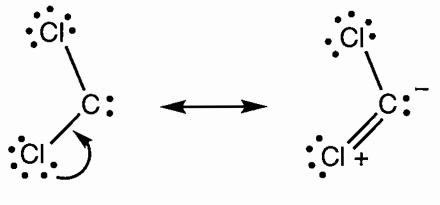
The trichloromethyl anion can lose a chloride ion to give the carbene.



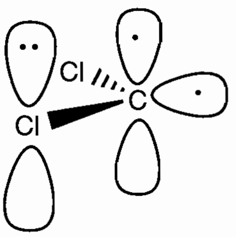
Problem 11.12 In the singlet state, the empty $2p$ orbital on carbon overlaps with a filled $3p$ orbital on chlorine. This resonance between the empty orbital and a filled orbital is not as stabilizing in the triplet because it is between an orbital with one electron and a filled orbital. The triplet will have three electrons in the π system, which means two electrons will be in the bonding orbital and one electron will be in the antibonding orbital. It is that one electron in the antibonding orbital that makes the triplet less stable than the singlet.



Singlet: Only one filled orbital on one of the Cl atoms is shown; the overlap with the empty $2p$ orbital on carbon is shown

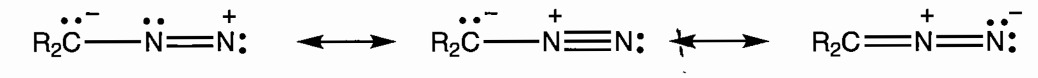


Resonance: We can represent the electron delocalization for the singlet carbene by drawing its resonance structure

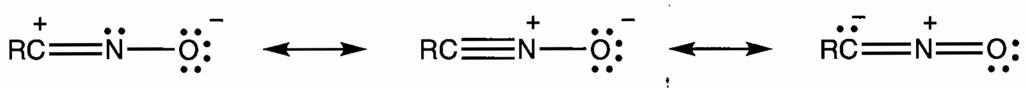


Triplet: The $2p$ orbital on carbon is half filled; overlap with the filled $3p$ orbital on either adjacent Cl atom is not as stabilizing as in the singlet

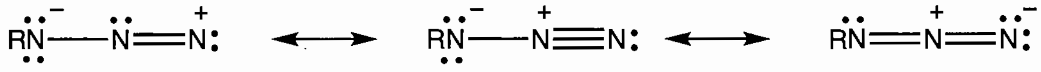
Problem 11.13 The resonance forms shown in Figure 11.45 emphasize the 1,3-dipolar nature of these reagents. Each of the resonance structures drawn for the 1,3-dipoles have all atoms with a filled octet. Other resonance structures can be drawn.



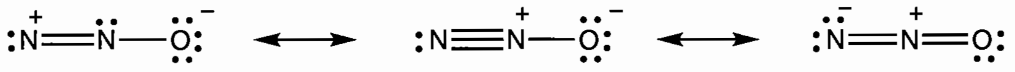
Diazo compounds



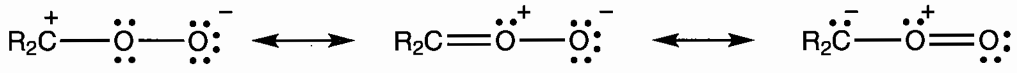
Nitrile oxides



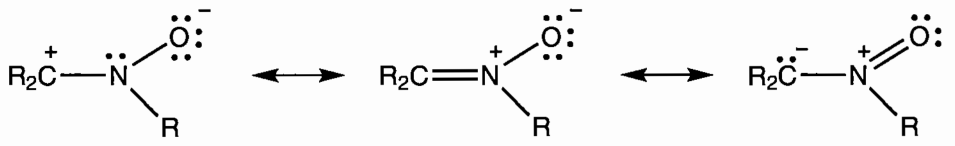
Azides



Nitrous oxide



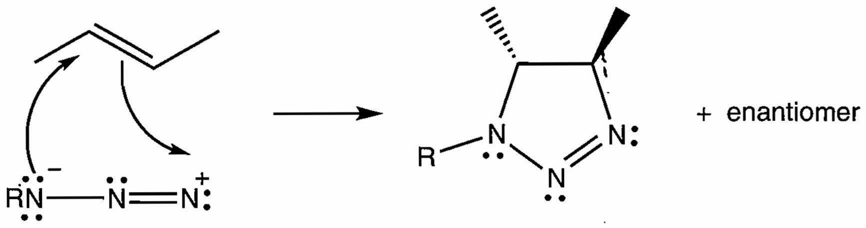
Carbonyl oxides



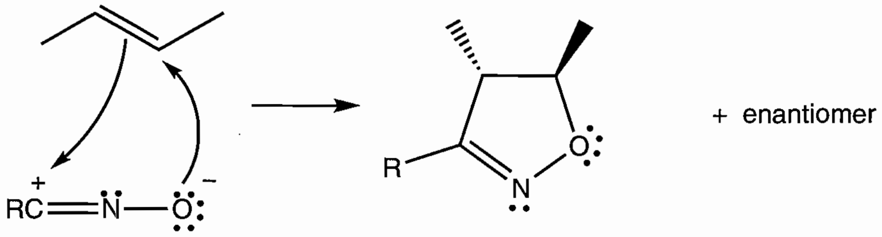
Nitrones

Problem 11.14

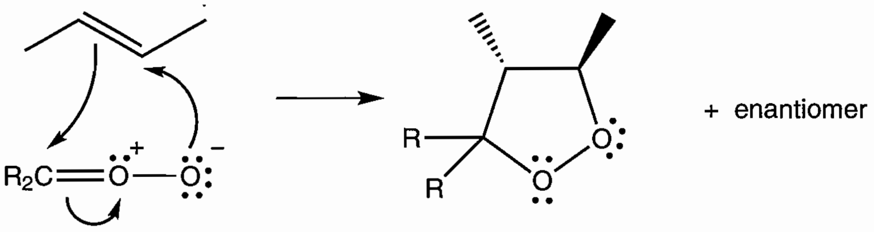
The reaction of an azide with (*E*)-2-butene:



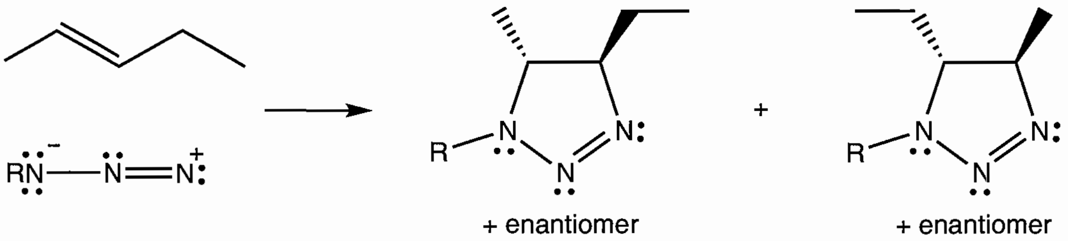
The reaction of a nitrile oxide with (*E*)-2-butene:



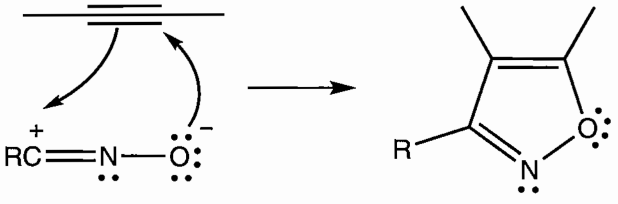
The reaction of a carbonyl oxide with (*E*)-2-butene:



Because the 1,3-dipole reagents are unsymmetrical, reaction of one of them with (*E*)-2-pentene will result in two products in each case. For example, here is a reaction with an azide with (*E*)-2-pentene:

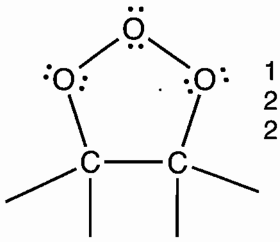


Because of symmetry, reaction of one equivalent of dipolar reagent with 2-butyne will give only one product. For example, here is the reaction of a nitrile oxide with 2-butyne:



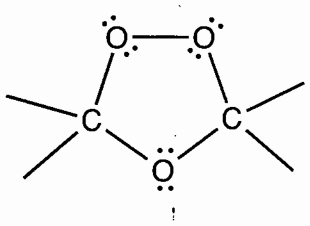
Problem 11.15 Some approximations must be made here. In this answer, we use the bond energy of ethane for the carbon–carbon bonds, the bond energy of a simple alcohol for the carbon–oxygen bonds, and the bond energy for di-*tert*-butyl peroxide for the oxygen–oxygen bonds. The final ozonide is much more stable than the primary ozonide.

Less stable
(weaker overall bonding)



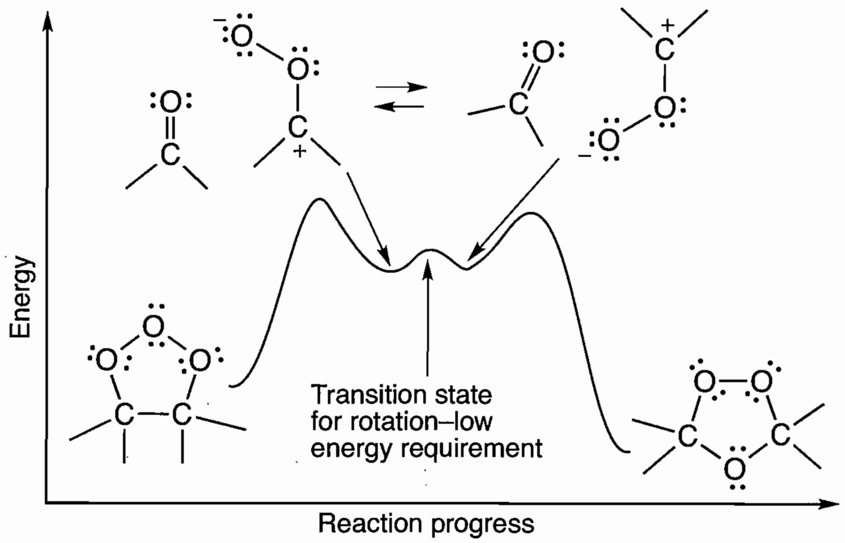
1 C—C	90
2 C—O	184
2 O—O	76
	350 kcal/mol

More stable
(stronger overall bonding)



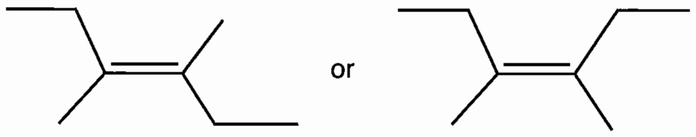
4 C—O	368
1 O—O	38
	406 kcal/mol

Problem 11.16 A full diagram includes the intermediates as well as starting material and products.



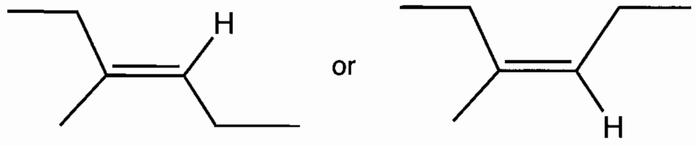
Problem 11.17

(a)



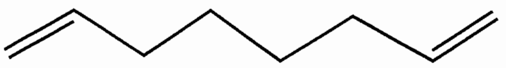
Either oxidative or reductive workup can be used

(b)



Since an aldehyde is one of the products, a reductive workup must be used

(d)



The products here are carboxylic acids, and so an oxidative workup must be used