you fill with your own writing in studying during the term.

5. Learn by teaching and explaining. Study with your student peers and practice explaining concepts and mechanisms to each other. Use the Learning Group Problems and other exercises your instructor may assign as vehicles for teaching and learning interactively with your peers.

6. Use the answers to the problems in the Study Guide in the proper way. Refer to the answers only in two circumstances: (1) When you have finished a problem, use the Study Guide to check your answer. (2) When, after making a real effort to solve the problem, you find that you are completely stuck, then look at the answer for a clue and go back to work out the problem on your own. The value of a problem is in solving it. If you simply read the problem and look up the answer, you will deprive yourself of an important way to learn.

7. Use the Introductory material in the Study Guide entitled "Solving the Puzzle—or—Structure Is Everything (Almost)" as a bridge from general chemistry to your beginning study of organic chemistry. You might find this section helpful as a way to see the relevance to organic chemistry of some of the concepts you learned in general chemistry, while at the same time refreshing these ideas in your mind and gearing you up to study organic chemistry. It is also meant to help you see that an understanding of certain fundamental principles, largely having to do with structure, can help immensely to reduce the complexity of the puzzle you may feel lies ahead of you. Indeed, once you have a firm understanding of structure, the puzzle of organic chemistry can become one of very manageable size and comprehensible pieces.

8. Use molecular models when you study. Because of the three-dimensional nature of most organic molecules, molecular models can be an invaluable aid to your understanding of them. Buy yourself an inexpensive molecular model set and use it when you need to see the three-dimensional aspect of the particular topic. An appendix in the Study Guide provides a set of highly useful molecular model exercises.

INTRODUCTION

"Solving the Puzzle", or
"Structure Is Everything (Almost)"

As you begin your study of organic chemistry it may seem like a puzzling subject. In fact, in many ways organic chemistry is like a puzzle—a jigsaw puzzle. But it is a jigsaw puzzle with useful pieces, and a puzzle with fewer pieces than perhaps you first thought. In order to put a jigsaw puzzle together you must consider the shape of the pieces and how one piece fits together with another. In other words, solving a jigsaw puzzle is about structure. In organic chemistry, molecules are the pieces of the puzzle. Much of organic chemistry, indeed life itself, depends upon the fit of one molecular puzzle piece with another. For example, when an antibody of our immune system acts upon a foreign substance, it is the puzzle-piece-like fit of the antibody with the invading molecule that allows "capture" of the foreign substance. When we smell the sweet scent of a rose, some of the neural impulses are initiated by the fit of a molecule called geraniol in an olfactory receptor site in our nose. When an adhesive binds two surfaces together, it does so by billions of interactions between the molecules of the two materials. Chemistry is truly a captivating subject.

As you make the transition from your study of general to organic chemistry, it is important that you solidify those concepts that will help you understand the structure of organic molecules. A number of concepts are discussed below using several examples. It is suggested that you consider the examples and the explanations given, and refer to information from your general chemistry studies when you need more elaborate information. There are also occasional references below to sections in your text. Solomon's and Frykle's Organic Chemistry, because some of what follows foreshadows what you will learn in the course.

SOME FUNDAMENTAL PRINCIPLES WE NEED TO CONSIDER

What do we need to know to understand the structure of organic molecules? First, we need to know where electrons are located around a given atom. To understand this we need to recall from general chemistry the ideas of electron configuration and valence shell electron orbitals, especially in the case of atoms such as carbon, hydrogen, oxygen, and nitrogen. We also need to use Lewis valence shell electron structures. These concepts are useful because the shape of a molecule is defined by its constituent atoms, and the placement of the atoms follows from the location of the electrons that bond the atoms. Once we have a Lewis structure for a molecule, we can consider orbital hybridization and valence shell electron pair repulsion (VSEPR) theory in order to generate a three-dimensional image of the molecule.

Secondly, in order to understand why specific organic molecular pieces fit together we need to consider the attractive and repulsive forces between them. To understand this we need to know how electronic charge is distributed in a molecule. We must
use tools such as formal charge and electronegativity. That is, we need to know which parts of a molecule are relatively positive and which are relatively negative—in other words, their polarity. Associations between molecules strongly depend on both shape and the complementarity of their electrostatic charges (polarity).

When it comes to organic chemistry it will be much easier for you to understand why organic molecules have certain properties and react the way they do if you have an appreciation for the structure of the molecules involved. Structure is, in fact, almost everything, in that whenever we want to know why or how something works we look ever more deeply into its structure. This is true whether we are considering a toaster, jet engine, or an organic reaction. If you can visualize the shape of the puzzle pieces in organic chemistry (molecules), you will see more easily how they fit together (react).

SOME EXAMPLES

In order to review some of the concepts that will help us understand the structure of organic molecules, let's consider three very important molecules—water, methane, and methanol (methyl alcohol). These three are small and relatively simple molecules that have certain similarities among them, yet distinct differences that can be understood on the basis of their structures. Water is a liquid with a moderately high boiling point that does not dissolve organic compounds well. Methanol is also a liquid, with a lower boiling point than water, but one that dissolves many organic compounds easily. Methane is a gas, having a boiling point well below room temperature. Water and methanol will dissolve in each other, that is, they are miscible. We shall study the structures of water, methanol, and methane because the principles we learn with these compounds can be extended to much larger molecules.

Water

\[ \text{HOH} \]

Let's consider the structure of water, beginning with the central oxygen atom. Recall that the atomic number (the number of protons) for oxygen is eight. Therefore, an oxygen atom also has eight electrons. (An ion may have more or less electrons than the atomic number for the element, depending on the charge of the ion.) Only the valence (outermost) electron shells are involved in bonding. Oxygen has six valence electrons—that is, six electrons in the second principal shell. (Recall that the number of valence electrons is apparent from the group number of the element in the periodic table, and the row number for the element is the principal shell number for its valence electrons.) Let's consider the electron configuration for oxygen. The sequence of atomic orbitals for the first three shells of any atom is shown below. Oxygen uses only the first two shells in its lowest energy state.

\[ 1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z \]

The \( p \) orbitals of any given principal shell (second, third, etc.) are of equal energy. Recall also that each orbital can hold a maximum of two electrons and that each orbital must accept one electron before a second can reside there (Hund's rule). So, for oxygen we place two electrons in the \( s \) orbital, two in the \( 2s \) orbital, and one in each of the \( 2p \) orbitals, for a subtotal of seven electrons. The final eighth electron is paired with another in one of the \( 2p \) orbitals. The configuration for the eight electrons of oxygen is, therefore

\[ 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1 1p_z^1 \]

Now, let's consider the shape of these orbitals. The shape of an \( s \) orbital is that of a sphere with the nucleus at the center. The shape of each \( p \) orbital is approximately that of a dumbbell or lobe-shaped object, with the nucleus directly between the two lobes. There is one pair of lobes for each of the three \( p \) orbitals \((p_x, p_y, p_z)\), and they are aligned along the \( x, y, \) and \( z \) coordinate axes, with the nucleus at the origin. Note that this implies that the three \( p \) orbitals are at 90° angles to each other.

Now, when oxygen is bonded to two hydrogens, bonding is accomplished by the sharing of an electron from each of the hydrogens with an unpaired electron from the oxygen. This type of bond, involving the sharing of electrons between atoms, is called a covalent bond. The formation of covalent bonds between the oxygen atom and the two hydrogen atoms is advantageous because each atom achieves a full valence shell by the sharing of these electrons. For the oxygen in a water molecule, this amounts to satisfying the octet rule.

A Lewis structure for the water molecule (which shows only the valence shell electrons) is depicted in the following structure. There are two nonbonding pairs of electrons around the oxygen as well as two bonding pairs.

\[ \text{H}_2\text{O} \]

In the left-hand structure the six valence electrons contributed by the oxygen are shown as dots, while those from the hydrogens are shown as \( x \)'s. This is done strictly for bookkeeping.
purposes. All electrons are, of course, identical. The right-hand structure uses the convention that a bonding pair of electrons can be shown by a single line between the bonded atoms.

This structural model for water is only a first approximation, however. While it is a proper Lewis structure for water, it is not an entirely correct three-dimensional structure. It might appear that the angle between the hydrogen atoms (or between any two pairs of electrons in a water molecule) would be 105°, but this is not what the true angles are in a water molecule.

The angle between the two hydrogens is in fact about 109.5°, and the nonbonding electron pairs are in a different plane than the hydrogen atoms. The reason for this arrangement is that groups of bonding and nonbonding electrons tend to repel each other due to the negative charge of the electrons. Thus, the ideal angles between bonding and nonbonding groups of electrons are those angles that allow maximum separation in three-dimensional space. This principle is built around it are called the valence shell electron pair repulsion (VSEPR) theory.

VSEPR theory predicts that the ideal separation between four groups of electrons around an atom is 109.5°, the so-called tetrahedral angle. At an angle of 109.5° all four electron groups are separated equally from each other, being oriented toward the corners of a regular tetrahedron. The exact tetrahedral angle of 109.5° is found in structures where the four groups of electrons and bonded groups are identical.

In water, there are two different types of electron groups—pairs bonding the hydrogens with the oxygen and nonbonding pairs. Nonbonding electron pairs repel each other with greater force than bonding pairs, so the separation between them is greater. Consequently, the angle between the pairs bonding the hydrogens to the oxygen in a water molecule is compressed slightly from 109.5°, being actually about 105°. As we shall see shortly, the angle between the four groups of bonding electrons in methane (CH₄) is the ideal tetrahedral angle of 109.5°. This is because the four groups of electrons and bound atoms are identical in a methane molecule.

Orbital hybridization is the reason that 109.5° is the ideal tetrahedral angle. As noted earlier, an s orbital is spherical, and each p orbital is shaped like two symmetrical lobes aligned along the x, y, and z coordinate axes. Orbital hybridization involves taking a weighted average of the valence electron orbitals of the atom, resulting in the same number of new hybridized orbitals. With four groups of valence electrons, as in the structure of water, one s orbital and three p orbitals from the second principal shell in oxygen are hybridized (the 2s and 2p₁, 2p₂, and 2p₃ orbitals). The result is four new hybrid orbitals of equal energy designated as sp³ orbitals (instead of the original three p orbitals and one s orbital). Each of the four sp³ orbitals has roughly 25% s character and 75% p character. The geometric result is that the major lobes of the four sp³ orbitals are oriented toward the corners of a tetrahedron with an angle of 109.5° between them.

In the case of the oxygen in a water molecule, where two of the four sp³ orbitals are occupied by nonbonding pairs, the angle of separation between them is larger than 109.5° due to additional electrostatic repulsion of the nonbonding pairs. Consequently, the angle between the bonding electrons is slightly smaller, about 105°.

More detail about orbital hybridization than provided above is given in Sections 1.10–1.14 of Organic Chemistry. With that greater detail it will be apparent from consideration of orbital hybridization that for three groups of valence electrons the ideal separation is 120° (trigonal planar), and for four groups of valence electrons the ideal separation is 109.5° (linear). VSEPR theory allows us to come to essentially the same conclusion as by the mathematical hybridization of orbitals, and it will serve us for the moment in predicting the three-dimensional shape of molecules.

Methane CH₄

Now let's consider the structure of methane (CH₄). In methane there is a central carbon atom bearing four bonded hydrogens. Carbon has six electrons in total, with four of them being valence electrons. (Carbon is in Group 4 in the periodic table.) In methane each valence electron is shared with an electron from a hydrogen atom to form four covalent bonds. This information allows us to draw a Lewis structure for methane (see below). With four groups of valence electrons the VSEPR theory allows us to predict that the three-dimensional shape of a methane molecule should be tetrahedral, with an angle of 109.5° between each of the bonded hydrogens. This is indeed the case. Orbital hybridization arguments can also be used to show that there are four equivalent sp³ hybrid orbitals around the carbon atom, separated by an angle of 109.5°.

The structure at the far right above uses the dash-wedge notation to indicate three dimensions. A solid wedge indicates that a bond projects out of the paper toward the reader. A dashed bond indicates that it projects behind the paper away from the viewer. Ordinary lines represent bonds in the plane of the paper. The dash-wedge notation is an important and widely used tool for depicting the three-dimensional structure of molecules.

Methanol CH₃OH

Now let's consider a molecule that incorporates structural aspects of both water and methane. Methanol (CH₃OH), or methyl alcohol, is such a molecule. In methanol, a central carbon atom has three hydrogens and an O–H group bonded to it. Three of the four valence electrons of the carbon atom are shared with a valence electron from the hydrogen atoms, forming three C–H bonds. The fourth valence electron of the carbon is shared with a valence electron from the oxygen atom, forming a C–O bond. The carbon atom now has an octet of valence electrons through the formation of four covalent bonds. The angles between these four covalent bonds is very near the ideal tetrahedral angle of 109.5°, allowing maximum separation between them. (The valence orbitals of the carbon are sp³ hybridized.) At the oxygen atom, the situation is very similar to that in water. The oxygen uses its two unpaired valence electrons to form covalent bonds. One valence electron is used in the bond with the carbon atom, and the other is paired with an electron from the hydrogen to form the O–H.
bond. The remaining valence electrons of the oxygen are present as two nonbonding pairs, just as in water. The angles separating the four groups of electrons around the oxygen are thus near the ideal angle of 109.5°, but reduced slightly in the C-O-H angle due to repulsion by the two nonbonding pairs on the oxygen. (The valence orbitals of the oxygen are also sp³ hybridized since there are four groups of valence electrons.) A Lewis structure for methanol is shown below, along with a three-dimensional perspective drawing.

\[ \text{H} - 
\text{C} = \text{O} - \text{H} \]

THE "CHARACTER" OF THE PUZZLE PIECES

With a mental image of the three-dimensional structures of water, methane, and methanol, we can ask how the structure of each, as a "puzzle piece," influences the interaction of each molecule with identical and different molecules. In order to answer this question we have to move one step beyond the three-dimensional shape of these molecules. We need to consider not only the location of the electron groups (bonding and nonbonding) but also the distribution of electronic charge in the molecules.

First, we note that nonbonding electrons represent a locus of negative charge, more so than electrons involved in bonding. Thus, water would be expected to have some partial negative charge localized in the region of the nonbonding electron pairs of the oxygen. The same would be true for a methanol molecule.

Secondly, the phenomenon of electronegativity influences the distribution of electrons, and hence the charge in a molecule, especially with respect to electrons in covalent bonds. Electronegativity is the propensit of an element to draw electrons toward it in a covalent bond. The trend among elements is that of increasing electronegativity toward the upper right corner of the periodic table. (Fluorine is the most electronegative element.) By observing the relative locations of carbon, oxygen, and hydrogen in the periodic table, we can see that oxygen is the most electronegative of these three elements. Carbon is more electronegative than hydrogen, although only slightly. Oxygen is significantly more electronegative than hydrogen. Thus, there is substantial separation of charge in a water molecule, due not only to the nonbonding electron pairs on the oxygen but also to the greater electronegativity of the oxygen with respect to the hydrogens. The oxygen tends to draw electron density toward itself in the bonds with the hydrogens, leaving the hydrogens partially positive. The resulting separation of charge is called polarity. The oxygen-hydrogen bonds are called polar covalent bonds due to this separation of charge. If one considers the net effect of the two nonbonding electron pairs in a water molecule as being a region of negative charge, and the hydrogens as being a region of positive charge, it is clear that a water molecule has substantial separation of charge, or polarity.

An analysis of polarity for a methanol molecule would proceed similarly to that for water. Methanol, however, is less polar than water because only one O-H bond is present. Nevertheless, the region of the molecule around the two nonbonding electron pairs of the oxygen is relatively negative, and the region near the hydrogen is relatively positive. The electronegativity difference between the oxygen and the carbon is not as large as that between oxygen and hydrogen, however, so there is less polarity associated with the C-O bond. Since there is even less difference in electronegativity between hydrogen and carbon in the three C-H bonds, these bonds contribute essentially no polarity to the molecule. The net effect for methanol is to make it a polar molecule, but less so than water due to the nonpolar character of the CH₃ region of the molecule.

Now let's consider methane. Methane is a nonpolar molecule. This is evident first because there are no nonbonding electron pairs, and secondly because there is relatively little electronegativity difference between the hydrogens and the central carbon. Furthermore, what little electronegativity difference there is between the hydrogens and the central carbon atom is negated by the symmetrical distribution of the C-H bonds in the tetrahedral shape of methane. The slight polarity of each C-H bond is canceled by the symmetrical orientation of the four C-H bonds. If considered as vectors, the vector sum of the four slightly polar covalent bonds oriented at 109.5° to each other would be zero.

The same analysis would hold true for a molecule with identical bonded groups, but groups having electronegativity significantly different from carbon, so long as there were symmetrical distribution of the bonded groups. Tetrachloromethane (carbon tetrachloride) is such a molecule. It has no net polarity.
INTERACTIONS OF THE PUZZLE PIECES

Now that you have an appreciation for the polarity and shape of these molecules it is possible to see how molecules might interact with each other. The presence of polarity in a molecule bestows upon it attractive or repulsive forces in relation to other molecules. The negative part of one molecule is attracted to the positive region of another. Conversely, if there is little polarity in a molecule, the attractive forces it can exert are very small (though not completely nonexistent, due to van der Waals forces (Section 2.14D in Organic Chemistry)). Such effects are called intermolecular forces (forces between molecules), and strongly depend on the polarity of a molecule or certain bonds within it (especially O-H, N-H, and other bonds between hydrogen and more electron-negative atoms with nonbonding pairs). Intermolecular forces have profound effects on physical properties such as boiling point, solubility, and reactivity. An important manifestation of these properties is that the ability to isolate a pure compound after a reaction often depends on differences in boiling point, solubility, and sometimes reactivity among the compounds present.

Boiling Point

An intuitive understanding of boiling points will serve you well when working in the laboratory. The polarity of water molecules leads to relatively strong intermolecular attraction between water molecules. One result is the moderately high boiling point of water (100°C, as compared to 65°C for methanol and ~162°C for methane, which we will discuss shortly). Water has the highest boiling point of these three example molecules because it will strongly associate with itself by attraction of the partially positive hydrogens of one molecule (from the electronegativity difference between the O and H) to the negatively charged region in another water molecule (where the nonbonding pairs are located).

The specific attraction between a partially positive hydrogen atom attached to a heteroatom (an atom with both nonbonding and bonding valence electrons, e.g., oxygen or nitrogen) and the nonbonding electrons of another heteroatom is called hydrogen bonding. It is a form of dipole–dipole attraction due to the polar nature of the hydrogen–heteroatom bond. A given water molecule can associate by hydrogen bonding with several other water molecules, as shown above. Each water molecule has two hydrogens that can associate with the nonbonding pairs of other water molecules, and two nonbonding pairs that can associate with the hydrogens of other water molecules. Thus, several hydrogen bonds are possible for each water molecule. It takes a significant amount of energy (provided by heat, for example) to give the molecules enough kinetic energy (motion) for them to overcome the polarity-induced attractive forces between them and escape into the vapor phase (evaporation or boiling).

Methanol, on the other hand, has a lower boiling point than water (65°C), in large part due to the decreased hydrogen bonding ability of methanol in comparison with water. Each methanol molecule has only one hydrogen atom that can participate in a hydrogen bond with the nonbonding electron pairs of another methanol molecule (as compared with two for each water molecule). The result is reduced intermolecular attraction between methanol molecules and a lower boiling point since less energy is required to overcome the lesser intermolecular attractive forces.

The CH₃ group of methanol does not participate in dipole–dipole attractions between molecules because there is not sufficient polarity in any of its bonds to lead to significant partial positive or negative charges. This is due to the small electronegativity difference between the carbon and hydrogen in each of the C-H bonds.

Now, on to methane. Methane has no hydrogens that are eligible for hydrogen bonding, since none is attached to a heteroatom such as oxygen. Due to the small difference in electronegativity between carbon and hydrogen there are no bonds with any significant polarity. Furthermore, what slight polarity there is in each C-H bond is canceled due to the tetrahedral symmetry of the molecule. The minute attractive forces that exist between methane molecules is due to van der Waals forces, but these are negligible in comparison to dipole–dipole interactions that exist when significant differences in electronegativity are present in molecules such as water and methanol.

Thus, because there is only a very weak attractive force between methane molecules, the boiling point of methane is very low (~162°C) and it is a gas at ambient temperature and pressure.

Solubility

An appreciation for trends in solubility is very useful in gaining a general understanding of many practical aspects of chemistry. The ability of molecules to dissolve other molecules or solutes is strongly affected by polarity. The polarity of water is frequently exploited during the isolation of an organic reaction product because water will not dissolve most organic compounds but will dissolve salts, many inorganic materials, and other polar byproducts that may be present in a reaction mixture. As to our example molecules, water and methanol are miscible with each other because each is polar and can interact with the other by dipole–dipole hydrogen bonding interactions. Since methane is a gas under ordinary conditions, for the purposes of this discussion let's consider a close relative of methanol - hexane. Hexane (C₆H₁₄) is a liquid having only carbon – carbon and carbon – hydrogen bonds. It belongs to the same chemical family as methane. Hexane is not soluble in water due to the essential absence of polarity in its bonds. Hexane is slightly soluble in methanol due to the compatibility of the nonpolar CH₃ region of methanol with hexane. The old saying “like dissolves like” definitely holds true. This can be extended to solutes, as well. Very polar substances, such as ionic compounds, are usually freely soluble in water. The high polarity of salts generally prevents...
most of them from being soluble in methanol, however. And, of course, there is absolutely no solubility of ionic substances in hexane. On the other hand, very nonpolar substances, such as oils, would be soluble in hexane.

Thus, the structure of each of these molecules we've used for examples (water, methanol, and methane) has a profound effect on their respective physical properties. The presence of nonbonding electron pairs and polar covalent bonds in water and methanol versus the complete absence of these features in the structure of methane imparts markedly different physical properties to these three compounds. Water, a small molecule with strong intermolecular forces, is a moderately high boiling liquid. Methane, a small molecule with only very weak intermolecular forces, is a gas. Methanol, a molecule combining structural aspects of both water and methane, is a relatively low boiling liquid, having sufficient intermolecular forces to keep the molecules associated as a liquid, but not so strong that mild heat can't disrupt their association.

Reactivity

While the practical importance of the physical properties of organic compounds may only be starting to become apparent, one strong influence of polarity is on the reactivity of molecules. It is often possible to understand the basis for a given reaction in organic chemistry by considering the relative polarity of molecules and the propensity, or lack thereof, for them to interact with each other.

Let us consider one example of reactivity that can be understood at the initial level by considering structure and polarity. When chloromethane (CH₃Cl) is exposed to hydroxide ions (OH⁻) in water a reaction occurs that produces methanol. This reaction is shown below:

\[
\text{CH}_3\text{Cl} + \text{HO}^- \rightarrow \text{HOCH}_3 + \text{Cl}^-
\]

This reaction is called a substitution reaction, and it is of a general type that you will spend considerable time studying in organic chemistry. The reason this reaction occurs readily can be understood by considering the principles of structure and polarity that we have been discussing. The hydroxide ion has a negative charge associated with it, and thus should be attracted to a species that has a positive charge. Now recall our discussion of electronegativity and polar covalent bonds, and apply these ideas to the structure of chloromethane. The chlorine atom is significantly more electronegative than carbon (note its position in the periodic table). Thus, the covalent bond between the carbon and the chlorine is polarized such that there is partial negative charge on the chlorine and partial positive charge on the carbon. This provides the positive site that attracts the hydroxide ion!

The intimate details of this reaction will be studied in Chapter 6 of your text. Suffice it to say for the moment that the hydroxide ion attacks the carbon atom using one of its nonbonding electron pairs to form a bond with the carbon. At the same time, the chlorine atom is pushed away from the carbon and takes with it the pair of electrons that used to bond it to the carbon. The result is substitution of OH for Cl at the carbon atom and the synthesis of methanol by calculating formal charges (Section 1.3 in the text) one can show that the oxygen of the hydroxide atom goes from having a formal negative charge in hydroxide to zero formal charge in chloromethane and a formal negative charge as a chloride ion after the reaction. The fact that the reaction takes place at all rests largely upon the complementary polarity of the interacting species. This is a pervasive theme in organic chemistry.

Acid-base reactions are also very important in organic chemistry. Many organic reactions involve at least one step in the overall process that is fundamentally an acid-base reaction. Both Bronsted-Lowry acid-base reactions (those involving proton donors and acceptors) and Lewis acid-base reactions (those involving electron pair acceptors and donors, respectively) are important. In fact, the reaction above can be classified as a Lewis acid-base reaction in that the hydroxide ion acts as a Lewis base to attack the partially positive carbon as a Lewis acid. It is strongly recommended that you review concepts you have learned previously regarding acid-base reactions. Chapter 3 in Organic Chemistry will help in this regard, but it is advisable that you begin some early review about acids and bases based on your previous studies. Acid-base chemistry is widely applicable to understanding organic reactions.

JOINING THE PIECES

Finally, while what we have said above has largely been in reference to three specific compounds, water, methanol, and methane, the principles involved find exceptionally broad application in understanding the structure, and hence reactivity, of organic molecules in general. You will find it constantly useful in your study of organic chemistry to consider the electronic structure of the molecules with which you are presented, the shape caused by the distribution of electrons in a molecule, the ensuing polarity, and the resulting potential for that molecule's reactivity. What we have said about these very small molecules of water, methanol, and methane can be extended to consideration of molecules with 10 to 100 times as many atoms. You would simply apply these principles to small sections of the larger molecule one part at a time. The following structure of Streptogramin A provides an example.

![Streptogramin A](image)

A natural antibacterial compound that blocks protein synthesis at the 70S ribosomes of Gram-positive bacteria.

We have not said much about how overall shape influences the ability of one molecule to interact with another, in the sense that a key fits in a lock or a hand fits in a glove.
This type of consideration is also extremely important, and will follow with relative ease if you have worked hard to understand the general principles of structure outlined here and expanded upon in the early chapters of Organic Chemistry. An example would be the following. Streptogramin A, shown above, interacts in a hand-in-glove fashion with the 70S ribosome in bacteria to inhibit binding of transfer RNA at the ribosome. The result of this interaction is the prevention of protein synthesis in the bacterium, which thus accounts for the antibacterial effect of Streptogramin A. Other examples of hand-in-glove interactions include the olfactory response to geraniol mentioned earlier, and the action of enzymes to speed up the rate of reactions in biochemical systems.

FINISHING THE PUZZLE

In conclusion, if you pay attention to learning aspects of structure during this initial period of "getting your feet wet" in organic chemistry, much of the three-dimensional aspects of molecules will become second nature to you. You will immediately recognize when a molecule is tetrahedral, trigonal planar, or linear in one region or another. You will see the potential for interaction between a given section of a molecule and that of another molecule based on their shape and polarity, and you will understand why many reactions take place. Ultimately, you will find that there is much less to memorize in organic chemistry than you first thought. You will learn how to put the pieces of the organic puzzle together, and see that structure is indeed almost everything, just applied in different situations!

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SOLUTIONS TO PROBLEMS

Another Approach to Writing Lewis Structures

When we write Lewis structures using this method, we assemble the molecule or ion from the constituent atoms showing only the valence electrons (i.e., the electrons of the outermost shell). By having the atoms share electrons, we try to give each atom the electronic structure of a noble gas. For example, we give hydrogen atoms two electrons because this gives them the structure of helium. We give carbon, nitrogen, oxygen, and fluorine atoms eight electrons because this gives them the electronic structure of neon. The number of valence electrons of an atom can be obtained from the periodic table because it is equal to the group number of the atom. Carbon, for example, is in group 4A and has four valence electrons; fluorine, in group 7A, has seven; hydrogen, in group 1A, has one. As an illustration, let us write the Lewis structure for CH₃F. In the example below, we will at first show a hydrogen’s electron as x, carbon’s electrons as o’s, and fluorine’s electrons as dots.

Example A

\[ \text{H}_3^+ \text{C}^2- \text{F}^- \]

are assembled as

\[
\begin{aligned}
\text{H} & \atop \text{o} \\
\text{H} & \atop \text{o} \\
\text{H} & \atop \text{o} \\
\text{C} & \atop \text{o} \\
\text{F} & \atop \text{o} \\
\end{aligned}
\]

H₃CO:F; or H:C:F:

\[ \text{H} \]

If the structure is an ion, we add or subtract electrons to give it the proper charge. As an example, consider the chlorate ion, ClO₃⁻.

Example B

\[ \text{Cl}^3+ \text{and } \begin{aligned}
\text{O} & \atop \text{o} \\
\text{O} & \atop \text{o} \\
\end{aligned} \text{ and an extra electron } \text{x} \]

are assembled as

\[
\begin{aligned}
\begin{bmatrix}
\text{O} \\
\text{O} \\
\text{O} \\
\text{Cl} \\
\text{O} \\
\end{bmatrix} & \text{ or } \\
\begin{bmatrix}
\text{O} \\
\text{O} \\
\text{O} \\
\text{Cl} \\
\text{O} \\
\end{bmatrix}
\end{aligned}
\]
1.1 (a) \( \text{H} - \overset{\cdot}{\text{H}} \quad (d) \text{H} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{O}} \quad (g) \text{H} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{H}} \)

(b) \( \text{H} - \overset{\cdot}{\text{H}} \quad (c) \underset{\text{H}}{\text{H}} - \text{O} - \text{H} \quad (h) \text{H} - \overset{\cdot}{\text{H}} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{H}} \)

(c) \( \overset{\cdot}{\text{H}} - \overset{\cdot}{\text{H}} \quad (f) \underset{\text{H}}{\text{H}} - \text{H} - \text{H} \quad (i) \text{H} - \overset{\cdot}{\text{C}} - \text{N} \)

1.2 (a) \( \overset{\cdot}{\text{N}} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{O}} \quad (c) \overset{\cdot}{\text{C}} - \text{N} : \quad (e) \text{H} - \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{C}} \)

(b) \( \text{H} - \overset{\cdot}{\text{N}} \quad (d) \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{O}} \quad (f) \text{H} - \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{C}} \quad \)

1.3 (a) \( \text{H} - \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{C}} + \quad (c) \text{H} - \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{C}} \quad (e) \text{H} - \overset{\cdot}{\text{N}} - \overset{\cdot}{\text{H}} \)

(b) \( \text{H} - \overset{\cdot}{\text{H}} \quad (d) \text{H} - \overset{\cdot}{\text{H}} - \overset{\cdot}{\text{H}} \quad (f) \text{H} - \overset{\cdot}{\text{H}} - \overset{\cdot}{\text{H}} \quad \)

1.4 (a) \( \text{H} - \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{C}} \quad \)

(b) and (c). Since the two resonance structures are equivalent, each should make an equal contribution to the overall hybrid. The C–O bonds should therefore be of equal length (they should be of bond order 1.5), and each oxygen atom should bear a 0.5 negative charge.

1.5 (a) In its ground state, the valence electrons of carbon might be disposed as shown in the following figure.

The electronic configuration of a ground state carbon atom. The \( p \) orbitals are designated \( 2p_x, 2p_y, \) and \( 2p_z \) to indicate their respective orientations along the \( x, y, \) and \( z \) axes. The assignment of the unpaired electrons to the \( 2p_x, \) and \( 2p_y, \) orbitals is arbitrary. They could also have been placed in the \( 2p_z, \) and \( 2p_x, \) or \( 2p_x, \) and \( 2p_y, \) orbitals.

(To have placed them both in the same orbital would not have been correct, however, for this would have violated Hund's rule.) (Section 1.10)

The formation of the covalent bonds of methane from individual atoms requires that the carbon atom overlap its orbitals containing single electrons with 1s orbitals of hydrogen atoms (which also contain a single electron). If a ground state carbon atom were to combine with hydrogen atoms in this way, the result would be that depicted below. Only two carbon-hydrogen bonds would be formed, and these would be at right angles to each other.

The hypothetical formation of \( \text{CH}_3 \) from a carbon atom in its ground state.

(b) An excited-state carbon atom might combine with four hydrogen atoms as shown in the figure above.

The promotion of an electron from the \( 2s \) orbital to the \( 2p \) orbital requires energy. The amount of energy required has been determined and is equal to 400 \( \text{kJ mol}^{-1} \). This expenditure of energy can be rationalized by arguing that the energy released when two additional covalent bonds form would more than compensate for that required to excite the electron. No doubt this is true, but it solves only one problem. The problems that cannot be solved by using an excited-state carbon as a basis for a model of methane are the problems of the carbon-hydrogen bond angles and the apparent equivalence of
CARBON COMPOUNDS AND CHEMICAL BONDS

All four carbon-hydrogen bonds. Three of the hydrogens—those overlapping their 1s orbitals with the three p orbitals—would, in this model, be at angles of 90° with respect to each other; the fourth hydrogen, the one overlapping its 1s orbital with the 2s orbital of carbon, would be at some other angle, probably as far from the other bonds as the confines of the molecule would allow. Basing our model of methane on this excited state of carbon gives us a carbon that is tetravalent but one that is not tetrahedral, and it predicts a structure for methane in which one carbon-hydrogen bond differs from the other three.

The hypothetical formation of CH₄ from an excited-state carbon atom.

1.6 (a) Cis-trans isomers are not possible.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

(b) \[ \text{H}_2\text{C} \quad \text{H}_2\text{C} \]

(c) Cis-trans isomers are not possible.

\[
\begin{align*}
\text{CH}_2\text{CH}_2 & \quad \text{CH}_2\text{CH}_2 \\
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{H}
\end{align*}
\]

(d) \[ \text{H}_2\text{C} \quad \text{H}_2\text{C} \]

1.7 If the geometry of the carbon atom were square planar, two isomeric compounds with the formula CH₃Cl should exist.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

1.8 (a) There are four bonding pairs. The geometry is tetrahedral.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

(b) There are two bonding pairs about the central atom. The geometry is linear.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

(c) There are four bonding pairs. The geometry is tetrahedral.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

(d) There are two bonding pairs and two nonbonding pairs. The geometry is angular.

\[
\text{H}_2\text{S}
\]

(e) There are three bonding pairs. The geometry is trigonal planar.

\[
\text{H}_2\text{B}
\]

(f) There are four bonding pairs around the central atom. The geometry is tetrahedral.

\[
\text{H}_2\text{F}
\]
(g) There are four bonding pairs around the central atom. The geometry is tetrahedral.

(b) There are three bonding pairs and one nonbonding pair around the central atom. The geometry is trigonal pyramidal.

1.10 H-C-O-C-H

1.11 (a) H₃C-CH₂-CH₂-CH₃ = \( \overset{\text{120°}}{\text{CH₃}} \)

(b) H₂C=CH₂-CH₂OH = \( \overset{\text{180°}}{\text{CH₃}} \)

(c) H₂C=CH₂-CH₂Cl = \( \overset{\text{120°}}{\text{CH₃}} \)

(d) H₂C-CH₂-CH₂-CH₃ = \( \overset{\text{120°}}{\text{CH₃}} \)

1.12 (a) \( \overset{\text{120°}}{\text{H₃C}} \)

(b) \( \overset{\text{120°}}{\text{H₃C}} \)

(c) \( \overset{\text{120°}}{\text{H₃C}} \)

(d) \( \overset{\text{120°}}{\text{H₃C}} \)

1.13 (a) H₃C-CH₂-CH₂-CH₂-CH₂-CH₃

(b) \( \overset{\text{120°}}{\text{CH₃}} \)

(c) \( \overset{\text{120°}}{\text{CH₃}} \)

1.14 (a) HCl

(b) Cl⁻ or \( \overset{\text{Cl₁}}{\text{CH₃}} \) and so on

(c) and others

(d) and others
1.15 (a) Na⁺ has the electronic configuration, 1s²2s²2p⁶, of Ne.
(b) Cl⁻ has the electronic configuration, 1s²2s²2p³3s²3p⁶, of Ar.
(c) F⁻ and (b) Br⁺ do not have the electronic configuration of a noble gas.
(d) H⁻ has the electronic configuration, 1s², of He.
(e) Ca²⁺ has the electronic configuration.
(f) S²⁻ has the electronic configuration, 1s²2s²2p⁶3s²3p⁶ of Ar.
(g) O²⁻ has the electronic configuration, 1s²2s²2p⁶ of Ne.

1.16 (a)  
(b)  
(c)  
(d) 

1.17 (a)  
(b)  

1.18 (a) (CH₃)₂CHCH₂OH
(b) (CH₂)₂CHCH(CH₃)₂

1.19 (a) C₄H₁₀
(b) C₃H₈

1.20 (a) Different compounds, not isomeric
(b) Constitutional isomers
(c) Same compound
(d) Same compound
(e) Same compound
(f) Constitutional isomers
(g) Different compounds, not isomeric
(h) Same compound

1.21 (a)  
(b)  
(c)  
(d)  
(e)  

1.22 (a)  
(b)  
(c)  
(d)  

1.23 CH₂=CHCH₂CH₃  CH₃CH=CHCH₃  CH₂=CH₂

1.24 H⁺C⁺N⁺O⁻  (Other structures are possible.)

1.25 (a) While the structures differ in the position of their electrons, they also differ in the positions of their nuclei and thus they are not resonance structures. (In cyanic acid the hydrogen nucleus is bonded to oxygen; in isocyanic acid it is bonded to nitrogen.)
(b) The anion obtained from either acid is a resonance hybrid of the following structures: ¹O=C=Nil ↔ ¹O=CNi⁺
1.26 (a) A + charge. \( F = 4 - \frac{1}{2} n + 1 \)
(b) A + charge. (It is called a methyl cation.)
(c) Trigonal planar, that is,
\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\]
(d) \( sp^3 \)

1.27 (a) A - charge. \( F = 4 - \frac{1}{2} - 2 = -1 \)
(b) A - charge. (It is called a methyl anion.)
(c) Trigonal pyramidal, that is,
\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\]
(d) \( sp^3 \)

1.28 (a) No formal charge. \( F = 4 - \frac{1}{2} - 1 = 0 \)
(b) No charge.
(c) \( sp^2 \), that is,
\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\]

1.29 (a) and (b)
(c) Because the two resonance structures are equivalent, they should make equal contributions to the hybrid and, therefore, the bonds should be the same length.
(d) Yes. We consider the central atom to have two groups or units of bonding electrons and one unshared pair.

1.30 Structures A and C are equivalent and, therefore, make equal contributions to the hybrid. The bonds of the hybrid, therefore, have the same length.

*1.31 (a)
\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{H}
\end{array}
\]
(b) \( \text{CH}_3\text{NH} \quad \text{CH}_3\text{CH}_2\text{NH}_3 \)
(c) \( \text{CH}_3\text{N} \quad \text{CH}_3\text{CH}_2\text{NHCH}_3 \quad \text{CH}_3\text{CH}_2\text{NH}_2 \quad \text{CH}_3\text{CH}_2\text{NH}_3 \)
(d) \( \text{NH}_2 \quad \text{H} \quad \text{CH} \)

*1.32 (a) constitutional isomers (b) the same
(c) resonance forms (d) constitutional isomers
(e) resonance forms (f) the same

*1.33 (a) \( \text{O} = \text{N} = \text{O} \)
(b) Linear
(c) Carbon dioxide

*1.34 Set A:

Set B:
CARBON COMPOUNDS AND CHEMICAL BONDS

12

1.6 Write another resonance structure for the formate ion.

H—\overset{\cdot}{C}—O—\overset{\cdot}{H}

Formate ion

1.7 In the boxes below write condensed structural formulas for constitutional isomers of CH₃(CH₂)₂CH₃.

1.8 Write a three-dimensional formula for a constitutional isomer of compound A given below. Complete the partial structure shown.

1.9 Consider the molecule (CH₃)₃B and give the following:

(a) Hybridization state of boron

(b) Hybridization state of carbon atoms

(c) Formal charge on boron

(d) Orientation of groups around boron

(e) Dipole moment of (CH₃)₃B

1.1 Which of the following is a valid Lewis dot formula for the nitrite ion (NO₂⁻)?

(a) \overset{\cdot}{\overset{\cdot}{\overset{\cdot}{N}}}—\overset{\cdot}{\overset{\cdot}{O}}—\overset{\cdot}{\overset{\cdot}{O}}

(b) \overset{\cdot}{O}—\overset{\cdot}{\overset{\cdot}{N}}—\overset{\cdot}{\overset{\cdot}{O}}

(c) \overset{\cdot}{\overset{\cdot}{\overset{\cdot}{O}}}—\overset{\cdot}{\overset{\cdot}{N}}—\overset{\cdot}{\overset{\cdot}{O}}

(d) Two of these

(e) None of the above

1.2 What is the hybridization state of the boron atom in BF₃?

(a) s

(b) p

(c) sp

(d) sp²

(e) sp³

1.3 BF₃ reacts with NH₃ to produce a compound, F—B—N—H. The hybridization state of B is

(a) s

(b) p

(c) sp

(d) sp²

(e) sp³

1.4 The formal charge on N in the compound given in Problem 1.3 is

(a) -2

(b) -1

(c) 0

(d) +1

(e) +2

1.5 The correct bond-line formula of the compound whose condensed formula is CH₃CHCICH₂CH(CH₃)CH₂CH₃ is

(a) 

(b) 

(c) 

(d) 

(e) 

1.7 (Continued)

1.8 (Continued)

1.9 (Continued)
1.10 Give the formal charge on oxygen in each compound.

(a) $\text{CH}_3\text{O}-\text{CH}_3$  
(b) $\text{CH}_3\text{C}\equiv\text{O}$

1.11 Write another resonance structure in which all of the atoms have a formal charge of zero.

$$\ce{H-C=N-H}$$

1.12 Indicate the direction of the net dipole moment of the following molecule.

[Diagram of molecule]

2.1 SOLUTIONS TO PROBLEMS

(a) $\text{H}^+\text{F}$  
(b) $\text{I}^-\text{Br}$

2.2 VSEPR theory predicts a planar structure for $\text{BF}_3$.

$$\ce{BF_3}$$

The vector sum of the bond moments of a trigonal planar structure would be zero, resulting in a prediction of $\mu = 0$ for $\text{BF}_3$. This correlates with the experimental observation and confirms the prediction of VSEPR theory.

2.3 The shape of $\text{CCl}_2\equiv\text{CCl}_3$ (below) is such that the vector sum of all of the $\text{C}-\text{Cl}$ bond moments is zero.

[Diagram of molecule]

2.4 The fact that $\text{SO}_2$ has a dipole moment indicates that the molecule is angular, not linear.

$$\mu = 1.63 \text{ D}$$

An angular shape is what we would expect from VSEPR theory, too.
The fact that CO₂ has no dipole moment indicates that its shape is linear, not angular.

\[
\begin{align*}
\text{linear} & : O=O \\
\text{angular} & : O \equiv O
\end{align*}
\]

\[\mu = 0\]

2.5 Again, this is what VSEPR theory predicts.

2.6 In CFC₃, the large C—F bond moment opposes the C—Cl moments, leading to a net dipole moment in the direction of the fluorine. Because hydrogen is much less electronegative than fluorine, no such opposing effect occurs in CHCl₃; therefore, it has a net dipole moment that is larger and in the direction of the chlorine atoms.

2.7 (a) Smaller net dipole moment
2.8 (a) net dipole moment
2.9 (a) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}\) and \(\text{CH}_3\text{CHCH}_2\text{Br}\)
2.10 (a) \(\text{CH}_3\text{CHF}\)
2.11 (a) \(\text{CH}_2\text{CH}_2\text{OH}\) and \(\text{CH}_3\text{CHCH}_2\text{OH}\)
2.12 (a) \(\text{CH}_3\text{CH}_2\text{OH}\)
2.13 (a) \(\text{CH}_3\text{CH}-\text{O}-\text{CH}_2\text{CH}_3\)
2.14 (a) \(\text{CH}_3\text{CH}_2\text{NH}_2\)
2.15 (a) only (b) (d.f) (c) (b, c, e, g)
2.16 (a) \(\text{CH}_3\text{NH}^- + \text{H}^+ \rightarrow \text{CH}_3\text{NH}^+ + \text{H}_2\text{O}\)
2.17 (a) CH₃CH₂CH₂CH₂OH would boil higher because its molecules can form hydrogen bonds to each other through the -O-H group.

(b) CH₃CH₂NHCH₃ would boil higher because its molecules can form hydrogen bonds to each other through the -N-H group.

(c) HOCH₂CH₂CH₂OH because by having two -O-H groups, it can form more hydrogen bonds.

2.18 Cyclopropane would have the higher melting point because its cyclic structure gives it a rigid compact shape that would permit stronger crystal lattice forces.

2.19 (a) Ketone
(b) Alkyne
(c) Alcohol
(d) Aldehyde
(e) Alcohol
(f) Alkene

2.20 (a) Three carbon-carbon double bonds (alkene) and a 2° alcohol
(b) Phenyl, carboxylic acid, amide, ester, and a 1° amine
(c) Phenyl and a 1° amine
(d) Carbon-carbon double bond and a 2° alcohol
(e) Phenyl, ester, and a 3° amine
(f) Carbon-carbon double bond and an aldehyde
(g) Carbon-carbon double bond and 2 ester groups

2.21 CH₃CH₂CH₂CH₃ Br  CH₃CH₂CH₃ Br
1° Alkyl halide 2° Alkyl halide

CH₃CH₂CH₂Br  CH₃CH₂Br
1° Alkyl halide 1° Alkyl halide

CH₃CH₂CH₂Br  CH₃CH₂Br
3° Alkyl halide 3° Alkyl halide

CH₃CH₂CH₂OH  CH₃CH₂OH
1° Alcohol 1° Alcohol

CH₃CH₂OH  CH₃CH₂OH
2° Alcohol 2° Alcohol

CH₃CH₂OH  CH₃CH₂OH
1° Alcohol 1° Alcohol

CH₃CH₂OH  CH₃CH₂OH
3° Alcohol 3° Alcohol

2.22 CH₃CH₂CH₂OH  CH₃CH₂CH₂OH
1° Alcohol 2° Alcohol

CH₃CH₂OH  CH₃CH₂OH
1° Alcohol 1° Alcohol

CH₃CH₂OH  CH₃CH₂OH
3° Alcohol 3° Alcohol

2.23 Any four of the following:

(a) CH₃CH₂OH
(b) CH₃CH₂CH₂OH
(c) CH₃CH₂CH₃
(d) CH₃CH₂Br

2.24 (a) 1° (b) 2° (c) 3° (d) 2° (e) 2°

2.25 (a) 2° (b) 1° (c) 3° (d) 2° (e) 2° (f) 3°

2.26 (a) CH₃OCH₂CH₂CH₃
(b) CH₃OCH₂CH₂CH₂OH
(c) CH₃OCH₃
(d) CH₃OCH₂CH₂OH
(e) CH₃OCH₂CH₂CH₃
(f) CH₃OCH₂CH₃
(g) CH₃OCH₂OH
(h) CH₃OCH₂CH₃
(i) CH₃OCH₂CH₂CH₂OH
2.27 (a) CH₃CH₂CH₂OH because its molecules can form hydrogen bonds to each other through its O—H group.

(b) HOCH₂CH₂OH because with two O—H groups, its molecules can form more hydrogen bonds with each other.

(c) —OH because its molecules can form hydrogen bonds to each other.

(d) OH⁻ [Same reason as (c)].

(e) because its molecules can form hydrogen bonds to each other through its N—H group.

(f) because its molecules will have a larger dipole moment. (The trans compound will have μ = 0.)

(g) —O⁻ [Same reason as (e)].

(h) Nonane, because of its larger molecular weight and larger size, will have larger van der Waals attractions.

(i) because its carbonyl group is far more polar than the double bond of

2.28 (a) The alcohol would have a broad absorption from the O—H group in the 3200 to 3500 cm⁻¹ region of its IR spectrum. The ether would have no such absorption.

(b) The ketone would have a strong absorption from its carbonyl group near 1700 cm⁻¹ in its IR spectrum. The alcohol would have a broad absorption due to its hydroxyl group in the 3200 to 3500 cm⁻¹ region of its IR spectrum.

(c) The ketone would have a strong absorption from its carbonyl group near 1700 cm⁻¹ in its IR spectrum. The ether would have no such absorption but would have an absorption between 1620 and 1680 cm⁻¹ due to C=O stretching.

(d) Same rationale as for (a).

(e) The secondary amine would have an absorption near 3300 to 3500 cm⁻¹ arising from N—H stretching. The tertiary amine would have no such absorption in this region since there is no N—H group present.

(f) Both compounds would exhibit absorptions near 1710 to 1780 cm⁻¹ due to carbonyl stretching vibrations. The carboxylic acid would also have a broad absorption somewhere between 2500 and 3500 cm⁻¹ due to its hydroxyl group. The ester would not have a hydroxyl absorption.

(g) The ketone would have a strong absorption from its carbonyl group near 1700 cm⁻¹ in its IR spectrum. The alcohol would have no such absorption but would have an absorption between 1620 and 1680 cm⁻¹ due to C=O stretching.

(h) The last one given above [i.e., HCN(CH₃)₂] because it does not have a hydrogen that is covalently bonded to nitrogen and, therefore, its molecules cannot form hydrogen bonds to each other. The other molecules all have a hydrogen covalently bonded to nitrogen and, therefore, hydrogen-bond formation is possible. With the first molecule, for example, hydrogen bonds could form in the following way:

2.30 An ester group.

2.31 The attractive forces between hydrogen fluoride molecules are the very strong dipole-dipole attractions that we call hydrogen bonds. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge of an ethyl fluoride molecule is buried in the ethyl group and is shielded by the surrounding electrons. Thus the positive end of one hydrogen fluoride molecule can approach the negative end of another hydrogen fluoride molecule much more closely, with the result that the attractive force between them is much stronger.)

2.32 (a) and (b) are polar and hence are able to dissolve ionic compounds. (c) and (d) are non-polar and will not dissolve ionic compounds.
2.33 (a) Dimethyl ether: There are four electron pairs around the central oxygen: two bonding pairs and two nonbonding pairs. We would expect $sp^3$ hybridization of the oxygen with a bond angle of approximately 109.5° between the methyl groups.

(b) Trimethylamine: There are four electron pairs around the central nitrogen: three bonding pairs and one nonbonding pair. We would expect $sp^3$ hybridization of the nitrogen with a bond angle of approximately 109.5° between the methyl groups.

(c) Trimethylboron: There are only three bonding electron pairs around the central boron. We would expect $sp^2$ hybridization of the boron with a bond angle of 120° between the methyl groups.

(d) Dimethylberyllium: There are only two bonding electron pairs around the central beryllium atom. We would expect $sp$ hybridization of the beryllium atom with a bond angle of 180° between the methyl groups.

2.34 (a) Without one (or more) polar bonds, a molecule cannot possess a dipole moment and, therefore, it cannot be polar. If the bonds are directed so that the bond moments cancel, however, the molecule will not be polar even though it has polar bonds.

2.35 Crixivan has the following functional groups:

2.36 Crixivan has the following functional groups:

2.37 Hydrogen bond

2.38 A B B'

The 1780-cm$^{-1}$ band is in the general range for C=O stretching so structure B' is considered one of the possible answers, but only B would have its C=O stretch at this high frequency (B' would be at about 1730 cm$^{-1}$).

2.39 (a) cis

(b) The cis isomer will have the 3572-cm$^{-1}$ band because only in it are the two hydroxyl groups close enough to permit intramolecular hydrogen-bonding. (Intermolecular hydrogen-bonding is not possible at high dilution in a non-polar solvent like CCl$_4$.)
2.40 (a) OH
     CH₃
     CH₃

(b) enantiomers

   OH     OH
   CH₃    CH₃
   H      H

   (Enantiomers and diastereomers are defined in Chapter 5.)

2.41 Which of the following pairs of compounds is not a pair of constitutional isomers?

(a) CH₃—O—CH=CH₂ and CH₂CH₂CH
(b)       and  CH₄CH=CH₂CH₃
(c) CH₃C—OH         and  HO—CH₂CH₂
(d) CH₃CH₂C≡CH      and  CH₃CH=CH₂CH₂
(e) CH₃CH₃CH(CH₃)₂  and  (CH₃)₂CHCH(CH₃)₂

2.42 Which of the answers to Problem 2.1 contains an ether group?

(a) A tertiary alcohol with the formula C₆H₁₂O
(b) An N,N-disubstituted amide with the formula C₄H₉NO
(c) The alkene isomer of C₅H₅Cl, that has no dipole moment
(d) An ester with the formula C₂H₆O₂
(e) The isomer of C₅H₅Cl, that cannot show cis-trans isomerism
(f) The isomer of C₅H₅O, that would have the lowest boiling point

2.43 Which of the following pairs of structures represents a pair of isomers?

(a) H₃C—C≡C—H     and  H₃C—C≡C—H₃
(b) CH₃C≡CH        and  CH₃CH₂C≡CH
(c) Cl—C—F         and  Cl—C—F
(d) CH₃CH₂CHCH₃    and  CH₃CH₃CHCH₃
(e) More than one of these pairs are isomers.

2.4 Give a structural formula for each of the following:

(a) A tertiary alcohol with the formula C₆H₁₂O
(b) An N,N-disubstituted amide with the formula C₄H₉NO
(c) The alkene isomer of C₅H₅Cl, that has no dipole moment
(d) An ester with the formula C₂H₆O₂
(e) The isomer of C₅H₅Cl, that cannot show cis-trans isomerism
(f) The isomer of C₅H₅O, that would have the lowest boiling point
(g) The isomer of C₂H₃N that would have the lowest boiling point

2.5 Write the bond-line formula for a constitutional isomer of the compound shown below that does not contain a double bond.

CH₃CH₂CH=CH₂

2.6 Circle the compound in each pair that would have the higher boiling point.

(a) CH₃CH₂CH₂OH or CH₃CH₂CHO
(b) CH₃CH₂NH or CH₃CH₂CH₃
(c) CH₃COCH₃ or CH₃CH₂OH
(d) CH₃OCH₂CH₂OH or CH₃OCH₂CH₃
(e) CH₃CH₂NHCCH₃ or CH₃CN(CH₃)₂

2.7 Give an acceptable name for each of the following:

(a) O
(b) CH₃NH₂
(c) CH₃C₅H₅N

3 AN INTRODUCTION TO ORGANIC REACTIONS: ACIDS AND BASES

SOLUTIONS TO PROBLEMS

3.1 (a) CH₃⁻ + H⁺ → CH₃CH₂⁺
(b) CH₃⁻ + AI⁻ → CH₃CH₂⁺
(c) CH₃⁻ + CH₃⁺ → CH₃CH₂⁺

3.2 (a) Lewis base (b) Lewis acid
(c) Lewis base (d) Lewis base
(e) Lewis acid (f) Lewis base

3.3 CH₃⁻ + H⁺ → CH₃CH₂⁺

3.4 (a) \[ K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = 1.77 \times 10^{-4} \]

Let \[ x = [\text{H}_3\text{O}^+] = [\text{HCO}_2^-] \] at equilibrium
then, \[ 0.1 - x = [\text{HCO}_2\text{H}] \] at equilibrium
but, since the \( K_a \) is very small, \( x \) will be very small and \( 0.1 - x = 0.1 \)
Therefore,
\[ \frac{[\text{H}_3\text{O}^+] x}{x} = 1.77 \times 10^{-4} \]
\[ 0.1 = 1.77 \times 10^{-5} \]
\[ x = 0.0042 = [\text{H}_3\text{O}^+] = [\text{HCO}_2^-] \]
(g) The isomer of $C_2H_4N$ that would have the lowest boiling point.

2.5 Write the bond-line formula for a constitutional isomer of the compound shown below that does not contain a double bond.

$$\text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2$$

2.6 Circle the compound in each pair that would have the higher boiling point.

(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{CHO}$
(b) $\text{CH}_3\text{N}^+\text{H}$ or $\text{CH}_3\text{NH}_2$
(c) $\text{CH}_3\text{OCH}_3$ or $\text{CH}_3\text{CH}_2\text{OH}$
(d) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ or $\text{CH}_3\text{OCH}_2\text{OCH}_3$
(e) $\text{CH}_3\text{CH}_2\text{CNHCH}_3$ or $\text{CH}_3\text{CN(CH}_3)_2$

2.7 Give an acceptable name for each of the following:

(a) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$
(b) $\text{CH}_3\text{C}==\text{NCH}_3$
(c) $\text{CH}_3\text{CH}==\text{NCH}_3$

3.1 (a) $\text{CH}_3\text{O}^-\text{H}^+$ + $\text{B}^-$ $\rightarrow$ $\text{CH}_3\text{O}^-\text{B}^-\text{H}^+$
(b) $\text{CH}_3\text{Cl}^+$ + $\text{AlCl}_3$ $\rightarrow$ $\text{CH}_3\text{Cl}^-\text{Al}^+\text{Cl}_3$
(c) $\text{CH}_3\text{O}^-\text{CH}_3^+$ + $\text{B}^-$ $\rightarrow$ $\text{CH}_3\text{O}^-\text{B}^-\text{CH}_3^+$

3.2 (a) Lewis base (b) Lewis acid
(c) Lewis base (d) Lewis base
(e) Lewis acid (f) Lewis base

3.3 $\text{CH}_3\text{N}^+\text{H}^- + \text{B}^-$ $\rightarrow$ $\text{CH}_3\text{N}\overset{\equiv}{\text{B}}\text{H}^-$

Lewis base Lewis acid

3.4 (a) $K_a = \frac{[\text{H}_2\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = 1.77 \times 10^{-4}$

Let $x = [\text{H}_2\text{O}^+] = [\text{HCO}_2^-]$ at equilibrium
then, $0.1 - x = [\text{HCO}_2\text{H}]$ at equilibrium
but, since the $K_a$ is very small, $x$ will be very small and $0.1 - x = 0.1$
Therefore,

\[
\frac{1}{x} \times x = 1.77 \times 10^{-4}
\]
3.10 Structures A and B make equal contributions to the overall hybrid. This means that the carbon-oxygen bonds should be the same length and that the oxygens should bear equal positive charges.

\[
\begin{align*}
A & \quad \text{Stronger acid} \\
B & \quad \text{Stronger base (from NaH)} \\
\end{align*}
\]

3.11 (a) CHCl₃CO₂H would be the stronger acid because the electron-withdrawing inductive effect of two chlorine atoms makes it more positive. The electron-withdrawing effect of the two chlorine atoms would also stabilize the dichloroacetate ion more effectively by dispersing its negative charge more extensively.

(b) CCl₄CO₂H would be the stronger acid for reasons similar to those given in (a), except here there are three versus two electron-withdrawing chlorine atoms involved.

(c) CH₃CO₂H would be the stronger acid because the electron-withdrawing effect of a fluorine atom is greater than that of a bromine atom (fluorine is more electronegative).

(d) CH₃CO₂H is the stronger acid because the fluorine atom is nearer the carboxyl group and is, therefore, better able to exert its electron-withdrawing inductive effect. (Remember: Inductive effects weaken steadily as the distance between the substituent and the group increases.)

3.12 All compounds containing oxygen and most compounds containing nitrogen will have an unshared electron pair in their oxygen or nitrogen atom. These compounds can, therefore, act as bases and accept a proton from concentrated sulfuric acid. When they accept a proton, these compounds become either oxonium ions or ammonium ions, and having become ionic, they are soluble in the polar medium of sulfuric acid. The only nitrogen compounds that do not have an electron pair on their nitrogen atom are quaternary ammonium compounds, and these, already being ionic, also dissolve in the polar medium of concentrated sulfuric acid.

3.13 (a) CH₂O⁻ + H⁺ \rightarrow \text{methanol} \rightarrow \text{CH}_2\text{O}⁻ + \text{H}_2

\[
\begin{align*}
\text{Stronger acid} & \quad \text{pK}_a = -16 \\
\text{Stronger base (from NaH)} & \quad \text{pK}_a = 35 \\
\end{align*}
\]

(b) CH₃CH₂O⁻ + NH₃ \rightarrow \text{ethanol} \rightarrow \text{CH}_3\text{CH}_2\text{O}⁻ + \text{NH}_3

\[
\begin{align*}
\text{Stronger acid} & \quad \text{pK}_a = 16 \\
\text{Stronger base (from NaNH₃)} & \quad \text{pK}_a = 38 \\
\end{align*}
\]
AN INTRODUCTION TO ORGANIC REACTIONS: ACIDS AND BASES

3.18 \( \text{H}_2\text{SO}_4 > \text{H}_2\text{O}^+ > \text{CH}_3\text{CO}_2\text{H} > \text{CH}_3\text{NH}_2^+ > \text{NH}_3 > \text{CH}_3\text{CH}_3 \)

3.19 (a) \( \text{CH}_3\text{CH}_2\text{Cl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CH}_2\text{Cl}^+ + \text{AlCl}_4^- \\
\text{Lewis base} \quad \text{Lewis acid} \\
\text{base} \quad \text{acid}
\)

(b) \( \text{CH}_3\text{OH} + \text{BF}_3 \rightarrow \text{CH}_3\text{B}^+ + \text{F}^- \\
\text{Lewis base} \quad \text{Lewis acid}
\)

(c) \( \text{CH}_3\text{C} \quad \text{CH} \quad \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{C} \quad $$ \quad \text{H}_2\text{O}_2^+ \\
\text{Lewis acid} \quad \text{Lewis base}
\)

3.20 (a) \( \text{CH}_3\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{OH}^+ + \text{Cl}^- \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\)

(b) \( \text{CH}_3\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^- \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\)

(c) \( \text{H} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{C} \quad \text{C} \quad \text{H}_2\text{O}_2 \quad \text{H}_2\text{O}_2^+ \\
\text{Lewis acid} \quad \text{Lewis base}
\)

3.21 Because the proton attached to the highly electronegative oxygen atom of \( \text{CH}_3\text{OH} \) is much more acidic than the protons attached to the much less electronegative carbon atom.

3.22 \( \text{CH}_3\text{CH}_2\text{O}_2\text{H} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2^+ + \text{H}-\text{C} \quad \text{H} \\
\text{C} \quad \text{C} \quad \text{H}_2\text{O}_2 \quad \text{H}_2\text{O}_2^+ \\
\text{Lewis acid} \quad \text{Lewis base}
\)

3.23 (a) \( K_a = \log 1.77 \times 10^{-4} = 4 - 0.248 = 3.752 \\
\text{pK}_a = 10^{-13}
\)

(b) Yes. Since \( \text{A}^- \) is the stronger base and \( \text{HB} \) is the stronger acid, the following acid-base reaction will take place.

\[ \text{A}^- + \text{HB} \rightarrow \text{A}^- \quad \text{H} \quad \text{B}^+ \]

\[ \text{Stronger base} \quad \text{Stronger acid} \quad \text{Weaker base} \quad \text{Weaker acid} \]

3.24 (a) \( \text{HB} \) is the stronger acid because it has the smaller \( \text{pK}_a \).

(b) Yes. Since \( \text{A}^- \) is the stronger base and \( \text{HB} \) is the stronger acid, the following acid-base reaction will take place.

\[ \text{A}^- + \text{HB} \rightarrow \text{A}^- \quad \text{H} \quad \text{B}^+ \]

\[ \text{Stronger base} \quad \text{Stronger acid} \quad \text{Weaker base} \quad \text{Weaker acid} \]
3.25 (a) \[ CH_3CH=CH_2 + HO^- \rightarrow CH_3CH=CH_2O^- + H^+ \]

(b) \[ C_6H_5COOH + HO^- \rightarrow C_6H_5COO^- + H^+ \]

(c) No appreciable acid-base reaction takes place because \( CH_3CH_2ONa \) is too weak a base to remove a proton from ethyne.

(d) \[ H-C≡C-H + CH_3CH_2 \text{hexane} \rightarrow H-C≡C^- + CH_3CH_3 \]

(e) \[ CH_3CH=C^- + CH_3CH_3 \text{hexane} \rightarrow CH_3CH-CH^- + CH_3CH_3 \]

3.26 (a) \[ C_6H_6 + NaNH_2 \rightarrow C_6H_5-Na^+ + NH_3 \]

(b) \[ CH_3-C-O-H + NaNH_2 \rightarrow CH_3-C-O^--Na^+ + NH_3 \]

(c) \[ CH_3CH_2CH_2OH + NaOH \rightarrow CH_3CH_2CH_2ONa + H_2 \]

3.27 (a) \( CH_3CH_2OH > CH_3CH_2NH_2 > CH_3CH_2CH_3 \)

Oxygen is more electronegative than nitrogen, which is more electronegative than carbon. The O-H bond is most polarized, the N-H bond is next, and the C-H bond is least polarized.

(b) \( CH_3CH_2O^- < CH_3CH_2NH^- < CH_3CH_2CH_2^- \)

The weaker the acid, the stronger the conjugate base.

3.28 (a) \[ CH_3C≡CH > CH_2=CHCH_2 > CH_3CH_2CH_3 \]

(b) \[ CH_3CHCO_2H > CH_3CH_2CO_2H > CH_3CO_2H \]

(c) \[ CH_3CH_2OH > CH_3CH_2OH > CH_3OH \]

3.29 (a) \[ CH_3NH_4^+ < CH_3NH_2 < CH_3NH^- \]

(b) \[ CH_3O^- < CH_3NH^- < CH_3CH_2^- \]

(c) \[ CH_3C≡C^- < CH_3CH=CH^- < CH_3CH_2CH_3^- \]

3.30 The acidic hydrogens must be attached to oxygen atoms. In \( H_2PO_3^- \), one hydrogen is bonded to a phosphorus atom:

3.31 (a) \[ H-CO^- + H^+ \rightarrow H-C-O^- + H^+ \]

(b) \[ H-CO^- + H^+ \rightarrow H-C-O^- + H^+ \]

(c) \[ H-C-O^- \rightarrow H-C-O^- + H^+ \]

(d) \[ H-O^- + CH_3^- \rightarrow H-O^- + CH_3^- \]

(e) \[ H-O^- + CH_3^- \rightarrow H-O^- + CH_3^- \]
3.32 (a) Assume that the acidic and basic groups of glycine in its two forms have acidities and basicities similar to those of acetic acid and methyamin. Then consider the equilibrium between the two forms:

\[
\begin{align*}
\text{Stronger} & \quad \text{Stronger} \\
\text{base} & \quad \text{acid} \\
\text{Weaker} & \quad \text{Weaker}
\end{align*}
\]

We see that the ionic form contains the groups that are the weaker acid and weaker base. The equilibrium, therefore, will favor this form.

(b) The high melting point shows that the ionic structure better represents glycine.

3.33 (a) The second carboxyl group of malonic acid acts as an electron-withdrawing group and stabilizes the conjugate base formed (i.e., HO₂⁻). When malonic acid loses a proton, [any factor that stabilizes the conjugate base of an acid always increases the strength of the acid (Section 3.10).] An important factor here may be an entropy effect as explained in Section 3.9.

(b) When "O₂⁻CH₂CO₂⁻H" loses a proton, it forms a dianion, "O₂⁻CH₂CO₂⁻". This dianion is destabilized by having two negative charges in close proximity.

3.34 HB is the stronger acid.

3.35 \[\Delta G^° = \Delta H^° - T \Delta S^°\]

\[= 6.3 \, \text{kJ mol}^{-1} - (298 \, \text{K} \times 0.0084 \, \text{kJ mol}^{-1} \text{K}^{-1})\]

\[= 3.8 \, \text{kJ mol}^{-1}\]

\[\log K_p = \log K_a = -\frac{\Delta G^°}{2.303RT}\]

\[pK_a = \frac{-\Delta G^°}{2.303RT}\]

\[pK_a = 3.8 \, \text{kJ mol}^{-1} \times \frac{1}{(2.303 \times 0.008314 \, \text{kJ mol}^{-1} \text{K}^{-1} \times 298 \, \text{K})}\]

\[pK_a = 0.66\]

3.36 The dianion is a hybrid of the following resonance structures:

3.37 (a) \(A\) is \(\text{CH}_3\text{CHO}^-\)

\(B\) is \(\text{CH}_3\text{OH}\)

\(C\) is \(\text{CH}_3\text{CH}_2\text{SCH}_2\text{CO}_2^-\)

\(D\) is \(\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}\)

\(E\) is \(\text{OH}^-\)

(b) \(\text{CH}_3\text{CH}_2\text{S}^-\text{H}^- + \text{CH}_3\text{O}^-\) \(\rightarrow\) \(\text{CH}_3\text{CH}_2\text{S}^-\text{CH}_3\) + \(\text{CH}_3\text{O}^-\)

\(\text{CH}_3\text{CH}_2\text{S}^-\text{H}^- + \text{CH}_2\text{CH}_2\) \(\rightarrow\) \(\text{CH}_3\text{CH}_2\text{S}^-\text{CH}_2\text{CH}_2\) + \(\text{H}^-\)

3.38 (a) \(\text{CH}_3\text{CH}_2\text{OD} + \text{CH}_3\text{CH}_2\text{Li} \rightarrow \text{CH}_3\text{CH}_2\text{O}^-\text{Li}^+ + \text{CH}_3\text{CH}_2\text{D}\)

Hexane could be used as solvent. Liquid ammonia and ethanol could not because they would compete with \(\text{CH}_3\text{CH}_2\text{OD}\) and generate mostly non-deuterio-labelled \(\text{CH}_3\text{CH}_2\text{D}\).

(b) \(\text{NH}_2^- + \text{CH}_3\text{C}==\text{CH} \rightarrow \text{NH}_3 + \text{CH}_3\text{C}==\text{C}^-\)

Hexane or liquid ammonia could be used; ethanol is too acidic and would lead to \(\text{CH}_3\text{CH}_2\text{OH}^-\) (ethoxide ion) instead of the desired alkynide ion.

(c) \(\text{HCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-\)

Hexane or ethanol could be used; liquid ammonia is too strong a base and would lead to \(\text{NH}_3^-\) instead of the desired ammonium ion.

3.39 (a) Since DMSO does not bind with (solvate) anions, their electron density remains high and their size small, both of which make nucleophiles more reactive.
3.6 Which would be the weakest base?
(a) CH₃CO₂Na  (b) CF₃CO₂Na  (c) CHF₂CO₂Na  (d) CH₂FCO₂Na

3.7 What acid-base reaction (if any) would occur when NaF is dissolved in H₂SO₄?

3.8 The pKₐ of CH₃NH₃⁺ equals 10.6; the pKₐ of (CH₃)₂NH₃⁺ equals 10.7. Which is the stronger base, CH₃NH₂ or (CH₃)₂NH?

3.9 Supply the missing reagents.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C} & \equiv \text{CH} + \quad \text{hexane} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{C} \equiv \text{C}^+ \text{Li}^+ + \text{CH}_3\text{CH}_2^- \\
\text{CH}_3\text{CH}_2\text{C} & \equiv \text{CD} + \text{LiOD}
\end{align*}
\]

3.10 Supply the missing intermediates and reagents.

\[
\begin{align*}
\text{CH}_3\text{Br} + 2\text{Li} & \rightarrow (a) + \text{LiBr} \\
\text{CH}_3\text{CHCH}_2\text{OT} + \text{LiOT} & \rightarrow (c)
\end{align*}
\]
4 ALKANES: NOMENCLATURE, CONFORMATIONAL ANALYSIS, AND AN INTRODUCTION TO SYNTHESIS

SOLUTIONS TO PROBLEMS

4.1

Heptane
2-Methylhexane
3-Methylhexane
2,2-Dimethylpentane
3,3-Dimethylpentane
2,3-Dimethylpentane
2,4-Dimethylpentane
3-Ethylpentane
2,2,3-Trimethylbutane

4.2

(a) CH₃CH₂CH₂CH₂CH₃
pentyl
CH₃CH₂CH(CH₃)CH₂CH₃
1-Methylbutyl
CH₃CH₂CH(CH₂)CH₂CH₃
3-Methylbutyl
CH₃CH₂CH₂CH₂CH₃
1,2-Dimethylpropyl
CH₃CH₂CH₂CH₂CH₂CH₃
1,1-Dimethylpropyl

(b) See the answer to Problem 4.1 for the names of C₇H₁₆ isomers.
**ALKANES**

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)

1-Pentanol

\( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)

2-Pentanol

\( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)

3-Pentanol

\( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

2,2-Dimethyl-1-propanol

CH

4.5 (a) \( 1-(1\text{-Methylethyl})-2-(1,1\text{-dimethylethyl})\text{cyclopentane or 1-tert-butyl-2-isopropylcyclopentane} \)

(b) \( 1\text{-Methyl-2-(2-methyIpropyl)cyclohexane or 1-isobutyl-2-methylcyclohexane} \)

(c) Butylcyclohexane

(d) \( 1\text{-Chloro-2,4-dimethylcyclohexane} \)

(e) \( 2\text{-Chlorocyclopentanol} \)

(f) \( 3\text{-[(1,1-Dimethylethyl)cyclohexanol or 3-tert-butylcyclohexanol} \)

4.6 (a) \( 2\text{-Chlorobicyclo[1.1.0]butane} \)

(b) Bicyclo[3.2.1]octane

(c) Bicyclo[2.1.1]hexane

(d) \( 9\text{-Chlorobicyclo[3.3.1]nonane} \)

(e) \( 2\text{-Methylbicyclo[2.2.2]octane} \)

(f) \( \text{Bicyclo[3.1.0]hexane or } \text{bicycle[2.1.1]hexane} \)

4.7 (a) trans-3-Heptene

(b) 2,5-Dimethyl-2-octene

(c) 4-Ethyl-2-methyl-1-hexene

(d) 3,5-Dimethylcyclohexene

(e) 4-Methyl-4-penten-2-ol

(f) 2-Chloro-3-methyl-3-cyclohexen-1-ol

4.8 (a) \( \text{=} \)

(b) \( \text{=} \)

(c) \( \text{=} \)

(d) \( \text{=} \)

(e) \( \text{=} \)

(f) \( \text{=} \)

(g) \( \text{=} \)

(h) \( \text{=} \)

(i) \( \text{=} \)

(j) \( \text{=} \)

4.9 1-Hexyne

2-Hexyne

3-Hexyne

3-Methyl-1-pentyne

4-Methyl-1-pentyne

4-Methyl-2-pentyne

4.10

<table>
<thead>
<tr>
<th>Potential Energy</th>
<th>Rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>50°</td>
</tr>
<tr>
<td>120°</td>
<td>180°</td>
</tr>
<tr>
<td>240°</td>
<td>300°</td>
</tr>
<tr>
<td>360°</td>
<td></td>
</tr>
</tbody>
</table>

Rotation →
4.11 \( \log K_{eq} = \frac{\Delta G^\circ}{-2.303RT} = \frac{-7600}{(-2.303)(8.314 \text{ J K}^{-1}\text{ mol}^{-1})(298 \text{ K})} = 1.32 \)

\( K_{eq} = 21.38 \)

Let \( e \) = amount of equatorial form
and \( a \) = amount of axial form

then, \( K_{eq} = \frac{e}{a} = 21.38 \)

\( e = 21.38a \)

\( \%e = \frac{21.38a}{a + 21.38a} \times 100 = 95.5\% \)

4.12 (a) \( \text{Cl} \)
(b) \( \text{Br} \)
(cis) (trans)

4.13 (a-d) CH₃-CH₂-CH₃

More stable because larger group is equatorial
Less stable because larger group is axial

4.14 (a) CH₃-CH₂-CH₂-CH₃

(b) Yes

(c) Less stable because the large tert-butyl group is axial
More stable because the large tert-butyl group is equatorial

(d) More stable because both methyl groups are equatorial
Less stable because both methyl groups are axial

4.15 CH₂=CHCH₃ → H₂ \( \overset{\text{Pd, Pt or Ni}}{\rightarrow} \) CH₃CH₂CHCH₃

4.16 CH₃CH=CHCH₃ → Zn \( \overset{\text{H}_2\text{O}^+}{\rightarrow} \) CH₃CHCHCH₃

4.17 HC≡C-CH₂-CH₃ \( \overset{\text{NaNH₃}}{\rightarrow} \) Na⁺:C≡CCH₂CH₃ \( \overset{\text{CH₃-Br}}{\rightarrow} \) (-NaBr)
4.18
(a) Nonane

\[
\text{HC} = \text{C}^- + \text{X(CH}_2\text{CH}_3} \rightarrow \text{CH}_3\text{C} = \text{C}^- + \text{X(CH}_2\text{CH}_3} \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{C}^- + \text{X(CH}_2\text{CH}_3} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C} = \text{C}^- + \text{X(CH}_2\text{CH}_3}
\]

Etc. (using the other alkyne and alkyl halide homolog pairs)

2-Methylheptadecane

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

(after hydrogenation of the alkyne from one of the possible retrosynthetic disconnections)

\[
\text{X} + \text{X} \rightarrow \text{X} + \text{X}
\]

(Note that is not a good choice because the alkyl halide is branched at the carbon adjacent to the halogen. Neither would work because the alkyl halide is secondary.)

(b) For any pair of reactants above that is a feasible retrosynthetic disconnection, the steps for the synthesis would be

\[
\text{RC} = \text{C}^- \overset{\text{NaNH}_2}{\longrightarrow} \text{RC} = \text{C}^- \overset{\text{R}^- \text{X}}{\longrightarrow} \text{R} = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

4.19
(a) \( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\overset{\text{Cl}}{\longrightarrow} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)

(b) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{Br}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(c) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CHCH}_2\overset{\text{Cl}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CHCH}_2\)

(d) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{CH}_3\text{CH}_2\text{CHCH}_2}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(e) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{CH}_3\text{CH}_2\text{CHCH}_2}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(f) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{CH}_3\text{CH}_2\text{CHCH}_2}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(g) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{CH}_3\text{CH}_2\text{CHCH}_2}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(h) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{CH}_3\text{CH}_2\text{CHCH}_2}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(i) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{OH}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(j) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{OH}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(k) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{OH}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(l) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{OH}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(m) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{OH}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

(n) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\overset{\text{OH}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CHCH}_2\)

4.20
(a) 3,3,4-Trimethylhexane

(b) 2,2-Dimethyl-1-butanol

(c) 3,5,7-Trimethylnonane

(d) 3-Methyl-4-heptanol

(e) 2-Bromobicyclo[3.3.1]nonane

(f) 2,5-Dibromo-4-ethylhexane

(g) Cyclobutyleclopentane

(h) 7-Chlorobicyclo[2.2.1]heptane

4.21 The two secondary carbon atoms in sec-butyl alcohol are equivalent; however, there are three five-carbon alcohols (pentyl alcohols) that contain a secondary carbon atom.
4.22 (a) \[ \text{CH}_3\text{C} = \text{C} = \text{CH}_3 \text{ H}_2 \text{C} \text{C} \text{H}_3 \]
2,2,3,3-Tetramethylbutane

(b) \[ \text{Cyclohexane} \]

(c) \[ \text{1,1-Dimethyliclohexane} \]

4.23 Each of the desired alkenes must have the same carbon skeleton as 2-methylbutane, \( \text{CH}_3 = \text{C} = \text{C} = \text{CH}_3 \); they are therefore

\[ \begin{align*}
\text{CH}_3 = \text{C} & \text{CH}_3 \\
\text{CH}_3 & \text{C} \text{CH}_3 \\
\text{CH}_3 & \text{C} \text{C} = \text{CHCH} = \text{CH}_3
\end{align*} \]

4.24 Only one isomer of \( \text{C}_6\text{H}_{14} \) can be produced from five isomeric hexyl chlorides (\( \text{C}_6\text{H}_6\text{Cl}_5 \)).

The alkane is 2-methylpentane, \( \text{CH}_3\text{C} \text{CH}_2\text{CH}_2\text{CH}_3 \). The five alkyl chlorides are

\[ \begin{align*}
\text{CH}_3 & \text{ClCH}_2\text{CH} \text{CH}_2\text{CH}_3 \\
\text{CH}_3 & \text{CC} \text{ClCH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3 & \text{ClCH} \text{CH} \text{CH}_2\text{CH}_2\text{CH}_3
\end{align*} \]

4.25 \( \text{CH}_3\text{CH} = \text{CHCH}_3 \) 2,3-Dimethylbutane

From two alkyl chlorides

\[ \begin{align*}
\text{CH}_3 & \text{C} \text{CH}_3 \\
\text{C} & \text{CH}_3 \\
\text{Cl} & \text{CH}_3 \\
\text{Cl} & \text{CH}_3
\end{align*} \]

\[ \text{Zn} \ \text{H}_2\text{O} \Rightarrow \text{CH}_3\text{CH} = \text{CHCH}_3 \]

4.26 From two alkenes

\[ \begin{align*}
\text{CH}_2 = \text{C} & \text{CH}_3 \\
\text{H} & \text{CH}_3
\end{align*} \]

\[ \xrightarrow{\text{H}_2 \ \text{Pd, Pt, or Ni pressure}} \]

\[ \text{CH}_3\text{CH} \text{CHCH}_3 \]

4.27 \( \text{(CH}_3\text{)}_3\text{CCH}_3 \) is the most stable isomer (i.e., it is the isomer with the lowest potential energy) because it evolves the least amount of heat on a molar basis when subjected to complete combustion.
A homologous series is one in which each member of the series differs from the one preceding it by a constant amount, usually a CH₃ group. A homologous series of alkyl halides would be the following:

\[
\begin{align*}
\text{CH}_3X \\
\text{CH}_3\text{(CH}_3\text{)}X \\
\text{CH}_3\text{(CH}_3\text{)}_2X \\
\text{CH}_3\text{(CH}_3\text{)}_3X \\
\text{etc.}
\end{align*}
\]

This conformation is less stable because 1,3-diaxial interactions with the large tert-butyl group cause considerable repulsion.

This conformation is more stable because 1,3-diaxial interactions with the smaller methyl group are less repulsive.

\[4.30\]

Cyclopentane  Methylcyclobutane  \(c\text{-is-1,2-Dimethylcyclopropane}\)

\[4.31\]

(a)  (b)  (c)  (d)

\[4.32\]

\[S - A + 1 = N\]

For cubane, \(S = 12\) and \(A = 8\). Thus \(12 - 8 + 1 = N\); \(N = 5\) rings in cubane.
4.35 (a) Pentane would boil higher because its chain is unbranched. Chain-branching lowers the boiling point.

(b) Heptane would boil higher because it has the larger molecular weight and would, because of its larger surface area, have larger van der Waals attractions.

(c) 2-Chloropropane because it is more polar and because it has a larger molecular weight.

(d) 1-Propanol would boil higher because its molecules would be associated with each other through hydrogen-bond formation.

(e) Propanone (CH₃COCH₃) would boil higher because its molecules are more polar.

4.36 C₇H₁₆

Bicyclo[1.1.0]butane

1-Butyne

The IR stretch at -2250 cm⁻¹ for the alkylne C≡C bond distinguishes these two compounds.

4.37 trans-1,2-Dimethycyclopropane would be more stable because there is less crowding between its methyl groups.

Less stable

More stable

4.38 (a)

trans

More stable because both methyl groups are equatorial in the most stable conformation

(cis

Less stable because one methyl group must be axial and so has the larger heat of combustion

(b)

trans

More stable because both methyl groups are equatorial in the most stable conformation

(cis

Less stable because one methyl group must be axial and so has the larger heat of combustion

4.39 (a)

More stable conformation because both alkyl groups are equatorial

(b)

More stable because larger group is equatorial

(c)

More stable conformation because both alkyl groups are equatorial

(d)

More stable because larger group is equatorial

4.40 If the cyclobutane ring were planar, the C—Br bond moments would exactly cancel in the trans isomer. The fact that trans-1,3-dibromocyclobutane has a dipole moment shows the ring is not planar.

Planar form

µ = 0

Bent form

µ ≠ 0
4.41 (a) \( \text{H}_2; \text{Pd, Pt, or Ni catalyst, pressure} \)
(b) (1) \( \text{NaNH}_2 \) (2) \( \text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)
(c) (1) \( \text{H}_2; \text{Pd, Pt, or Ni catalyst, pressure} \)
(d) \( \text{H}_2; \text{Pd, Pt, or Ni catalyst, pressure} \)
(e) \( \text{X} = \text{CH}_2\text{CCH}_3 \)
(f) \( \text{X} = \text{CH}_2\text{CCH}_3 \)

4.42 (a) \( \text{cis-1,2-dimethyloctane} \)
(b) From Table 4.8 we find that this is \( \text{cis-1,2-dimethyloctane} \).
(c) Since catalytic hydrogenation produces the cis isomer, both hydrogen atoms must have added from the same side of the double bond. (As we shall see in Section 7.14, this type of addition is called a syn addition.)

\[
\begin{align*}
\text{cis-1,2-Dimethyloctane} & \quad \text{cis isomer is produced when both hydrogen atoms add from the same side.}
\end{align*}
\]

4.43 (a) From Table 4.8 we find that this is \( \text{trans-1,2-dichlorocyclohexane} \).
(b) Since the product is the trans isomer, we can conclude that the chlorine atoms have added from opposite sides of the double bond.

\[
\begin{align*}
\text{trans-1,2-Dichlorocyclohexane} & \quad \text{trans isomer is produced when the chlorine atoms add from opposite sides of the double bond.}
\end{align*}
\]

4.44 If \( \text{trans-1,3-di-tert-butylcyclohexane} \) were to adopt a chair conformation, one tert-butyl group would have to be axial. It is, therefore, more energetically favorable for the molecule to adopt a twist boat conformation.

4.45 (a) More rules are needed (see Chapter 7) to indicate relative stereochemistry for these 1-bromo-2-chloro-1-fluorothiophenes.
(b) \( \text{Bicyclo[4.4.0]dec-2-ene} \) (or decalin)
(c) \( \text{Bicyclo[4.4.0]dec-2-ene} \) (or \( \Delta^1 \)-octalin)
(d) \( \text{Bicyclo[4.4.0]dec-2-ene} \) (or \( \Delta^1 \)-octalin)

**Note:** The common name decalin comes from decahydrophthalene, the derivative of phthalene (\( \text{C}_8\text{H}_4\text{O}_2 \)) that has had all of its five double bonds converted to single bonds by addition of 10 atoms of hydrogen. Certain similarly comes from octaohydrophthalene and contains one surviving double bond. When using these common names derived from phthalene, their skeletons are usually numbered like that of phthalene. When, as in case (d), a double bond does not fit between the indicated carbon and the next higher numbered carbon, its location is specified as shown.

Also, the symbol \( \Delta \) is one that has been used with common names to indicate the presence of a double bond at the position specified by the accompanying superscript number(s).

4.46 \( \text{D-glucose} \) has all of its attached groups equatorial in the lowest energy chair conformation. Other sugars have at least one group axial in their lowest energy chair conformation.

Because if the configuration of stereocenters is changed, not all of the ring substituents can simultaneously be in the preferred equatorial position, as they are in glucose.

4.47

The \( \text{trans isomer} \) would be more stable because it can have both of its rings in the favored chair conformation, avoiding the many eclipsing interactions found in the doubly boat conformation of the \( \text{cis isomer} \) (which would actually increase its stability slightly by twisting to avoid some eclipsing interactions).

4.48

\[
\begin{align*}
\text{H} &= \text{C} \quad \text{C} &= \text{C} \quad \text{H} \\
\text{2 mol equiv. } \text{LiNH}_2 &\quad \text{2 mol equiv. } \text{CH}_3\text{C}_2\text{H}_2\text{Br} \\
\text{CH}_3\text{C}_2\text{H}_2\text{C} &= \text{C} \quad \text{C} &= \text{C} \quad \text{CH}_3\text{C}_2\text{H}_2\text{C}_2\text{H}_3 \\
\text{H}_2 &\quad \text{Pt catalyst} &\quad \text{CH}_3\text{C}_2\text{H}_2\text{C}_2\text{H}_3
\end{align*}
\]
QUIZ

4.1 Consider the properties of the following compounds:

<table>
<thead>
<tr>
<th>NAME</th>
<th>FORMULA</th>
<th>BOILING POINT (°C)</th>
<th>MOLECULAR WEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>CH₃CH₃</td>
<td>-88.2</td>
<td>30</td>
</tr>
<tr>
<td>Fluoromethane</td>
<td>CH₃F</td>
<td>-78.6</td>
<td>34</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>+64.7</td>
<td>32</td>
</tr>
</tbody>
</table>

Select the answer that explains why methanol boils so much higher than ethane or fluoromethane, even though they all have nearly equal molecular weights.
(a) Ion-ion forces between molecules.
(b) Weak dipole-dipole forces between molecules.
(c) Hydrogen bonding between molecules.
(d) Van der Waals forces between molecules.
(e) Covalent bonding between molecules.

4.2 Select the correct name of the compound whose structure is

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

(a) 2,5-Diethyl-6-methyloctane
(b) 2,4-Diethyl-3-methyloctane
(c) 4-Ethyl-3,7-dimethyloctane
(d) 6-Ethyl-3,7-dimethyloctane
(e) More than one of the above

4.3 Select the correct name of the compound whose structure is CH₃CH₃CH₃Cl

(a) Butyl chloride
(b) Isobutyl chloride
(c) sec-Butyl chloride
(d) tert-Butyl chloride
(e) More than one of the above

4.4 The structure shown in Problem 4.2 has:
(a) 1°, 2°, and 3° carbon atoms
(b) 1° and 2° carbon atoms only
(c) 1° and 3° carbon atoms only
(d) 2° and 3° carbon atoms only
(e) None of the above

4.5 How many isomers are possible for C₅H₇Br?
(a) 1 (b) 2 (c) 3 (d) 4 (e) 5

4.6 Which isomer of 1,3-dimethylcyclohexane is more stable?
(a) cis (b) trans (c) Both are equally stable
(d) Impossible to tell

4.7 Which is the lowest energy conformation of trans-1,4-dimethylcyclohexane?

(a) (b) (c) (d) (e) More than one of the above

4.8 Supply the missing structures

(a) (b)

2-Bromobicyclo[2.2.1]heptane
(c) Newman projection for a gauche form of 1,2-dibromoethane

4.9 Supply the missing reagents:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{Cl}
\end{array}
\quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{Cl}
\end{array}
\quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{Cl}
\end{array}
\]

4.10 The most stable conformation of trans-1-isopropyl-3-methylcyclohexane:

5. STEREOCHEMISTRY:
CHIRAL MOLECULES

5.1 (a) Achiral (c) Chiral (e) Chiral (g) Chiral
(b) Achiral (d) Chiral (f) Chiral (h) Achiral

5.2 (a) Yes (b) No (c) No

5.3 (a) They are the same molecule. (b) They are enantiomers.

5.4 (a), (b), and (f) do not have stereocenters.

\[
\begin{array}{c}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{OH}
\end{array}
\quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{OH}
\end{array}
\quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{OH}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHBr}
\end{array}
\quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHBr}
\end{array}
\quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHBr}
\end{array}
\end{array}
\]
STEREOCHEMISTRY: CHIRAL MOLECULES

5.5
(a) Limonene
(b) Thalidomide

5.6
(a) Two in each instance.

5.7
The following items possess a plane of symmetry, and are, therefore, achiral.
(a) A screwdriver
(b) A baseball bat (ignoring any writing on it)
(h) A hammer

5.8
In each instance below, the plane defined by the page is a plane of symmetry.

5.9

5.10
(c) (1) is (S)
  (2) is (R)
(d) (1) is (S)
  (2) is (R)
(e) (1) is (S)
  (2) is (R)
(g) (1) is (S)
  (2) is (R)
(h) (1) is (S)
  (2) is (R)
5.11 (a) -Cl > -SH > -OH > -H
(b) -CH₂Br > -CH₂Cl > -CH₂OH > -CH₃
(c) -OH > -CHO > -CH₃ > -H
(d) -C(CH₃)₃ > -CH=CH₂ > -CH(CH₃)₂ > -H
(e) -OCH₃ > -N(CH₃)₂ > -CH₃ > -H

5.12 (a) (S)  (b) (R)  (c) (S)

5.13 (a) Enantiomers
(b) Two molecules of the same compound
(c) Enantiomers

5.14

(S)-(+) Carvone  (R)-(−) Carvone

5.15 (a) Enant. Excess = \frac{\text{observed rotation}}{\text{specific rotation of pure enantiomer}} \times 100

= \frac{+1.151^\circ}{+5.756^\circ} \times 100

= 20.00\%

(b) since the (R) enantiomer (see Section 5.7C) is +, the (R) enantiomer is present in excess.

5.16 (a) (b) (c)

(S)-Ibuprofen  (S)-Methylidopa  (S)-Penicillamine

5.17 (a) Diastereomers.
(b) Diastereomers in each instance.
(c) No, diastereomers have different melting points.
(d) No, diastereomers have different boiling points.
(e) No, diastereomers have different vapor pressures.

### STUDY AID

An Approach to the Classification of Isomers

We can classify isomers by asking and answering a series of questions:

1. **Do the compounds have the same molecular formula?**
   - **Yes**
   - **No**

2. **Are they different?**
   - **Yes**  They are not isomers.
   - **No**

3. **They are isomers.**
   - **Do they differ in connectivity?**
     - **Yes**  They are constitutional isomers.
     - **No**  They are stereoisomers.

4. **Are they mirror images of each other?**
   - **Yes**  They are enantiomers.
   - **No**  They are diastereomers.
5.18 (a) It would be optically active.
(b) It would be optically active.
(c) No, because it is a meso compound.
(d) No, because it would be a racemic form.

5.19 (a) Represents A
(b) Represents C
(c) Represents B

5.20 (a) Enantiomers
(b) Enantiomers
(c) Enantiomers

5.21 B is (2S,3S)-2,3-Dibromobutane
C is (2R,3S)-2,3-Dibromobutane

5.22 (a) (1) is (2S,3S)-2,3-Dichlorobutane
(2) is (2R,3R)-2,3-Dichlorobutane
(3) is (2R,3S)-2,3-Dichlorobutane
(b) (1) is (2S,4S)-2,4-Pentanediol
(2) is (2R,4R)-2,4-Pentanediol
(3) is (2R,4S)-2,4-Pentanediol
(c) (1) is (2S,3R)-1,4-Dichloro-2,3-difluorobutane
(2) is (2S,3S)-1,4-Dichloro-2,3-difluorobutane
(3) is (2R,3S)-1,4-Dichloro-2,3-difluorobutane
(d) (1) is (2S,4S)-4-Chloro-2-pentanol
(2) is (2R,4R)-4-Chloro-2-pentanol
(3) is (2S,4R)-4-Chloro-2-pentanol
(4) is (2R,4S)-4-Chloro-2-pentanol
(e) (1) is (2S,3S)-2-Bromo-3-fluorobutane
(2) is (2R,3R)-2-Bromo-3-fluorobutane
(3) is (2S,3R)-2-Thromo-3-fluorobutane
(4) is (2R,3S)-2-Bromo-3-fluorobutane
STEREOCHEMISTRY: CHIRAL MOLECULES

5.23

\[
\text{Chloramphenicol}
\]

5.24
(a) No  (b) Yes  (c) No  (d) No  (e) Diastereomers  (f) Diastereomers

5.25
Meso compound

5.26
(a) \( (1R,2R) \) Enantiomers (both cis)  (b) \( (1R,2S) \) Enantiomers (both trans)  (c) Achiral (trans)  (d) Achiral (cis)

5.27 See Problem 5.26. The molecules in (c) are achiral, so they have no (R,S) designation.

5.28
\[
\begin{align*}
\text{(S)-(+) Glyceraldehyde} & \rightarrow \text{(S)+(+) Glyceric acid} \\
\text{HO-C-H} & \rightarrow \text{HO-C-OH} \\
\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OH} & \text{(5)-(+) Isoserine} \\
\text{HO-C-H} & \rightarrow \text{HO-C-OH} & \text{(See the following reaction, also.)} \\
\text{HgO} & \rightarrow \text{HNO}_2 & \text{(S)-(+) Isoserine} \\
\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OH} & \text{(R)-(++) 3-Bromo-2-hydroxypropanoic acid} \\
\text{HO-C-H} & \rightarrow \text{HO-C-OH} & \text{(S)-(+) Lactic acid} \\
\text{HNO}_2 & \rightarrow \text{HBr} & \text{(S)-(+) Isoserine} \\
\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O} & \text{(R)-(++) 3-Bromo-2-hydroxypropanoic acid} \\
\text{HO-C-H} & \rightarrow \text{HO-C-OH} & \text{(S)-(+) Lactic acid}
\end{align*}
\]
STEREOCHEMISTRY: CHIRAL MOLECULES

5.29  
\[
\begin{align*}
\text{(S)+(+)1-Chloro-2-methylbutane} & \quad \text{Zn, D}^+ \text{ (s.g. DCI) in D}_2 \text{O} \\
\text{(R)-l-Deuterio-2-methylbutane}
\end{align*}
\]

5.30  (a), (b), (f) and (g) only

5.31  (a) Seven.
(b) (R)- and (S)-3-Methylhexane and (R)- and (S)-2,3-dimethylpentane.

5.32  (a) and (b)

(c) Four
(d) Because a trans arrangement of the one carbon bridge is structurally impossible. Such a molecule would have too much strain.

5.33  (a) A is (R,S)-2,3-dichlorobutane; B is (S,S)-2,3-dichlorobutane; C is (R,R)-2,3-dichlorobutane.
(b) A

5.34  (a)  
\[
\begin{align*}
\text{CH}_3 & \quad \text{or} \quad \text{CH}_2\text{CH}_3 \\
\text{etc.}
\end{align*}
\]

(b)  
\[
\begin{align*}
\text{CH}_3 & \quad \text{and} \quad \text{H}_2\text{C} \\
\text{etc.}
\end{align*}
\]

(c)  
\[
\begin{align*}
\text{CH}_3 & \quad \text{and} \quad \text{CH}_2\text{CH}_3 \\
\text{etc.}
\end{align*}
\]

(d)  
\[
\begin{align*}
\text{H} & \quad \text{CH} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{and} \quad \text{CH}_2\text{CH}_3
\end{align*}
\]

5.35  (j) Enantiomers that are interconvertible by a ring flip
(b) Enantiomers
(c) Diastereomers
(d) Same
(e) Same
(f) Constitutional isomers
(g) Diastereomers
(h) Enantiomers
(i) Same

5.36  All of these molecules are expected to be planar. Their stereochemistry is identical to that of the corresponding haloethenes. (a) can exist as cis and trans isomers. Only one compound exists in the case of (b) and (c).

5.37  (a)  
\[
\begin{align*}
\text{(1)} & \quad \text{(2)} & \quad \text{(3)} & \quad \text{(4)}
\end{align*}
\]

(b) (3) and (4) are chiral and are enantiomers of each other.
(c) Three fractions: a fraction containing (1), a fraction containing (2), and a fraction containing (3) and (4) [because, being enantiomers, (3) and (4) would have the same vapor pressure].
(d) None

5.38  (a)  
\[
\begin{align*}
\text{(b)} & \quad \text{(c)} & \quad \text{(d)}
\end{align*}
\]

(b) No, they are not superposable.
(c) No, and they are, therefore, enantiomers of each other.
(d)
(c) No, they are not superposable.
(f) Yes, and they are therefore just different conformations of the same molecule.

5.39 (a) 

(b) Yes, and therefore trans-1,4-dieethylcyclohexane is achiral.
(c) No, they are different orientations of the same molecule.
(d) Yes, cis-1,4-dieethylcyclohexane is a stereoisomer (a diastereomer) of trans-1,4-dieethylcyclohexane.

(cis-1,4-Dieethylcyclohexane)

(e) No, it, too, is superposable on its mirror image. (Notice, too, that the plane of the page constitutes a plane of symmetry for both cis-1,4-dieethylcyclohexane and for trans-1,4-dieethylcyclohexane as we have drawn them.)

5.40 trans-1,3-Dieethylcyclohexane can exist in the following enantiomeric forms.

trans-1,3-Dieethylcyclohexane enantiomers

cis-1,3-Dieethylcyclohexane consists of achiral molecules because they have a plane of symmetry. [The plane of the page (below) is a plane of symmetry.]

(cis-1,3-Dieethylcyclohexane)

5.41 (a) Since it is optically active and not resolvable, it must be the meso form:

(b) (c) (d) A racemic modification

5.42 (a) \[
\alpha = \frac{-30^\circ}{0.10 \text{ g/mL}(1.0 \text{ dm})} = -300^\circ
\]

(b) \[
\alpha = \frac{163^\circ}{0.05 \text{ g/mL}(1.0 \text{ dm})} = +330^\circ
\]

The two rotation values can be explained by recognizing that this is a powerfully optically active substance and that the first reading, assumed to be \(-30^\circ\), was really \(+330^\circ\). Making this change the \(\alpha\) becomes \(+330^\circ\) in both cases.

(c) No, the apparent \(0^\circ\) rotation could actually be \(+0^\circ\) or \(-360^\circ\) (an integral multiple of these values).

5.43 Yes, it could be a meso form or an enantiomer whose stereocenters, by rare coincidence, happen to cancel each others activities.

5.44 A compound \(\text{C}_4\text{H}_8\text{O}_2\) has an index of hydrogen deficiency of 1. Thus, it could possess a carbon-carbon double bond, a carbon-oxygen double bond, or a ring.

The IR spectral data rule out a carbonyl group but indicate the presence of an \(-\text{OH}\) group.

No stable structure having molecular formula \(\text{C}_4\text{H}_8\text{O}_2\) with a C=O bond can exist in stereoisomeric forms and 1,2-cyclopropanediol can exist in three stereoisomeric forms.

Only ethylene oxide (oxirane) derivatives are possible for \(Y\):

\[\text{CH}_2\text{OH} \quad \text{HOCH}_2\]

QUIZ

5.1 Describe the relationship between the two structures shown.

(a) Enantiomers (b) Diastereomers (c) Constitutional isomers (d) Conformations (e) Two molecules of the same compound

(a) (b) (c)

5.2 Which of the following molecule(s) possess(es) a plane of symmetry?

(a) (b) (c)

(d) More than one of these (e) None of these
5.3 Give the (R-S) designation of the structure shown.

(a) (R) (b) (S) (c) Neither, because this molecule has no stereocenter (d) Impossible to tell

5.4 Select the words that best describe the following structure:

(a) Chiral (b) Meso form (c) Achiral (d) Has a plane of symmetry (e) More than one of these

5.5 Select the words that best describe what happens to the optical rotation of the alkene shown when it is hydrogenated to the alkane according to the following equation:

\[ \text{CH}_3\text{CH}_{2}\text{CH} = \text{CH}_2 + \text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3\text{CH}_{2}\text{CH}_2\text{CH}_3 \]

(a) Increases (b) Drops to zero (c) Changes sign (d) Stays the same (e) Impossible to predict

5.6 There are two compounds with the formula C₇H₁₄ that are capable of existing as enantiomers. Write three-dimensional formulas for the (S) isomer of each.

5.7 Compound A is optically active and is the (S) isomer.

\[ \text{A} \xrightarrow{\text{H}_2, \text{Ni}} \text{CH}_3\text{CHCHCH}_2\text{CH}_3 \]

5.8 Compound B is a hydrocarbon with the minimum number of carbon atoms necessary for it to possess a stereocenter and, as well, alternative stereoisomers about a double bond.
6.3 (a) We know that when a secondary alkyl halide reacts with hydroxide ion by substitution, the reaction occurs with inversion of configuration because the reaction is $S_N^2$. If we know that the configuration of (−)-2-butanol (from Section 5.7C) is that shown here, then we can conclude that (+)-2-chlorobutane has the opposite configuration.

(b) Again the reaction is $S_N^2$. Because we now know the configuration of (+)-2-chlorobutane to be (S) [cf., part (a)], we can conclude that the configuration of (−)-2-iodobutane is (R).

6.4 (a) (b)
6.6 (a) Being primary halides, the reactions are most likely to be \( S_N2 \), with the nucleophile in each instance being a molecule of the solvent (i.e., a molecule of ethanol).

(b) Steric hindrance is provided by the substituent or substituents on the carbon \( \beta \) to the carbon bearing the leaving group. With each addition of a methyl group at the carbon (below), the number of pathways open to the attacking nucleophile becomes fewer.

6.7 Protic solvents are those that have an \( H \) bonded to an oxygen or nitrogen (or to another strongly electronegative atom). Therefore, the protic solvents are formic acid, \( HCOH \); formamide, \( HCNH_2 \); ammonia, \( NH_3 \); and ethylene glycol, \( HOCH_2CH_2OH \).

Aprotic solvents lack an \( H \) bonded to a strongly electronegative element. Aprotic solvents in this list are acetone, \( CH_3CH_2CHO \); acetonitrile, \( CH_3CN \); sulfur dioxide, \( SO_2 \); and trimethyleneimine, \( (CH_2)_3N \).

6.8 The reaction is an \( S_N2 \) reaction. In the polar aprotic solvent (DMF), the nucleophile (\( CN^- \)) will be relatively unencumbered by solvent molecules, and, therefore, it will be more reactive than in ethanol. As a result, the reaction will occur faster in \( N,N \)-dimethylformamide.

6.9 (a) \( CH_3O^- \)
(b) \( H_2S \)
(c) \( (CH_2)_3P \)

6.10 (a) Increasing the percentage of water in the mixture increases the polarity of the solvent. (Water is more polar than methanol.) Increasing the polarity of the solvent increases the rate of the solvolysis because separated charges develop in the transition state. The more polar the solvent, the more the transition state is stabilized (Section 6.1-4d).

(b) In an \( S_N2 \) reaction of this type, the charge becomes dispersed in the transition state:

\[
\begin{align*}
  \text{I}^- + CH_3CH_2Cl & \rightarrow CH_3CH_2^-Cl^- \rightarrow CH_3CH_2^- + Cl^- \\
\text{Reactants} \quad \text{Charge is concentrated} \quad \text{Transition state} \quad \text{Charge is dispersed}
\end{align*}
\]

Increasing the polarity of the solvent increases the stabilization of the reactant \( \text{I}^- \) more than the stabilization of the transition state, and thereby increases the free energy of activation, thus decreasing the rate of reaction.

6.11 \( CH_3OSO_2CF_3 \rightarrow CH_3I \rightarrow CH_3Br \rightarrow CH_3Cl \rightarrow CH_3F \rightarrow ^3CH_3OH \)

(Most reactive)

6.12 (a) \( CH_3CH_2O + CH_3CH_2H \rightarrow CH_3CH_2O + Na^+ Br^- \)
(b) \( CH_3CO + CH_3CH_2H \rightarrow CH_3CO + Na^+ Br^- \)
(c) \( CH_3S + CH_3CH_2H \rightarrow CH_3S + Na^+ Br^- \)

6.13 (a) \( CH_3CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2OH + NaBr \)
(b) \( CH_3CH_2CH_2Br + Na \rightarrow CH_3CH_2CH_2Na + NaBr \)
(c) \( CH_3CH_2CH_2Br + CH_3CH_2ONa \rightarrow CH_3CH_2CH_2OCH_2CH_3 + NaBr \)
(d) \( CH_3CH_2Br + CH_3Na \rightarrow CH_3CH_2CH_2CH_3 + NaBr \)
(e) \( CH_3CH_2CH_2Br + CH_3CO \rightarrow CH_3CH_2CH_2OCH_2CH_3 + NaBr \)
(f) \( CH_3CH_2CH_2Br + CH_3CN \rightarrow CH_3CH_2CH_2CN + NaBr \)
(g) \( CH_3CH_2CH_2Br + CH_3CO \rightarrow CH_3CH_2CH_2CN + NaBr \)
(h) \( CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CH_2CN + NaBr \)
(i) \( CH_3CH_2CH_2Br + NaSh \rightarrow CH_3CH_2CH_2SH + NaBr \)

6.14 (a) 1-Bromopropane would react more rapidly because, being a primary halide, it is less hindered.
(b) 1-Iodobutane, because iodide ion is a better leaving group than chloride ion.

de 1-Chlorobutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylpropane.

d) 1-Chloro-3-methylbutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylbutane.

e) 1-Chlorohexane because it is a primary halide. Phenyl halides are unreactive in $S_n^2$ reactions.

6.15 (a) Reaction (1) because ethoxide ion is a stronger nucleophile than ethanol.

(b) Reaction (2) because the ethyl sulfide ion is a stronger nucleophile than the ethoxide ion in a protic solvent. (Because sulfur is larger than oxygen, the ethyl sulfide ion is less solvated and it is more polarizable.)

c) Reaction (2) because triphenylphosphine [($\text{C}_6\text{H}_5)_3\text{P}$] is a stronger nucleophile than triphenylamine. (Phosphorus atoms are larger than nitrogen atoms.)

d) Reaction (2) because in an $S_n^2$ reaction the rate depends on the concentration of the substrate and the nucleophile. In reaction (2) the concentration of the nucleophile is twice that of the reaction (1).

6.16 (a) Reaction (2) because bromide ion is a better leaving group than chloride ion.

(b) Reaction (1) because water is a more polar solvent than methanol, and $S_n^1$ reactions take place faster in more polar solvents.

c) Reaction (2) because the concentration of the substrate is twice that of reaction (1). (The major reaction would be $S_n^2$. However, the problem asks us to consider that small portion of the overall reaction that proceeds by an $S_n^1$ pathway.)

(d) Both reactions would take place at the same rate because, being $S_n^2$, reactions, they are independent of the concentration of the nucleophile. (The major reaction would be $S_n^2$. However, the problem asks us to consider that small portion of the overall reaction that proceeds by an $S_n^1$ pathway.)

(e) Reaction (1) because the substrate is a tertiary halide. Phenyl halides are unreactive in $S_n^1$ reactions.

6.17 Possible methods are given here.

(a) $\text{CH}_3\text{Cl} + \text{HO}^- \rightarrow \text{CH}_3\text{SH}$

(b) $\text{CH}_3\text{CH}_2\text{Cl} + \text{HO}^- \rightarrow \text{CH}_3\text{CH}_2\text{SH}$

(c) $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{OH}$

(f) $\text{CH}_3\text{CH}_2\text{Cl} + \text{SH}^- \rightarrow \text{CH}_3\text{CH}_2\text{SH}$

(g) $\text{CH}_3\text{Cl} + \text{CN}^- \rightarrow \text{CH}_3\text{CN}$

(h) $\text{CH}_3\text{CH}_2\text{Cl} + \text{CN}^- \rightarrow \text{CH}_3\text{CH}_2\text{CN}$

(i) $\text{CH}_3\text{OH} + \text{Na}^+ \rightarrow \text{CH}_3\text{ONa}$

(j) $\text{CH}_3\text{CH}_2\text{OH} + \text{Na}^+ \rightarrow \text{CH}_3\text{CH}_2\text{ONa}$

(k) $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{OH}$

6.18 (a) The reaction will not take place because the leaving group would have to be a methyl anion, a very powerful base, and a very poor leaving group.

(b) The reaction will not take place because the leaving group would have to be a hydride ion, a very powerful base, and a very poor leaving group.

(c) The reaction will not take place because the leaving group would have to be a carbanion, a very powerful base, and a very poor leaving group.

(d) The reaction will not take place by an $S_n$ mechanism because the substrate is a tertiary halide, and it, therefore, not susceptible to $S_n^2$ attack because of the steric hindrance. (A very small amount of $S_n^1$ reaction may take place, but the main reaction will be $S_n^2$ to produce a carbocation.)

(e) The reaction will not take place because the leaving group would have to be a $\text{CH}_3\text{O}^-$ anion, a strong base, and a very poor leaving group.

(f) The reaction will not take place because the first reaction that would take place would be an acid-base reaction that would convert the ammonia to an ammonium ion. An ammonium ion, because it lacks an electron pair, is not nucleophilic.

$$\text{NH}_3 + \text{CH}_3\text{OH} \rightarrow \text{NH}_4^+ + \text{CH}_3\text{OH}$$
6.19 The better yield will be obtained by using the secondary halide, 1-bromo-1-phenylethane, because the desired reaction is E2. Using the primary halide will result in substantial S_N2 reaction as well, producing the alcohol instead of the desired alkene.

6.20 Reaction (2) would give the better yield because the desired reaction is an S_N2 reaction, and the substrate is a methyl halide. Use of reaction (1) would, because the substrate is a secondary halide, result in considerable elimination by an E2 pathway.

6.21 (a) The major product would be CH(CH_3)_2CHCH_2CH_2OH (by an S_N2 mechanism) because the substrate is primary and the nucleophile base is not hindered. Some CH(CH_3)_2CHCH_2CH_3 would be formed by an E2 mechanism.

(b) The major product would be CH(CH_3)_2CHCH_2CH_2Cl (by an E2 mechanism), even though the substrate is primary because the base is a hindered strong base. Some CH(CH_3)_2CHCH_2CH_2OCH(CH_3)_2 would be produced by an S_N2 mechanism.

(c) For all practical purposes, (CH_3)_2CH=CH_2 (by an E2 mechanism) would be the only product because the substrate is tertiary and the base is strong.

d) Same answer as (c) above.

(e) Because the substrate is tertiary and the only nucleophile is the solvent, mechanism is S_N1. The two products that follow would be formed.

(f) (formed by an S_N2 mechanism) would, for all practical purposes, be the only product. Iodide ion is a very weak base and a good nucleophile.

(g) CH(CH_3)_2CHCH_2CH_3 (by an E2 mechanism) would be the major product because the substrate is secondary and the base/nucleophile is a strong base. Some of the ether, CH(CH_3)_2CHCH_2CH_3, would be formed by an S_N2 pathway.

(h) The major product would be CH(CH_3)_2CHCH_2CH_2OH (by an S_N2 mechanism) because the acetate ion is a weak base. Some CH(CH_3)_2CHCH_2CH_3 might be formed by an E2 pathway.

(i) CH(CH_3)_2CHCH_2CH_3 and CH=CHCH_2CH_3 (by E2) would be major products, and (5) CH(CH_3)_2CHCH_2CH_3 (by S_N2) would be the minor product.

(j) (2)-CH(CH_3)_2CHCH_2CH_3 and CH(CH_3)_2CHCH_3 (by S_N1) would be the major product.

(k) (R)-CH(CH_3)_2CHCH_2CH_3 (by S_N2) would be the only product.

6.22 (a), (b), and (c) are all S_N2 reactions and, therefore, proceed with inversion of configuration. The products are

6.23 Isobutyl bromide is more sterically hindered than ethyl bromide because of the methyl groups on the β carbon atom.

6.24 (a) S_N2 because the substrate is a 1° halide.

(b) Rate = k [CH(CH_3)_3C][I^-]^2

(c) 1 X 10^-6 mol L^{-1} s^{-1}
6.25 (a) CH$_3$NH$^-$ because it is the stronger base.
(b) CH$_3$O$^-$ because it is the stronger base.
(c) CH$_3$SH because sulfur atoms are larger and more polarizable than oxygen atoms.
(d) (C$_6$H$_5$)$_3$P because phosphorus atoms are larger and more polarizable than nitrogen atoms.
(e) H$_2$O because it is the stronger base.
(f) NH$_3$ because it is the stronger base.
(g) HS$^-$ because it is the stronger base.
(h) OH$^-$ because it is the stronger base.

6.26 (a) H$_2$C=CH$_2$Br + OH$^-$ \( \rightleftharpoons \) H$_2$Br + OCH$_2$CH$_3$ + Br$^-$
(b) H$_2$C=CH-Br + OH$^-$ \( \rightleftharpoons \) H$_2$C=CH-CH$_3$ + Br$^-$

6.27 Iodic acid is a good nucleophile and a good leaving group; it can rapidly convert an alkyl chloride or allyl bromide into an alkyl iodide, and the alkyl iodide can then react rapidly with another nucleophile. With methyl bromide in water, for example, the following reaction can take place:

\[
\text{CH}_3\text{Br} \xrightarrow{\text{H}_2\text{O} \text{ alone}} \text{CH}_3\text{OH}^+ + \text{Br}^- \\
\text{CH}_3\text{Br} \xrightarrow{\text{H}_2\text{O} \text{ containing I}} \text{CH}_3I \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{OH}_2^- + \text{I}^- 
\]

6.28 tert-Butyl alcohol and tert-butyl methyl ether are formed via an S$_\text{N}_2$ mechanism. The rate of the reaction is independent of the concentration of methoxide ion (from sodium methoxide). This, however, is only one reaction that causes tert-butyl bromide to disappear. A competing reaction that also causes tert-butyl bromide to disappear is an E2 reaction in which methoxide ion reacts with tert-butyl bromide. This reaction is dependent on the concentration of methoxide ion; therefore, increasing the methoxide ion concentration causes an increase in the rate of disappearance of tert-butyl bromide.

6.29 (a) You should use a strong base, such as RO$^-$, at a higher temperature to bring about an E2 reaction.
(b) Here we want an S$_\text{N}_2$ reaction. We use ethanol as the solvent and as the nucleophile, and we carry out the reaction at a low temperature so that elimination will be minimized.

6.30 l-Bromobicyclo[2.2.1]heptane is unreactive in an S$_\text{N}_2$ reaction because it is a tertiary halide and its ring structure makes the backside of the carbon bearing the leaving group completely inaccessible to attack by a nucleophile.

\[
\text{Na}^+ \xrightarrow{\text{Et}_3\text{O}(-\text{H}_2)} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\
\text{CH}_3\text{CH}_2\text{CHCH}_3 \xrightarrow{\text{O}^- \text{Na}^+} \text{CH}_3\text{CH(CH}_2\text{CH}_3) \xrightarrow{\text{(-NaBr)}} \text{CH}_3\text{CH(CH}_2\text{CH}_3)\text{C}^- \text{Br}^- \\
\text{(CH}_3)_2\text{C}^- \text{S}^- \xrightarrow{\text{Na}^+ \text{Et}_3\text{O}(-\text{H}_2)} \text{(CH}_3)_2\text{C}^- \text{S}^- \xrightarrow{\text{(-NaBr)}}
\]

6.31 The cyanide ion has two nucleophilic atoms; it is what is called an ambident nucleophile.

\[
\text{CN}^- \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{CN}^- \\
\text{CN}^- \xrightarrow{\text{Na}^+ \text{Et}_3\text{O}(-\text{H}_2)} \text{H}_2\text{CN}^- \xrightarrow{\text{O}^- \text{Na}^+} \text{CH}_3\text{CH(CN)} \xrightarrow{\text{(-NaBr)}} \\
\text{CN}^- \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{CN}^- \xrightarrow{\text{Na}^+ \text{Et}_3\text{O}(-\text{H}_2)} \text{H}_2\text{CN}^- \xrightarrow{\text{O}^- \text{Na}^+} \text{CH}_3\text{CH(CN)} \xrightarrow{\text{(-NaBr)}}
\]

6.32 (a) CH$_3$CH$_2$CH$_2$CH$_3$ + NaH \( \rightarrow \) CH$_3$CH$_2$CH$_2$CH$_3$ \( + \) Na$^+$
(b) (CH$_3$)$_3$CSNa \( \rightarrow \) (CH$_3$)$_3$C$^-$Na$^+$ \( \rightarrow \) (CH$_3$)$_3$C$^-$Br$^-$
**6.33** (a) 

![Chemical structure](image1)

(Formation of this product depends on the fact that bromide ion is a much better leaving group than chloride ion.)

(b) CH₃CH₂CH₃CH₂CH₂CH₂Cl⁻ → CH₃CH₂CH₃CH₂CH₂Cl⁻ + Na⁺

(Formation of this product depends on the greater reactivity of 1° substrates in S_N2 reactions.)

(c) S⁻CH₂CH₂N⁻

(Here two S_N2 reactions produce a cyclic molecule.)

(d) Cl⁻CH₂CH₂CH₂CH₂OH + Na⁺ + Et₂O → Cl⁻CH₂CH₂CH₂CH₂Na⁺ + Et₂O

(e) CH₃CH₃CH₃ + Na⁺ + HO⁻ → (CH₃)₃CHNa⁺ + HO⁻

(6.34) The rate-determining step in the S_N1 reaction of tert-buty1 bromide is the following:

$$\text{(CH₃)}₃\text{C}⁻ + \text{Br}⁻ \rightarrow \text{(CH₃)}₃\text{C}^+ \text{Br}⁻ + \text{H⁺}$$

$$\text{(CH₃)}₃\text{C}^+ \rightarrow \text{(CH₃)}₂\text{COH}⁻$$

(6.35) Two different mechanisms are involved. (CH₃)₂CBr reacts by an S_N1 mechanism, and apparently this reaction takes place faster. The other three alkyl halides react by an S_N2 mechanism, and their reactions are slower because the nucleophile (H₂O) is weak. The reaction rates of CH₃Br, CH₂CH₂Br, and (CH₃)₂CHBr are affected by the steric hindrance, and thus their order of reactivity is CH₃Br > CH₂CH₂Br > (CH₃)₂CHBr.
6.36: The nitrite ion is an ambident nucleophile; that is, it is an ion with two nucleophilic sites. The equivalent oxygen atoms and the nitrogen atom are nucleophilic.

\[ \text{Nucleophilic site} \quad \overset{\ddots}{\ddots} \text{N} \longrightarrow \overset{\ddots}{\ddots} \text{O} \quad \text{Nucleophilic site} \]

6.37: (a) The transition state has the form:

\[ \ddagger^* \quad \ddagger^- \quad \text{Nu} \longrightarrow R \quad \text{L} \]

in which charges are developing. The more polar the solvent, the better it can solvate the transition state, thus lowering the free energy of activation and increasing the reaction rate.

(b) The transition state has the form:

\[ \ddagger^* \quad \ddagger^* \quad R \longrightarrow \text{L} \]

in which the charge is becoming dispersed. A polar solvent is less able to solvate this transition state than it is to solvate the reactant. The free energy of activation, therefore, will become somewhat larger as the solvent polarity increases, and the rate will be slower.

6.38: (a) \[ \text{Cl} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{I} \]

(b) \[ \text{HO} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{Cl} + \text{some alkene} \]

6.39: (a) In an S_12 reaction the carbocation intermediate reacts rapidly with any nucleophile it encounters in a Lewis acid–Lewis base reaction. In the case of the S_1,2 reaction, the leaving group departs only when "pushed out" by the attacking nucleophile, and some nucleophiles are better than others.

(b) \( \text{CN}^- \) is a much better nucleophile than ethanol and hence the nitrite is formed in the S_1,2 reaction of \( \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \). In the case of \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \), the tert-buty1 cation reacts chiefly with the nucleophile present in higher concentration, here the ethanol solvent.

6.40: \[ \Delta H^\circ, \text{kJ mol}^{-1} \]

\[ (\text{CH}_3)_2\text{C}^- \quad \text{Cl} \quad \longrightarrow \quad (\text{CH}_3)_2\text{C}^+ \quad + \quad \ddagger^- \quad +328 \quad \text{Homolytic bond dissociation energy} \]

\[ (\text{CH}_3)_2\text{C}^- \quad \longrightarrow \quad (\text{CH}_3)_2\text{C}^+ \quad + \quad \ddagger^* \quad +715 \quad \text{Ionization potential} \]

\[ \ddagger^* \quad + \quad \ddagger^- \quad \longrightarrow \quad \text{Cl}^- \quad -330 \quad \text{Electron affinity} \]

\[ (\text{CH}_3)_2\text{C}^- \quad \longrightarrow \quad (\text{CH}_3)_2\text{C}^+ \quad + \quad \text{Cl}^- \quad +713 \quad \text{Heterolytic bond dissociation energy} \]

6.41: (a) The entropy term is slightly favorable. (The enthalpy term is highly unfavorable.)

\[ \Delta G^\circ = \Delta H^\circ + T \Delta S^\circ \]

\[ = 26.6 \text{ kJ mol}^{-1} + (298)(0.00481 \text{ kJ mol}^{-1}) \]

\[ = 25.2 \text{ kJ mol}^{-1} \]

(c) \[ \log K_{eq} = \frac{-\Delta G^\circ}{2.303RT} \]

\[ = \frac{-25.2 \text{ kJ mol}^{-1}}{(2.303)(0.008314 \text{ kJ mol}^{-1} K^{-1})(298 \text{ K})} \]

\[ = -4.165 \]

\[ K_{eq} = 10^{-4.165} = 3.85 \times 10^{-5} \]

(d) The equilibrium is very much more favorable in aqueous solution because solvation of the products (ethanol, hydroxide ions, and chloride ions) takes place and thereby stabilizes them.

6.42: The mechanism for the reaction involves the participation of the carboxylate group. In step 1 (see following reaction) an oxygen of the carboxylate group attacks the stereocenter from the backside and displaces bromide ion. (Silver ion aids in this process in much the same way that protonation assists the ionization of an alcohol.) The configuration of the stereocenter inverts in step 1, and a cyclic ester called an \( \alpha \)-lactone forms:

\[
\text{Step 1: }
\begin{align*}
\text{H}_3\text{C} & \quad \text{Br} \quad \text{Ag}^+ \\
\text{H} & \quad \text{CH}_3 \\
\text{CH} & \quad \text{Br} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

\[ \rightarrow \quad \text{C}^- \quad \text{C}^+ \quad \text{Ag}^+ \quad \text{Br}^- \quad \text{Ag}^+ \\
\]

An \( \alpha \)-lactone

The highly strained three-membered ring of the \( \alpha \)-lactone opens when it is attacked by a water molecule in step 2. This step also takes place with an inversion of configuration:

\[
\text{Step 2: }
\begin{align*}
\text{CH} & \quad \text{Br} \quad \text{OH} \\
\text{H} & \quad \text{CH}_3 \\
\text{C} & \quad \text{O} \\
\end{align*}
\]

\[ \rightarrow \quad \text{C}^- \quad \text{C}^+ \quad \text{OH}^- \quad \text{H}^+ \quad \text{H}^+ \\
\]

The net result of two inversions (in steps 1 and 2) is an overall retention of configuration.
*6.43 (a) and (b) 

\[ \text{Ag}_2O \quad \text{H}_2O \quad \text{retention} \]

\[ \text{HO} \quad \text{CO}_3^2- \quad \text{H} \quad \text{CH}_2 \quad \text{CO}_2^2- \]

\[ \text{(S)-(-)-Chlorosuccinic acid} \]

\[ \text{KOH} \quad \text{inversion} \]

\[ \text{HO} \quad \text{CO}_3^2- \quad \text{H} \quad \text{CH}_2 \quad \text{CO}_2^2- \]

\[ \text{(R)(+)-Chlorosuccinic acid} \]

(c) The reaction takes place with retention of configuration.

\[ \text{(S)(-)-Malic acid} \]

\[ \text{KOH} \quad \text{inversion} \]

\[ \text{HO} \quad \text{CO}_3^2- \quad \text{H} \quad \text{CH}_2 \quad \text{CO}_2^2- \]

\[ \text{(R)(+)-Chlorosuccinic acid} \]

(d) 

\[ \text{SOCl}_2 \]

\[ \text{HO}_2C\text{CH}_2\text{CHO}_2\text{C}_2\text{H}_4 \]

\[ \text{(S)(-)-Chlorosuccinic acid} \]

\[ \text{KOH} \quad \text{inversion} \]

\[ \text{HO}_2C\text{CH}_2\text{CHO}_2\text{C}_2\text{H}_4 \]

\[ \text{(R)(+)-Chlorosuccinic acid} \]

*6.44 

No change of configuration occurs, just a change in the relative priority of a group at the stereocenter.

\[ \text{CH}_3 \quad \text{O} \quad \text{CH}_2 \quad \text{H} \quad \text{CH}_3 \]

\[ \text{CH}_2 \quad \text{Cl} \]

\[ \text{A} \quad \text{B} \]

\[ \text{H}_3\text{C} \quad \text{C} \quad \text{H} \quad \text{CH}_2 \quad \text{Cl} \]

\[ \text{H}_3\text{C} \quad \text{C} \quad \text{H} \quad \text{CH}_2 \quad \text{N}_3 \]

\[ \text{C} \quad \text{C} \quad \text{H} \quad \text{CH}_2 \quad \text{Cl} \]

*6.45 Comparison of the molecular formulas of starting material and product indicates a loss of HCl. The absence of IR bands in the 1620–1680 cm\(^{-1}\) region rules out the presence of the alkene function.

A nucleophilic substitution agrees with the evidence:

\[ \text{HO} \quad \text{Cl} \quad \text{S} \quad \text{H} \quad \text{C} \]

*6.46 The IR evidence indicates that C possesses both an alkene function and a hydroxyl group. An E2 reaction on this substrate produces enantiomeric unsaturated alcohols.
6.1 Which set of conditions would you use to obtain the best yield in the reaction shown?

\[
\begin{align*}
\text{CH}_2\text{-CH}_2\text{-Br} & \quad ? \quad \text{CH}_2\text{-CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

(a) \( \text{H}_2\text{O}, \text{heat} \)  (b) \( \text{CH}_3\text{CH}_2\text{ONa/CH}_3\text{CH}_2\text{OH, heat} \)  (c) \( \text{Heat alone} \)  (d) \( \text{H}_2\text{SO}_4 \)  (e) None of the above

6.2 Which of the following reactions would give the best yield?

(a) \( \text{CH}_3\text{ONa} + (\text{CH}_3)_2\text{CHBr} \rightarrow \text{CH}_3\text{OCH(CH}_3)_2 \)
(b) \( (\text{CH}_3)_2\text{CHONa} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{OCH(CH}_3)_2 \)
(c) \( \text{CH}_3\text{OH} + (\text{CH}_3)_2\text{CHBr} \rightarrow \text{CH}_3\text{OCH(CH}_3)_2 \)

6.3 A kinetic study yielded the following reaction rate data:

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial Concentration</th>
<th>Initial Rate of disappearance of ( \text{R-Br} ) and formation of ( \text{R-OH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Which of the following statements best describe this reaction?

(a) The reaction is second order.  (b) The reaction is first order.
(c) The reaction is \( S_n \).  (d) Increasing the concentration of \( \text{OH}^- \) has no effect on the rate.
(e) More than one of the above.

6.4 There are four compounds with the formula \( \text{C}_4\text{H}_8\text{Br} \). List them in order of decreasing reactivity in an \( S_n \) reaction.

6.5 Supply the missing reactants, reagents, intermediates, or products.

\[
\begin{align*}
\text{A} & \quad (\text{C}_3\text{H}_7\text{Br)} \\
\text{B} & \quad (\text{Minor product}) \\
\text{C} & \quad (\text{Major product}) \\
\text{D} & \quad (\text{Minor product}) \\
\end{align*}
\]

6.6 Which \( S_n \) reaction will occur most rapidly. (Assume the concentrations and temperatures are all the same.)

(a) \( \text{CH}_3\text{O}^- + \text{CH}_3\text{CH}_2\text{-F} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_3 + \text{F}^- \)
(b) \( \text{CH}_3\text{O}^- + \text{CH}_3\text{CH}_2\text{-I} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_3 + \text{I}^- \)
(c) \( \text{CH}_3\text{O}^- + \text{CH}_3\text{CH}_2\text{-Cl} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_3 + \text{Cl}^- \)
(d) \( \text{CH}_3\text{O}^- + \text{CH}_3\text{CH}_2\text{-Br} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_3 + \text{Br}^- \)

6.7 Provide three-dimensional structures for the missing boxed structures and formulas for missing reagents.

\[
\begin{align*}
\text{(S)-A} & \quad (\text{C}_5\text{H}_7\text{Br)} \\
\text{(S)-B} & \quad (\text{C}_9\text{H}_{15}) \\
\text{(S)-C} & \quad (\text{C}_5\text{H}_{17}) \\
\end{align*}
\]
7

ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

SOLUTIONS TO PROBLEMS

7.1 (a) (E)-1-Bromo-1-chloro-1-pentene
(b) (E)-2-Bromo-1-chloro-1-iodo-1-butene
(c) (Z)-3,5-Dimethyl-2-hexene
(d) (Z)-1-Chloro-1-bromo-2-methyl-1-butene
(e) (2,4S,3,4-Dimethyl-2-hexene
(f) (Z,3S)-1-Bromo-2-chloro-3-methyl-1-hexene

7.2 (a) \[ \text{CH}_3 \text{CH}=\text{CH} \text{CH}_3 \] (2-Methyl-1-butene (disubstituted)
\[ \text{H}_3 \text{Pt} \rightarrow \text{CH}_3 \text{CH} \text{CH=CHCH}_3 \] \( \Delta H^\circ = -119 \text{ kJ mol}^{-1} \)

(b) \[ \text{CH}_3 \text{CH}=\text{CHCH}=\text{CH}_2 \] (3-Methyl-1-butene (monosubstituted)
\[ \text{H}_3 \text{Pt} \rightarrow \text{CH}_3 \text{CH}_2 \text{CHCHCH}_3 \] \( \Delta H^\circ = -127 \text{ kJ mol}^{-1} \)

(c) \[ \text{CH}_3 \text{CH}=\text{CHCH}_3 \] (2-Methyl-2-butene (trisubstituted)
\[ \text{H}_3 \text{Pt} \rightarrow \text{CH}_3 \text{CHCHCHCH}_3 \] \( \Delta H^\circ = -113 \text{ kJ mol}^{-1} \)

(c) Yes, because hydrogenation converts each alkene into the same product.

(d) \[ \text{CH}_3 \text{CH}=\text{CHCH}_3 > \text{CH}_3 \text{CH} \text{CH=CHCH}_3 > \text{CH}_3 \text{CHCH}=\text{CH}_3 \] (trisubstituted) (disubstituted) (monosubstituted)

Notice that this predicted order of stability is confirmed by the heats of hydrogenation. 2-Methyl-2-butene evolves the least heat; therefore, it is the most stable. 3-Methyl-1-butene evolves the most heat; therefore, it is the least stable.

7.3 (a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetra-substituted. 2-Methyl-2-pentene has a trisubstituted double bond.
(b) trans-3-Hexene would be the more stable because alkenes with trans double bonds are more stable than those with cis double bonds.
(c) cis-3- Hexene would be more stable because its double bond is disubstituted. The double bond of 1-hexene is monosubstituted.
(d) 2-Methyl-2-pentene would be the more stable because its double bond is trisubstituted. The double bond of trans-2-hexene is disubstituted.

7.4 The relative stabilities of the pairs of alkenes in parts (b) and (c) in Problem 7.3 could be determined by measuring heats of hydrogenation, because in each instance the two alkenes would yield the same product. Heats of combustion could be used to determine the relative stabilities of the alkene pairs in parts (a) and (d)  and also those in parts (b) and (c) because on complete combustion the alkenes produce the same number of molar equivalents of CO2 and H2O.

7.5 (a) \[ \text{Br} \] (trisubstituted, more stable)
\[ \text{CO}, \text{H} \text{O}, \text{heat} \] (monosubstituted, less stable)

(b) \[ \text{Br} \] (tetrasubstituted, more stable)
\[ \text{CO}, \text{H} \text{O}, \text{heat} \] (dissubstituted, less stable)

7.6 An anti-periplanar transition state allows the molecule to assume the more stable staggered conformation.
whereas a syn periplanar transition state requires the molecule to assume the less stable eclipsed conformation:

7.7 *cis*-1-Bromo-4-tert-butylcyclohexane can assume an anti periplanar transition state in which the bulky tert-butyl group is equatorial:

The conformation (above), because it is relatively stable, is assumed by most of the molecules present, and, therefore, the reaction is rapid.

On the other hand, for *trans*-1-bromo-4-tert-butylcyclohexane to assume an anti periplanar transition state, the molecule must assume a conformation in which the large tert-butyl group is axial:

Such a conformation is of high energy; therefore, very few molecules assume this conformation. The reaction, consequently, is very slow.

7.8 (a) *Anti* periplanar elimination can occur in two ways with the *cis* isomer.

(b) *Anti* periplanar elimination can occur in only one way with the *trans* isomer.

7.9 (a) (1) \[ \text{CH}_3-\text{CH}-\text{OH} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3-\text{CH}-\text{O}-\text{H} + \text{H}_2\text{SO}_4 \]

(b) By donating a proton to the \(-\text{OH}\) group of the alcohol in step (1), the acid allows the loss of a relatively stable, weakly basic, leaving group (\(\text{H}_2\text{O}\)) in step (2). In the absence of an acid, the leaving group would have to be the strongly basic \(\text{OH}^-\) ion, and such steps almost never occur.

7.10 (1) \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{HA} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^- \]

(2) \[ \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \]

(3) \[ \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 \]
ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

1.3 (a) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{PCl}_3, \text{HCl} \rightarrow \text{CH}_3\text{C}\equiv\text{CH}_2 \) (1) 3 \( \text{NaNH}_2 \), mineral oil, heat
(2) \( \text{NH}_4^+ \)
(b) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{PCl}_3, \text{HCl} \rightarrow \text{CH}_3\text{C}=\text{CH}_2 
(c) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{PCl}_3, \text{HCl} \rightarrow \text{CH}_3\text{C}=\text{CH}_2 
(d) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{PCl}_3, \text{HCl} \rightarrow \text{CH}_3\text{C}=\text{CH}_2 

7.14 (a) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 \) (1) 3 \( \text{NaNH}_2 \), mineral oil, heat
(2) \( \text{NH}_4^+ \)
(b) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 
(c) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 
(d) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 
(e) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 

7.15 (a) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 \) (1) 3 \( \text{NaNH}_2 \), mineral oil, heat
(2) \( \text{NH}_4^+ \)
(b) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 
(c) \( \text{CH}_3\text{C}=\text{CH}_2 + \text{NaNH}_2 \rightarrow \text{CH}_3\text{C}=\text{CH}_2 

7.16 (a) \( \text{C}_6\text{H}_{12} = \text{formula of alkane} \)
\( \text{C}_6\text{H}_{12} = \text{formula of 2-hexene} \)
\( \text{H}_2 = \text{difference} = 1 \text{ pair of hydrogen atoms} \)
Index of hydrogen deficiency = 1
(b) \( \text{C}_6\text{H}_{12} = \text{formula of alkane} \)
\( \text{C}_6\text{H}_{12} = \text{formula of methylcyclopentane} \)
\( \text{H}_2 = \text{difference} = 1 \text{ pair of hydrogen atoms} \)
Index of hydrogen deficiency = 1
(c) No, all isomers of \( \text{C}_6\text{H}_{12} \), for example, have the same index of hydrogen deficiency.
9.6 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

(d) No

(e) $C_6H_{14}$ = formula of alkane
$C_6H_{12}$ = formula of 2-hexyne

$H_4$ = difference = 2 pairs of hydrogen atoms

Index of hydrogen deficiency = 2

(f) $C_6H_{12}$ (alkane)
$C_6H_{16}$ (compound)

$H_4$ = difference = 3 pairs of hydrogen atoms

Index of hydrogen deficiency = 3

The structural possibilities are thus:

3 double bonds
1 double bond and one triple bond
2 double bonds and 1 ring
1 double bond and 2 rings
3 rings
1 triple bond and one ring

7.17 (a) $C_6H_{13}$ = formula of alkane
$C_6H_{11}$ = formula of zingiberene

$H_4$ = difference = 4 pairs of hydrogen atoms

Index of hydrogen deficiency = 4

(b) Since 1 mol of zingiberene absorbs 3 mol of hydrogen, one molecule of zingiberene must contain three double bonds. (We are told that molecules of zingiberene do not contain any triple bonds.)

(c) If a molecule of zingiberene has three double bonds and an index of hydrogen deficiency equal to 4, it must have one ring. (The structural formula for zingiberene can be found in Problem 23.2.)

7.18 (a) We designate the position of the double bond by using the lower number of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is trans-2-pentene

(b) We must choose the longest chain for the base name. The correct name is 2-methylpropene.

7.19 (a) $CH(CH_3)_2CH_2=CH=CH_2$
(b) $CH_2=CHCH_2CH_2CH_3$
(c) $CH_2=CHCH_2CH_2CH_3$
(d) $CH_2=CHCH_2CH_2CH_3$
(e) $CH_2=CHCH_2CH_2CH_3$
(f) $CH_2=CHCH_2CH_2CH_3$
(g) $CH_2=CHCH_2CH_2CH_3$
(h) $CH_2=CHCH_2CH_2CH_3$
(i) $CH_2=CHCH_2CH_2CH_3$
(j) $CH_2=CHCH_2CH_2CH_3$
(k) $CH_2=CHCH_2CH_2CH_3$
(l) $CH_2=CHCH_2CH_2CH_3$
7.20 (a) \((Z,4R)-4\text{-Bromo-2-hexene}\)  \((Z,4S)-4\text{-Bromo-2-hexene}\)  
\((E,4R)-4\text{-Bromo-2-hexene}\)  \((E,4S)-4\text{-Bromo-2-hexene}\) 

(b) \((3R,4Z)-3\text{-Chloro-1,4-hexadiene}\)  \((3S,4Z)-3\text{-Chloro-1,4-hexadiene}\)  
\((3R,4E)-3\text{-Chloro-1,4-hexadiene}\)  \((3S,4E)-3\text{-Chloro-1,4-hexadiene}\) 

(c) \((2E,4R)-2,4\text{-Dichloro-2-pentene}\)  \((2Z,4R)-2,4\text{-Dichloro-2-pentene}\)  
\((2E,4S)-2,4\text{-Dichloro-2-pentene}\)  \((2Z,4S)-2,4\text{-Dichloro-2-pentene}\) 

(d) \((3R,4Z)-5\text{-Bromo-3-chloro-4-hexen-1-yne}\)  \((3S,4Z)-5\text{-Bromo-3-chloro-4-hexen-1-yne}\)  
\((3R,4E)-5\text{-Bromo-3-chloro-4-hexen-1-yne}\)  \((3S,4E)-5\text{-Bromo-3-chloro-4-hexen-1-yne}\) 

7.21 (a) \((E)-3,5\text{-Dimethyl-1-2-hexene}\) 
(b) 4-Chloro-3-methylcyclopentene 
(c) 6-Methyl-3-3-heptyne 
(d) 1-sec-Butyl-2-methylcyclohexene or 1-methyl-2-[(1-methylpropyl)cyclohexene 
(e) \((Z,3R)-3\text{-Chloro-4-hepen-1-yne}\) 
(f) 2-Pentyl-1-hepene 

7.22 (a) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{(\text{CH}_3)\text{COH}} \text{CH}_3\text{CH} = \text{CH}_2\) 
(b) \(\text{CH}_3\text{CHCH}_3 \xrightarrow{\text{Cl}, \text{NaOH}} \text{CH}_3\text{CH} = \text{CH}_2\) 
(c) \(\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}, \text{heat}} \text{CH}_3\text{CH} = \text{CH}_2\) 
(d) \(\text{CH}_3\text{CHCH}_3\text{OH} \xrightarrow{\text{Zn}, \text{CH}_3\text{COH}} \text{CH}_3\text{CH} = \text{CH}_2\) 
(e) \(\text{CH}_3\text{CHCH}_3\text{Br} \xrightarrow{\text{H}_2, \text{NaI} \text{P} \text{Se}} \text{CH}_3\text{CH} = \text{CH}_2\) 
(f) \(\text{CH}_3\text{C} = \text{CH} \xrightarrow{\text{Ni}, \text{Na}} \text{CH}_3\text{CH} = \text{CH}_2\) 

7.23 (a) \(\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{NaOH}, \text{aq.}} \text{CH}_3\text{C} = \text{CH}_2\) 
(b) \(\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{Zn}} \text{CH}_3\text{CH}_2\text{CH}_3\) 
(c) \(\text{CH}_3\text{CH}==\text{CH}_2 \xrightarrow{\text{H}, \text{heat}} \text{CH}_3\text{CH}_2\text{CH}_3\) 

7.24 (a) \(\text{HC}==\text{C} \xrightarrow{\text{NaNH}_2, \text{aq.} \text{NH}_3} \text{HC}==\text{C}^{+} \xrightarrow{\text{CH}_3\text{CH}==\text{CH}_2} \text{HC}==\text{C} == \text{CH}_3\) 
(b) \(\text{HC}==\text{C} \xrightarrow{\text{NaNH}_2, \text{aq.} \text{NH}_3} \text{HC}==\text{C}^{+} \xrightarrow{\text{CH}_3\text{CH}==\text{CH}_2} \text{HC}==\text{C} == \text{CH}_3\) 
(c) \(\text{HC}==\text{C} \xrightarrow{\text{NaNH}_2, \text{aq.} \text{NH}_3} \text{HC}==\text{C}^{+} \xrightarrow{\text{CH}_3\text{CH}==\text{CH}_2} \text{HC}==\text{C} == \text{CH}_3\) 
(d) \(\text{CH}_3\text{C}==\text{CH} \xrightarrow{\text{H}, \text{NaI} \text{P} \text{Se}} \text{CH}_3\text{C} == \text{CH}_3\)
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(f) \( \text{HC} = \text{C} \overset{\text{Br}}{\text{Na}} \rightarrow \text{HC} = \text{C} - \text{CH}_2\text{CH}_3 \)

(g) \( \text{CH}_2\text{CH}_2\text{C} = \text{CH} \rightarrow \text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 \overset{\text{NaNH}_2}{\text{liq. NH}_4} \rightarrow \text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 \)

(h) \( \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{CH}_2\text{Cl} \overset{\text{H}_2}{\text{Ni}_2\text{B}} \) (P-2)

(i) \( \text{CH}_3\text{CH}_2\text{C} = \text{C} \overset{\text{Br}}{\text{Na}} \rightarrow \text{HC} = \text{C} - \text{CH}_2\text{CH}_3 \overset{\text{NaNH}_2}{\text{liq. NH}_4} \rightarrow \text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 \)

(k) \( \text{CH}_2\text{CH}_3\text{C} = \text{C} \overset{\text{Br}}{\text{Na}} \rightarrow \text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 \)

(l) \( \text{CH}_2\text{C} = \text{C} \overset{\text{Br}}{\text{Na}} \rightarrow \text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 \)

7.25 We notice that the deuterium atoms are cis to each other, and we conclude, therefore, that we need to choose a method that will cause a syn addition of deuterium. One way would be to use D_2 and a metal catalyst (Section 7.13).

7.26 Dehydration of trans-2-methylcyclohexanol proceeds through the formation of a carbocation (through an E1 reaction of the protonated alcohol) and leads preferentially to the more stable alkene. 1-Methylcyclohexene (below) is more stable than 3-methylcyclohexene (the minor product of the dehydration) because its double bond is more highly substituted.

7.27 (a) \( \text{C}_6\text{H}_5\text{C} = \text{CH}_2 \overset{\text{Br}_3}{\text{3 NaNH}_2} \) (mineral oil, heat) \( \rightarrow \text{C}_6\text{H}_5\text{C} = \text{C} \overset{\text{Na}}{\text{Cl}} \rightarrow \text{C}_6\text{H}_5\text{C} = \text{CH}_2 \)

(b) \( \text{C}_6\text{H}_5\text{CH} = \text{CH}_2 \overset{\text{Br}_3}{\text{3 NaNH}_2} \) (mineral oil, heat) \( \rightarrow \text{C}_6\text{H}_5\text{C} = \text{C} \overset{\text{Na}}{\text{Cl}} \rightarrow \text{C}_6\text{H}_5\text{C} = \text{CH}_2 \)

(c) \( \text{C}_6\text{H}_5\text{C} = \text{CH}_2 \overset{\text{Br}_3}{\text{3 NaNH}_2} \) (mineral oil, heat) \( \rightarrow \text{C}_6\text{H}_5\text{C} = \text{C} \overset{\text{Na}}{\text{Cl}} \rightarrow \text{C}_6\text{H}_5\text{C} = \text{CH}_2 \)

(d) \( \text{C}_6\text{H}_5\text{C} = \text{C} \overset{\text{Br}_3}{\text{3 NaNH}_2} \) (mineral oil, heat) \( \rightarrow \text{C}_6\text{H}_5\text{C} = \text{C} \overset{\text{Na}}{\text{Cl}} \rightarrow \text{C}_6\text{H}_5\text{C} = \text{CH}_2 \)

7.28 Cyclobutane is less stable than any of the butene isomers.

7.29 1-Pentene, 3375 kJ mol\(^{-1}\)

cis-2-Pentene, 3369 kJ mol\(^{-1}\)

trans-2-Pentene, 3365 kJ mol\(^{-1}\)

2-Methyl-1-butene, 3361 kJ mol\(^{-1}\)

2-Methyl-2-butene, 3355 kJ mol\(^{-1}\)
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7.30 1-Pentanol > 1-pentene > pentane
(See Section 3.7 for the explanation.)

7.31 (a) \( \text{CH}_3\text{CHCHCH}_3 \xrightarrow{\text{NaOEt, EtOH, heat}} \text{CH}_3\text{C}==\text{CH}_3 + \text{CH}_3\text{CHCHCH}_3 \) 

(b) \( \text{CH}_3\text{C}==\text{CH}_3 \xrightarrow{\text{NaOEt, EtOH, heat}} \text{CH}_3\text{CHCHCH}_3 \)

(c) \( \text{CH}_3\text{CHCHCHCH}_3 \xrightarrow{\text{NaOEt, EtOH, heat}} \text{CH}_3\text{C}==\text{CH}_3 \) (major) + \( \text{CH}_3\text{CHCHCH}_3 \) (minor)

(d) \( \text{BrCH}_2\text{CH}_3 \xrightarrow{\text{NaOEt, EtOH, heat}} \text{C}_5\text{H}_{10} \) (major) + \( \text{CH}==\text{CH}_3 \) (minor)

(e) \( \text{C}_5\text{H}_{11} \xrightarrow{\text{NaOEt, EtOH, heat}} \text{C}_5\text{H}_{10} \) (major) + \( \text{CH}==\text{CH}_3 \) (minor)

7.32 (a) \( \text{CH}_3\text{CHCHCH}_3 \xrightarrow{\text{KOH-Bu, t-BuOH, heat}} \text{CH}_3\text{C}==\text{CH}_3 \) (major) + \( \text{CH}_3\text{CHCHCH}_3 \) (minor)

(b) \( \text{CH}_3\text{C}==\text{CHCH}_2\text{CH}_3 \xrightarrow{\text{KOH-Bu, t-BuOH, heat}} \text{CH}_3\text{C}==\text{CH}_3 \) (only)

(c) \( \text{CH}_3\text{CHCHCHCH}_3 \xrightarrow{\text{KOH-Bu, t-BuOH, heat}} \text{CH}_3\text{C}==\text{CHCHCH}_3 \) (major) + \( \text{CH}_3\text{CHCHCH}_3 \) (minor)

(d) \( \text{CH}_3\text{CHCHCHCH}_3 \xrightarrow{\text{KOH-Bu, t-BuOH, heat}} \text{CH}_3\text{C}==\text{CHCHCH}_3 \) (major) + \( \text{CH}_3\text{CHCHCH}_3 \) (minor)

(e) \( \text{C}_5\text{H}_{11} \xrightarrow{\text{KOH-Bu, t-BuOH, heat}} \text{C}_5\text{H}_{10} \) (major) + \( \text{CH}==\text{CH}_3 \) (minor)

7.33 (a) \( \text{CH}_3\text{CHCHCHCH}_3 \xrightarrow{\text{CH(OH)COH}} \text{CH}_3\text{CHCHCH}==\text{CH}_3 \)

(b) \( \text{CH}_3\text{CHCHCHCH}_3 \xrightarrow{\text{CH(OH)COH}} \text{CH}_3\text{CHCHCH}==\text{CH}_3 \)

(c) \( \text{CH}_3\text{CHCHCHCH}_3 \xrightarrow{\text{CH(OH)COH}} \text{CH}_3\text{CHCHCH}==\text{CH}_3 \)

(d) \( \text{H}_2\text{C}==\text{CHBr} \xrightarrow{\text{CH(OH)COH}} \text{CH}_3\text{CH}==\text{CH}_2 \)

(e) \( \text{BrCH}_2\text{CH}_3 \xrightarrow{\text{CH(OH)COH}} \text{H}_2\text{C}==\text{CH}_3 \)

7.34 \( \text{CH}_3\text{CHCHCHCH}_3 \xrightarrow{\text{EtOH, heat}} \text{CH}_3\text{CHCHCHCH}_3 \)

7.35 (a) \( \text{CH}_3\text{C}==\text{CHCHCHCH}_3 \xrightarrow{\text{H}^+, \text{H}_2\text{O}} \text{CH}_3\text{CHCHCHCH}_3 \)

(b) \( \text{CH}_3\text{C}==\text{CHCHCHCH}_3 \xrightarrow{\text{H}^+, \text{H}_2\text{O}} \text{CH}_3\text{CHCHCHCH}_3 \)

(c) \( \text{CH}_3\text{C}==\text{CHCHCHCH}_3 \xrightarrow{\text{H}^+, \text{H}_2\text{O}} \text{CH}_3\text{CHCHCHCH}_3 \)

(d) \( \text{CH}_3\text{C}==\text{CHCHCHCH}_3 \xrightarrow{\text{H}^+, \text{H}_2\text{O}} \text{CH}_3\text{CHCHCHCH}_3 \)

7.36 The alkene cannot be formed because the double bond in the product is too highly strained. Recall that the atoms at each carbon of a double bond prefer to be in the same plane.
7.37 Only the deuterium atom can assume the anti periplanar orientation necessary for an E2 reaction to occur.

7.38 (a) A hydride shift occurs.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{H^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}^+ \xrightarrow{(-\text{H}_2\text{O})} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \]

(b) A methanide shift occurs.

\[ \text{H}_2\text{C} \xrightarrow{H^+} \text{H}_2\text{C} \xrightarrow{(-\text{H}_2\text{O})} \text{H}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \]

7.39 In the first step, cholesterol reacts with bromine to form the vic-dibromide. This product is then purified by crystallization, and then treatment with zinc in ethanol converts the pure vic-dibromide back to cholesterol. (Recrystallization of the vic-dibromide is especially easy because it has a higher melting point than cholesterol.)

7.40 (a) Caryophyllene has the same molecular formula as zingiberene (Problem 7.13); thus, it, too, has an index of hydrogen deficiency equal to 4. That 1 mol of caryophyllene absorbs 2 mol of hydrogen on catalytic hydrogenation indicates the presence of two double bonds per molecule.

(b) Caryophyllene molecules must also have two rings. (See Problem 23.2 for the structure of caryophyllene.)

7.41 (a) \( \text{C}_9\text{H}_{16} \) = formula of an alkane

\( \text{C}_9\text{H}_{16} \) = formula of squalene

Index of hydrogen deficiency = 6

(b) Molecules of squalene contain six double bonds.

(c) Squalene molecules contain no rings. (See Problem 23.2 for the structural formula of squalene.)

7.42 (a) We are given (Section 7.3A) the following heats of hydrogenation:

\[ \text{cis-2-Butene} + \text{H}_2 \xrightarrow{\text{Pt}} \text{butene} \quad \Delta H^\circ = -120 \text{ kJ mol}^{-1} \]

\[ \text{trans-2-Butene} + \text{H}_2 \xrightarrow{\text{Pt}} \text{butene} \quad \Delta H^\circ = -115 \text{ kJ mol}^{-1} \]

Thus, for

\[ \text{cis-2-Butene} \rightarrow \text{trans-2-butene} \quad \Delta H^\circ = -5.0 \text{ kJ mol}^{-1} \]

(b) Converting \text{cis-2-butene} into \text{trans-2-butene} involves breaking the \( \pi \) bond. Therefore, we would expect the energy of activation to be at least as large as the \( \pi \)-bond strength, that is, at least 264 kJ mol\(^{-1}\).
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7.43 (a) \( \text{Optically active (the enantiomeric form is an equally valid answer)} \)

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]
\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \]

(b) \( \text{Optically active (the enantiomeric form is an equally valid answer)} \)

\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH} = \text{CH}_2 \quad \text{H} \quad \text{H} \quad \text{H} \]

7.44 That \( I \) and \( J \) rotate plane-polarized light in the same direction tells us that \( I \) and \( J \) are not enantiomers of each other. Thus, the following are possible structures for \( I, J, \) and \( K \). (The enantiomers of \( L, J, \) and \( K \) would form another set of structures, and other answers are possible as well.)

\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{H} \quad \text{H} \]
\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{H} \quad \text{H} \]

7.45 The following are possible structures:

(a) With either the \((1R,2R)\)- or the \((1S,2S)\)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of the \( \text{H}^- \) and \( \text{Br}^- \). In either case, the elimination leads only to \((Z)-1\)-bromo-1,2-diphenylethene:

\[ \text{B}^+ \quad \text{Ph}^- \quad \text{Ph}^- \quad \text{Br}^- \quad \text{Br}^- \]
\[ \text{(1R,2R)-1,2-Dibromo-1,2-diphenylethane (anti periplanar orientation of H^- and Br^-)} \]

\[ \text{(Z)-1-Bromo-1,2-diphenylethene} \]

(b) With \((1R,2S)\)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of the \( \text{H}^- \) and \( \text{Br}^- \). In this case, the elimination leads only to \((E)-1\)-bromo-1,2-diphenylethene:

\[ \text{(1R,2S)-1,2-Dibromo-1,2-diphenylethane (anti periplanar orientation of H^- and Br^-)} \]

\[ \text{(E)-1-Bromo-1,2-diphenylethene} \]
(c) With (1R,2S)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of both bromine atoms. In this case, the elimination leads only to (E)-1,2-diphenylethene:

\[
\text{(E)-1,2-Diphenylethene}
\]

7.1 Which conditions/reagents would you employ to obtain the best yields in the following reaction?

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Br}_2 &\rightarrow \overset{?}{\text{CH}_3\text{CH}_2\text{CH}==\text{CH}_3} \\
\text{(a) H}_2\text{O, heat} &\quad \text{(b) CH}_3\text{CH}_2\text{ONa/CH}_3\text{CH}_2\text{OH, heat} \\
&\quad \text{(c) (CH}_3\text{)}_2\text{CO/(CH}_3\text{)}_2\text{COH, heat} \\
&\quad \text{(d) Reaction cannot occur as shown}
\end{align*}
\]

7.2 Which of the following names is incorrect?

(a) 1-Butene  (b) trans-2-Butene  (c) (Z)-2-Chloro-2-pentene  (d) 1,1-Dimethylcyclopentene  (e) Cyclohexene

7.3 Select the major product of the reaction

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}==\text{CH}(\text{CH}_3)_2 + \text{Br}_2 &\rightarrow \overset{?}{\text{CH}_3\text{CH}_2\text{C}==\text{CH}==\text{CH}(\text{CH}_3)_2} \\
\text{(a) CH}_3\text{CH}_2\text{C}==\text{CH}(\text{CH}_3)_2 &\quad \text{(b) CH}_3\text{CH}_2\text{C}==\text{CH}(\text{CH}_3)_2 \\
&\quad \text{(c) CH}_3\text{CH}==\text{CH}==\text{CH}(\text{CH}_3)_2 \\
&\quad \text{(d) CH}_3\text{CH}==\text{CH}==\text{CH}(\text{CH}_3)_2 \\
&\quad \text{(e) CH}_3\text{CH}_2\text{C}==\text{CH}(\text{CH}_3)_2
\end{align*}
\]

7.4 Supply the missing reagents.

\[
\begin{align*}
\text{(a) } &\rightarrow \text{trans-2-butene} \\
\text{2-Butyne} &\rightarrow \text{cis-2-butene} \\
&\rightarrow \text{butane}
\end{align*}
\]
7.5 Arrange the following alkenes in order of decreasing stability.  
1-pentene, cis-2-pentene, trans-2-pentene, 2-methyl-2-butene

Most stable > > > Least stable

7.6 Complete the following synthesis.

Propene $\xrightarrow{Br_2/CCl_4}$  
3 $\text{NaNH}_2$, liquid NH$_3$  
mineral oil 110-160°C  
$\Rightarrow$  
$\text{Cl}$

8.1 $\text{CH}_3\text{CHCH}_2\text{I}$  
$\xrightarrow{Br}$  
2-Bromo-1-iodopropane

8.2 (a) $\text{CH}_3\text{CH}_2\text{C}=$CH$_2$  
$\xrightarrow{\text{H-Br}}$  
$\xrightarrow{\text{Br}}$  
$\text{Br}$

(b) $\text{CH}_3\text{C}=$CH$_2$  
$\xrightarrow{8^\circ\text{C}}$  
$\text{Cl}$

(c) $\text{CH}_3$  
$\xrightarrow{8^\circ\text{C}}$  
$\text{H-I}$  
$\xrightarrow{\text{H-I}}$  
$\text{H}_2\text{C}$

8.3 (a) $\text{CH}_3\text{CH}-\text{CH}=$CH$_2$  
$\xrightarrow{8^\circ\text{C}}$  
$\text{H}$  
2° Carbocation  
1,2-hydride shift  
$\text{Cl}$

(b) $\text{CH}_3\text{C}=$CH$_2$  
$\xrightarrow{\text{Cl}}$  
$\text{Cl}$

(c) $\text{H}_2\text{Cl}$

Unrearranged 2° carbocation  
2-Chloro-2-methylbutane  
(from unrearranged carbocation)
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3-Chloro-2,2-dimethylbutane
(from unarranged carbocation)

2-Chloro-2,3-dimethylbutane
(from rearranged carbocation)

8.4 \[ \text{CH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_2\text{OSO}_3\text{H} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4 \]

(b) Use a high concentration of water because we want the carbocation produced to react with water. And use a strong acid whose conjugate base is a very weak nucleophile. (For this reason we would not use HI, HBr, or HCl.) An excellent method, therefore, is to use dilute sulfuric acid.

8.5 (a) Use a low concentration of water (i.e., use concentrated H_{2}SO_{4}) and use a higher temperature to encourage elimination.

(c) 1-Methylcyclohexanol would be the product because a 3° carbocation would be formed as the intermediate.

8.6 \[ \text{CH}_2=\text{CH}_2 \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_3\text{CH}==\text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}==\text{CH}_2 \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_3\text{CH}==\text{CH}_2 \]

8.7 The order reflects the relative ease with which these alkenes accept a proton and form a carbocation. (CH_{3})_{2}C=CH_{2} reacts faster because it leads to a tertiary carbocation.

Recall that formation of the carbocation is the rate-determining step in acid-catalyzed hydration and that the order of stabilities of carbocations is the following:

\[ 3^\circ > 2^\circ > 1^\circ > ^\circ \text{CH}_3 \]
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8.8 \[ \text{CH}_3\text{C} = \text{CH}_2 \rightarrow \text{CH}_3\text{C} = \text{CH}_3 \]

8.9 \[ \text{Br}_2 \rightarrow \text{Br}_2 \text{Br}_2 \rightarrow \text{Br}_2 \text{Br}_2 \]

8.10 \[ \text{Br}_2 \text{Br}_2 \rightarrow \text{Br}_2 \text{Br}_2 \rightarrow \text{Br}_2 \text{Br}_2 \]

Because paths (a) and (b) occur at equal rates, these enantiomers are formed at equal rates.

8.11 \[ \text{CH} = \text{CH}_2 + \text{Br}^+ \rightarrow \text{Br}^- \text{CH} = \text{CH}_2 + \text{Br}^- \]

8.12 (a) \[ \text{Cl} \text{Cl} \text{Cl} \text{Cl} + \text{enantiomer} \]

8.13 \[ \text{KOC(CH}_3 )_3 \text{Br} \rightarrow \text{KOC(CH}_3 )_3 \text{Br} \]

8.14 \[ \text{CH}_2\text{CH}_2 \rightarrow \text{Br}_2 \text{Br}_2 \rightarrow \text{Br}_2 \text{Br}_2 \]

8.15 (a) \[ \text{OsO}_4,\text{pyridine, 25°C} \]

(b) \[ \text{CH}_2\text{CH}_2 \rightarrow \text{Br}_2 \text{Br}_2 \rightarrow \text{Br}_2 \text{Br}_2 \]

(c) \[ \text{OsO}_4,\text{pyridine, 25°C} \]
8.16 (a) Syn-hydroxylation at either face of (Z)- or cis-alkene leads to the meso compound

\[(2R,3S)-2,3	ext{-butanediol.}\]

(b) Syn-hydroxylation at one face of the (E)- or trans-alkene leads to the \((2R,3R)\)-enantiomer; at the other face, which is equally likely, it leads to the \((2S,3S)\)-enantiomer.

8.17 (a) 

\[
\begin{align*}
\text{CH}_3
\end{align*}
\]

\[
\text{H}_2\text{C} = \text{CH} - \text{CH} - \text{CH}_3
\]

\[
(1) \text{O}_3 (2) \text{Zn, HOAc}
\]

\[
\begin{align*}
\text{H}_2\text{C} &= \text{O} + \text{O} = \text{C} - \text{CH}_3
\end{align*}
\]

(b) 

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH} &= \text{CH} - \text{CH}_3
\end{align*}
\]

\[
(1) \text{O}_3 (2) \text{Zn, HOAc}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_3\text{CH} &= \text{O}
\end{align*}
\]

(c) 

\[
\begin{align*}
\text{CH}_3
\end{align*}
\]

\[
(1) \text{O}_3 (2) \text{Zn, HOAc}
\]

\[
\begin{align*}
\text{CH} &= \text{C} + \text{O} = \text{C}
\end{align*}
\]

8.18 Ordinary alkenes are more reactive toward electrophilic reagents. But the alkenes obtained from the addition of an electrophilic reagent to an alkane have at least one electronegative atom (\(\text{Cl}, \text{Br}, \text{etc.}\)) attached to a carbon atom of the double bond.

These alkenes are less reactive than alkenes toward electrophilic addition because the electronegative group makes the double bond "electron poor."

8.19 The molecular formula and the formation of octane from A and B indicate that both compounds are unbranched octanes. Since A yields only \(\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2\text{CO}_2\text{H}\) on ozonolysis, A must be the symmetrical octane \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\). The IR absorption for B shows the presence of a terminal triple bond. Hence B is \(\text{CH}_3\text{CH}_2\text{C} = \text{CH}_2\text{CH}_2\text{C} = \text{CH}_2\).

Since C \((\text{C}_8\text{H}_{16})\) gives \(\text{HO}_2\text{C} = \text{CH}_2\text{CH}_2\text{CO}_2\text{H}\) on ozonolysis, C must be cyclic octane. This is supported by the molecular formula of C and the fact that it is converted to \(\text{C}_8\text{H}_{10}\) (cyclooctane) on catalytic hydrogenation.

Answer to the Study Problem related to cholesterol biosynthesis, page 355.

In cholesterol biosynthesis an anti-Markovnikov addition occurs between C10 (once it becomes like a tertiary carbocation) and C15, forming the six-membered "C" ring of cholesterol (see the reactions in the text, page 355). This process results in a developing secondary carbocation at C14, which adds to C16 to form the five-membered "D" ring of cholesterol. If, on the other hand, Markovnikov addition occurred between C10 and C14 instead of anti-Markovnikov addition between C10 and C15, as shown in the following scheme, a developing tertiary carbocation would result at C15, along with formation of a five-membered "C" ring. Then, Markovnikov addition of C15 (as it becomes like a tertiary carbocation) to C18 would lead to a four-membered "D" ring and a tertiary carbocation at C19.

\[
\text{Squalene}
\]

\[
(3S)-2,3\text{-Oxidosqualene}
\]

which is the same as:

\[
\begin{align*}
\text{HO} &
\end{align*}
\]

\[
\text{HO}
\]

and
8.20 By converting the 3-hexyne to cis-3-hexene using H₂/Ni-B (P-2).

\[
\text{Et} \quad \xrightarrow{\text{B} \quad \text{Ni-B (P-2)}} \quad \text{Et}
\]

Then, addition of bromine to cis-3-hexene will yield (3R,4R), and (3S,4S)-3,4-dibromohexane as a racemic form.

\[
\text{H}_2\text{C} \quad \text{Br} \quad \text{Et} \quad \text{and addition} \quad \xrightarrow{\text{B} \quad \text{Ni-B (P-2)}} \quad \begin{cases} 
\text{Br} & \text{Et} \\
\text{H} & \text{Et}
\end{cases} \quad \text{(3S, 4S)} \quad \text{Br} \quad \text{Et} \quad \text{H} \quad \text{Et} \quad \text{(3R, 4R)}
\]

**Racemic 3,4-dibromohexane**

8.21

(a) CH₃CH₂CHCH₃
(b) CH₃CH₂CH₂CH₃
(c) CH₂CH₂CHCH₃
OH
(d) CH₃CH₂CHCH₃
OSO₂H
(e) CH₃CH₂CHCH₃
OH
(f) CH₃CH₂CHCH₃
Br
(g) CH₃CH₂CHCH₂Br
Br
(h) CH₃CH₂CH=CH₂
OH
(i) CH₃CH₂CHCH₂Br
OH
(j) CH₃CH₂CHCH₃
Cl
(k) CH₃CH₂CHCH₂OH
OH
(l) CH₃CH₂CH + H₂CH
(m) CH₃CH₂CHCH₂OH
OH
(n) CH₃CH₂CO₂H + CO₂

8.22

(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)

8.23

(a) CH₃CH₂C=CHBr
(b) CH₃CH₂C=CH₂
Br
(c) CH₃CH₂CH₂CH₃
(d) CH₃CH₂CH₂CH₃
(e) CH₃CH₂CH=CH₂
(f) CH₃CH₂C≡CCH₃
(g) CH₃CH₂C≡CH and CH₂C≡CH₃ [An E2 reaction would take place when CH₃CH₂C≡CNa is treated with (CH₂)₂CBr.]

8.24

(a) CH₃C=CHCH₃
Br
(b) CH₃CBr₂CH₂CH₃
(c)
(d) CH₃CBr₂CH₂CH₃
(e) H₂C=CHCH₃
Br
(f) H₂C=CBrCH₃
(g) H₂C=C=CH₂
Br
(h) CH₃CH₂CH=CH₃
(i) CH₃CH₂CH₂CH₃
(j) CH₃CO₂H (2 molar equivalents) (k) CH₃CO₂H (2 molar equivalents) (l) no reaction

8.25

(a) CH₃CH₂CH=CH₂
Br₃
CCl₄
CH₃CH₂CHCH₂CH₃
Br
Br
3NaNH₃
mineral oil, heat
CH₃CH₂C≡CNa
NHCl
CH₃CH₂C≡CH
(b) CH₃CH₂CHCHCl
r-BoOCl
r-BoOH, heat
CH₃CH₂CH=CH₂
Then as in (a)
(c) CH₃CH₂CH=CHCl
2NaNH₃
mineral oil, heat
CH₃CH₂C≡CNa
NHCl
CH₃CH₂C≡CH
(d) CH₃CH₂CHCH₂Cl
3NaNH₃
mineral oil, heat
CH₃CH₂C≡CNa
NHCl
CH₃CH₂C≡CH
(e) H≡C=CH
NaNH₃
Et₃NH₃
H≡C≡CNa
CH₃CH₂Br
CH₃CH₂C≡CH
ALKENES AND ALKYNES II: ADDITION REACTIONS

8.26 (a) \( \text{CH}_3 \text{C} = \text{CH}_2 \xrightarrow{\text{H}_2\text{O}, \text{H}_2\text{O}} \text{CH}_3 \text{CH}_2 \text{CH}_3 \)

(b) \( \text{CH}_3 \text{C} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_3 \text{CH}_2 \text{Cl} \)

(c) \( \text{CH}_3 \text{C} = \text{CH}_2 \xrightarrow{\text{HBr}} \text{CH}_3 \text{CH}_2 \text{Br} \)

(d) \( \text{CH}_3 \text{C} = \text{CH}_2 \xrightarrow{\text{HF}} \text{CH}_3 \text{CH}_2 \text{F} \)

(e) \( \text{CH}_3 \text{C} = \text{CH}_2 \xrightarrow{\text{Cl}_2, \text{H}_2\text{O}} \text{CH}_3 \text{CCH}_2 \text{Cl} \)

8.27 (a) \( \text{C}_{10}\text{H}_{22} \) (saturated alkane)
   \( \text{C}_{10}\text{H}_{16} \) (formula of myrcene)

   \( \text{H}_a = 3 \) pairs of hydrogen atoms

   Index of hydrogen deficiency (IHD) = 3

(b) Myrcene contains no rings because complete hydrogenation gives \( \text{C}_{10}\text{H}_{22} \), which corresponds to an alkane.

(c) That myrcene absorbs three molar equivalents of \( \text{H}_2 \) on hydrogenation indicates that it contains three double bonds.

(d) Three structures are possible; however, only one gives 2,6-dimethyloctane on complete hydrogenation. Myrcene is therefore

\[ \text{CH}_3 \text{C} = \text{CHCHCH}_2 \text{CH} = \text{CH}_3 \]

(e) \( \text{O} = \text{CHCH}_2 \text{CH}_2 \text{CH} = \text{O} \)

8.28 \( \text{CH}_3 \text{CH} = \text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3 \text{CH} - \text{CH}_2 \text{Cl} \)

\[ \text{CH}_3 \text{CHCH}_3 \xrightarrow{\text{HCl}} \text{CH}_3 \text{CHCH}_3 \]

8.29 The rate-determining step in each reaction is the formation of a carbocation when the alkene accepts a proton from \( \text{HCl} \). When 2-methylpropene reacts, it forms a 3° carbocation (the most stable); therefore, it reacts fastest. When ethene reacts, it forms a 1° carbocation (the least stable); therefore, it reacts the slowest.

\[ \text{CH}_3 \text{C} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_3 \text{CH} = \text{CH}_2 \rightarrow \text{CH}_3 \text{CCH}_3 \]

8.30 \( \text{CH}_3 \text{C} = \text{CHCHCH}_2 \text{CH} = \text{CH}_3 \)

2,6,10-Trimethylidodecane

8.31 (1) \( \text{O}_2 \)
   (2) \( \text{Zn}, \text{H}_2\text{OAc} \)

\[ \text{CH}_3 \text{CH} = \text{CH}_2 + \text{H}_2\text{OAc} \rightarrow \text{CH}_3 \text{C} = \text{CH}_2 + \text{CH}_3 \text{CH} = \text{CH}_2 \text{CH}_3 \]

8.32 Limonene

8.33 \( \text{C}_8\text{H}_8 \)

1,2-hydride shift

\[ \text{C}_8\text{H}_8 \xrightarrow{\text{HCl}} \text{C}_8\text{H}_7 \text{C} = \text{CH}_2 \rightarrow \text{C}_8\text{H}_7 \text{C} = \text{CHCH}_2 \text{Cl} \rightarrow \text{C}_8\text{H}_7 \text{C} = \text{CH}_3 \rightarrow \text{C}_8\text{H}_7 \text{C} = \text{CH}_3 \rightarrow \text{C}_8\text{H}_7 \text{C} = \text{CH}_3 \]
ALKENES AND ALKynes II: Addition Reactions

8.34
\[
\begin{align*}
\text{CH}_3&:\text{OH} \xrightarrow{\text{H}_2, \text{Pt}} \text{CH}_3&:\text{CH}-\text{CH}-\text{CH}_3 \\
&\xrightarrow{\text{1,2-methanide shift}} \text{CH}_3&:\text{CH}-\text{CH}-\text{CH}_3 \\
2^\circ \text{Carbocation}
\end{align*}
\]

8.35 (a) The hydrogenation experiment discloses the carbon skeleton of the pheromone.

\[\text{C}_{13}\text{H}_{22} \xrightarrow{2 \text{H}, \text{Pt}} \text{C}_{13}\text{H}_{22} \text{OH} \]

Coding moth pheromone

The ozonolysis experiment allows us to locate the position of the double bonds.

8.36 Retrosynthetic analysis

(a) Syn addition

\[\xrightarrow{\text{H}_2, \text{Pt}} \text{CH}_3&:\text{OH} \xrightarrow{\text{H}_2, \text{Pt}} \text{CH}_3&:\text{CH}-\text{CH}-\text{CH}_3 \]

8.37 Retrosynthetic analysis

(a) Syn addition through syn addition

(b) Anti addition through anti addition

(c) Markovnikov addition

(d) Markovnikov addition through anti addition

8.38 Syn hydrogenation of the triple bond is required. So use \( \text{H}_2 \) and \( \text{Ni}_2\text{B}(\text{P}-2) \) or \( \text{H}_2 \) and Lindlar's catalyst.
ALKENES AND ALKynes II: ADDITION REACTIONS

8.40  (a) (2S,3R)-[the enantiomer is (2R,3S)-]
(b) (2S,3S)-[the enantiomer is (2R,3R)-]
(c) (2S,3R)-[the enantiomer is (2R,3S)-]
(d) (2S,3S)-[the enantiomer is (2R,3R)-]

8.41

The bromonium ion reacts with a chloride ion to produce the trans-1-bromo-2-chlorocyclohexane enantiomers.

8.42  (a) 1-Pentene has IR absorption at about 3300 cm\(^{-1}\) due to its terminal triple bond. Pentane does not absorb in that region.
(b) 1-Pentene absorbs in the 1620–1680 cm\(^{-1}\) region due to the alkene function. Pentane does not exhibit absorption in that region.
(c) See parts (a) and (b).
(d) 1-Bromopentane shows C-Br absorption in the 690-515 cm\(^{-1}\) region while pentane does not.
(e) For 1-pentene, see (n). The interior triple bond of 2-pentene gives relatively weak absorption in the 2100–2260 cm\(^{-1}\) region.
(f) For 1-pentene, see (b). 1-Pentanol has a broad absorption band in the 3200–3550 cm\(^{-1}\) region.
(g) See (f).
(h) 1-Bromo-2-pentene has double bond absorption in the 1620–1680 cm\(^{-1}\) region which 1-bromopentane lacks.
(i) 2-Penten-1-ol has double bond absorption in the 1620–1680 cm\(^{-1}\) region not found in 1-pentanol.

8.43 Because of the electron-withdrawing nature of chlorine, the electron density at the double bond is greatly reduced and attack by the electrophilic bromine does not occur.

8.44 The index of hydrogen deficiency of A, B, and C is two.

\[
\begin{align*}
\text{C}_2H_4 & \quad \text{C}_2H_8 \\
H_4 & = 2 \text{ pairs of hydrogen atoms}
\end{align*}
\]

This result suggests the presence of a triple bond, two double bonds, a double bond and a ring, or two rings. The fact that A, B, and C all decolorize Br\(_2\)/CCl\(_4\) and dissolve in concd. H\(_2\)SO\(_4\) suggests they all have a carbon-carbon multiple bond.

A must be a terminal alkene, because of IR absorption at about 3300 cm\(^{-1}\).

Since A gives hexane on catalytic hydrogenation, A must be 1-hexene.

CH\(_3\)(CH\(_2\))\(_2\)C\(=\)CH \(\xrightarrow{2\text{H}_2/\text{Pt}}\) CH\(_3\)(CH\(_2\))\(_2\)CH\(_3\)

This is confirmed by the oxidation experiment

\[
CH_3(CH_2)_2C\equiv CH \xrightarrow{(1) \text{KMnO}_4, \text{OH}^-, \text{heat}} CH_3(CH_2)_2CO_2H + CO_2
\]

Hydrogenation of B to hexane shows that its chain is unbranched, and the oxidation experiment shows that B is 3-hexyne.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C} \equiv \text{CCH}_2\text{CH}_3 & \xrightarrow{(1) \text{KMnO}_4, \text{OH}^-, \text{heat}} \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \\
\text{CH}_3\text{CH}_2\text{C} \equiv \text{CCH}_2\text{CH}_3 & \xrightarrow{(2) \text{H}_2\text{O}^+} \text{CH}_3\text{CH}_2\text{CO}_2\text{H}
\end{align*}
\]

8.45 (a) Four

(b) CH\(_3\)(CH\(_2\))\(_2\)OH \(\xrightarrow{(1) \text{KMnO}_4, \text{OH}^-, \text{heat}}\) + enantiomer

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{(1) \text{KMnO}_4, \text{OH}^-, \text{heat}} \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \\
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{(2) \text{H}_2\text{O}^+} \text{CH}_3\text{CH}_2\text{CO}_2\text{H}
\end{align*}
\]

8.46 Hydroxylation of K\(_2\)MnO\(_4\) are syn hydroxylation (cf. Section 8.9). Thus, maleic acid must be the cis-dicarboxylic acid:

Maleic acid

\[
\xrightarrow{\text{K}_2\text{MnO}_4, \text{synhydroxylation}} \text{meso-Tartaric acid}
\]

Fumaric acid must be the trans-dicarboxylic acid:

Fumaric acid

\[
\xrightarrow{\text{K}_2\text{MnO}_4, \text{synhydroxylation}} (\pm)-\text{Tartaric acid}
\]
The addition of bromine is an anti addition. Thus, fumaric acid yields a meso compound.

\[
\begin{align*}
\text{HO}_2\text{C} - \text{C}=\text{O} & \quad \xrightarrow{\text{Br}_2} \quad \text{HO}_2\text{C} - \text{C}=\text{O} \\
\text{HO}_2\text{C} - \text{C}=\text{O} & \quad \xrightarrow{\text{anti add.}} \quad \text{HO}_2\text{C} - \text{C}=\text{O}
\end{align*}
\]

The addition of bromine is an i pale.

\[
\begin{align*}
\text{H}_2\text{C}=\text{C}-\text{H} & \quad \xrightarrow{\text{Br}_2} \quad \text{H}_2\text{C}=\text{C}-\text{H} \\
\text{H}_2\text{C}=\text{C}-\text{H} & \quad \xrightarrow{\text{anti add.}} \quad \text{H}_2\text{C}=\text{C}-\text{H}
\end{align*}
\]

Maleic acid adds bromine to yield a racemic modification.

\[
\begin{align*}
\text{HC}=\text{C}-\text{H} & \quad \xrightarrow{\text{Br}_2} \quad \text{HC}=\text{C}-\text{H} \\
\text{HC}=\text{C}-\text{H} & \quad \xrightarrow{\text{anti add.}} \quad \text{HC}=\text{C}-\text{H}
\end{align*}
\]

Optically active (the other enantiomer is an equally valid answer)

Optically inactive (nonresolvable)

C. In contrast to its cis isomer, would exhibit no intramolecular hydrogen-bonding. This would be proven by the absence of infrared absorption in the 3500- to 3600-cm\(^{-1}\) region when studied as a very dilute solution in CCl\(_4\). C would only show free O—H stretch at about 3625 cm\(^{-1}\).
8.1 A hydrocarbon whose molecular formula is C₆H₁₃ on catalytic hydrogenation (excess H₂/Pt) yields C₆H₁₄. The original hydrocarbon adds bromine and also exhibits an IR absorption band at 3500 cm⁻¹. Which of the following is a plausible choice of structure for the original hydrocarbon?

(a) (b) (c) CH₃CH=CHCH=CHCH₂CH₃
(d) CH₃CH₂CH₂C≡CHCH₃
(e) CH₃CH₂CH₂CH₂CH=CH₂

8.2 Select the major product of the dehydration of the alcohol, CH₃C—CHCH₂CH₃.

(a) CH₃C—CH≡CH₃ (b) CH₃C—CHCH₂CH₂CH₃ (c) CH₃C≡CH₃ (d) CH₃CH=CHCH₂CH₃ (e) CH₃CH₂CH₂C≡CH₂

8.3 Give the major product of the reaction of cis-2-pentene with bromine.

(a) (b) (c) (d) (e) A racemic mixture of (c) and (d)

8.4 The compound shown here is best prepared by which sequence of reactions?

(a) CH₃C—CH₂CH₂CH₂CH₂CH₃ → [product]
(b) CH₂CH₂C≡CH + NaNH₂ → then CH₃CH₂CH₂Br → [product]
(c) CH₂CH₂C≡CH₂CH₃ + H₂ → [product]
(d) CH₃CH₂CH₂CH₂CH₂Br + NaOCH₃ → [product]

8.5 A compound whose formula is C₄H₁₀ (Compound A) reacts with H₂/Pt in excess to give a product C₄H₁₂, which does not decolorize Br₂/CCl₄. Compound A does not show IR absorption in the 3300–3400 cm⁻¹ region. Ozonolysis of A gives 1 mol of HCH and 1 mol of ＯHazO. Give the structure of A.

(a) (b) CH₃CH₂CH₂CH₂C≡CH₃ (c) CH₃CH₂CH₂CH₃ (d) (e) CH₃CH₂CH₂C≡CH₂

8.6 Compound B (C₄H₁₀) does not dissolve in cold, concentrated H₂SO₄. What is B?

(a) CH₃CH₂CH₂CH₂CH₃ (b) CH₃CH₂CH₂CH₂CH₂H
(c) (d) (e) (f) (g) (h) (i) (j) (k) (l) (m) (n) (o) (p) (q) (r) (s) (t) (u) (v) (w) (x) (y) (z)

8.7 Which reaction sequence converts cyclohexene to cis-1,2-cyclohexanediol? That is, the reaction shown here is best prepared by which sequence of reactions?

(a) Cold, dilute, aqueous KMnO₄, OH⁻ (b) (1) O₃ (2) Zn/H₂O
(c) (1) OsO₄ (2) NaHSO₃ (d) (1) ROOH (2) H₂O/H₂O
(e) More than one of these

8.8 Which of the following sequences leads to the best synthesis of the compound CH₃CH₂CH₂C≡CH ? (Assume that the quantities of reagents are sufficient to carry out the desired reaction.)

(a) CH₃CH₂CH₂CH₂CH₃ → Br → NaOH → H₂O → NaNH₃
(b) CH₃CH₂CH₂CH₂CH₂CH₂H → Br → H₂SO₄ → NaNH₃
(c) CH₃CH₂CH₂CH₂CHBr₂ → Br → H₂SO₄ → NaNH₃
(d) CH₃CH₂CH₂CH₂CH₂H → light → O₂ → NaNH₃ → Zn/H₂O
(e) CH₃CH₂CH₂CH₂CH₂H → Br → NaOH → H₂O → NaNH₃
10 RADICAL REACTIONS

SOLUTIONS TO PROBLEMS

10.1 (a) H—H + F—F \[ \rightarrow \] 2 H—F
\[ (\Delta H^\circ = 435) \] \[ (\Delta H^\circ = 159) \]
+594 kJ mol\(^{-1}\) is required for bond cleavage
\[ \Delta H^\circ = +594 - 1138 \]
\[ = -544 \text{ kJ mol}^{-1} \]

(b) CH\(_2\)-H + F—F \[ \rightarrow \] CH\(_3\)-F + H—F
\[ (\Delta H^\circ = 435) \] \[ (\Delta H^\circ = 159) \]
+594 kJ mol\(^{-1}\) is required for bond cleavage
\[ \Delta H^\circ = +594 - 1021 \]
\[ = -427 \text{ kJ mol}^{-1} \]

(c) CH\(_2\)-H + Cl—Cl \[ \rightarrow \] CH\(_3\)-Cl + H—Cl
\[ (\Delta H^\circ = 435) \] \[ (\Delta H^\circ = 243) \]
+678 kJ mol\(^{-1}\) is required for bond cleavage
\[ \Delta H^\circ = +678 - 780 \]
\[ = -102 \text{ kJ mol}^{-1} \]

(d) CH\(_3\)-H + Br—Br \[ \rightarrow \] CH\(_3\)-Br + H—Br
\[ (\Delta H^\circ = 435) \] \[ (\Delta H^\circ = 192) \]
+627 kJ mol\(^{-1}\) is required for bond cleavage
\[ \Delta H^\circ = +627 - 659 \]
\[ = -32 \text{ kJ mol}^{-1} \]

10.2 The compounds all have different boiling points. They could, therefore, be separated by careful fractional distillation. Or, because the compounds have different vapor pressures, they could easily be separated by gas chromatography. GC/MS (gas chromatography/mass spectrometry) could be used to separate the compounds as well as provide structural information from their mass spectra. Their mass spectra would show contributions from the naturally occurring \(^{35}\text{Cl}\) and \(^{37}\text{Cl}\) isotopes. The natural abundance of...
10.4 A small amount of ethane is formed by the combination of two methyl radicals:

$$2 \text{CH}_3 : \rightarrow \text{CH}_3 \cdot + \text{CH}_3 \cdot$$

This ethane then reacts with chlorine in a substitution reaction (see Section 10.6) to form chloroethane.

The significance of this observation is that it is evidence for the proposal that the combination of methyl radicals is one of the chain-terminating steps in the chlorination of methane.

10.5 The use of a large excess of chlorine allows all of the chlorinated methanes (CH,Cl, CH,Cl, and CHCl, to react with chlorine.

10.6 Chain Initiation

Step 1  \( \text{F}^- + \text{F}^- \rightarrow 2 \text{F}^- \cdot \quad \Delta H^\circ = +159 \text{ kJ mol}^{-1} \)  

(DH° = 159)

Chain Propagation

Step 2  \( \text{CH}_3^- + \text{H}^- \rightarrow \text{CH}_3^+ + \text{H}^- \cdot \quad \Delta H^\circ = -134 \text{ kJ mol}^{-1} \)  

(DH° = 455)

Step 3  \( \text{CH}_3^+ + \text{F}^- \rightarrow \text{CH}_3^+ + \text{F}^- \cdot \quad \Delta H^\circ = -293 \text{ kJ mol}^{-1} \)  

(DH° = 452)

Chain Termination

\( \text{CH}_3^+ + \text{F}^- \rightarrow \text{CH}_3^- + \text{F}^- \cdot \quad \Delta H^\circ = -452 \text{ kJ mol}^{-1} \)  

(DH° = 452)

\( \text{CH}_3^+ + \text{CH}_3^- \rightarrow \text{CH}_3^+ + \text{CH}_3^- \cdot \quad \Delta H^\circ = -368 \text{ kJ mol}^{-1} \)  

(DH° = 368)

\( \text{F}^- + \text{F}^- \rightarrow \text{F}^- + \text{F}^- \cdot \quad \Delta H^\circ = -159 \text{ kJ mol}^{-1} \)  

(DH° = 159)

10.7  \( \text{CH}_3^- + \text{H}^- \rightarrow \text{CH}_3^- + \text{H}^- \cdot \quad \Delta H^\circ = -134 \text{ kJ mol}^{-1} \)  

\( \text{CH}_3^- + \text{F}^- \rightarrow \text{CH}_3^- + \text{F}^- \cdot \quad \Delta H^\circ = -293 \text{ kJ mol}^{-1} \)  

\( \text{CH}_3^- + \text{H}^- + \text{F}^- \rightarrow \text{CH}_3^- + \text{H}^- + \text{F}^- \cdot \quad \Delta H^\circ = -427 \text{ kJ mol}^{-1} \)  

10.8 (a) Reactions (3), (5), and (6) should have \( E_{\text{net}} = 0 \) because these are gas-phase reactions in which small radicals combine to form molecules.

(b) Reactions (1), (2), and (4) should have \( E_{\text{net}} > 0 \) because in them covalent bonds are broken.

(c) Reactions (1) and (2) should have \( E_{\text{net}} = \Delta H^\circ \) because in them bonds are broken homolytically but no bonds are formed.
The hydrogen abstraction step for ethane,  
$\text{CH}_3\text{CH}_2\text{H} + \text{Cl}^\cdot \rightarrow \text{CH}_3\text{CH}_2^\cdot + \text{HCl}$  
has a much lower energy of activation than the corresponding step for methane:  
$\text{CH}_3\text{H} + \text{Cl}^\cdot \rightarrow \text{CH}_3^\cdot + \text{HCl}$  
Therefore, ethyl radicals form much more rapidly in the mixture than methyl radicals, and this leads to the more rapid formation of ethyl chloride.

10.10 (a) There is a total of eight hydrogen atoms in propane. There are six equivalent $1^\circ$ hydrogen atoms, replacement of any one of which leads to propyl chloride, and there are two equivalent $2^\circ$ hydrogen atoms, replacement of any one of which leads to isopropyl chloride.  
$\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{Cl}^\cdot$  

10.11 (b) The hydrogen abstraction step for ethane,  
$\text{CH}_3\text{CH}_2\text{H} + \text{Cl}^\cdot \rightarrow \text{CH}_3\text{CH}_2^\cdot + \text{HCl}$  
$E_{\text{act}} = +4.2 \text{ kJ mol}^{-1}$  
$\Delta H^\circ = -21 \text{ kJ mol}^{-1}$  
$\text{CH}_3\text{CH}_2^\cdot + \text{HCl}$  

10.12 (a) There is a total of eight hydrogen atoms in propane. There are six equivalent $1^\circ$ hydrogen atoms, replacement of any one of which leads to propyl chloride, and there are two equivalent $2^\circ$ hydrogen atoms, replacement of any one of which leads to isopropyl chloride.  
$\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{Cl}^\cdot$
If all the hydrogen atoms were equally reactive, we would expect to obtain 75% propyl chloride and 25% isopropyl chloride:

\[
\% \text{ Propyl chloride} = \% \times 100 = 75% \\
\% \text{ Isopropyl chloride} = \% \times 100 = 25%
\]

(b) Reasoning in the same way as in part (a), we would expect 90% isobutyl chloride and 10% tert-butyl chloride, if the hydrogen atoms were equally reactive.

\[
\text{CH}_3\text{C}^\text{H} + \text{Cl}_2 \rightarrow (\text{CH}_3)\text{C}\text{CH}_2\text{Cl} + (\text{CH}_3)\text{CCl}
\]

\[
\% \text{ Isobutyl chloride} = \% \times 100 = 90% \\
\% \text{ tert-Butyl chloride} = \% \times 100 = 10%
\]

(c) In the case of propane (see Section 10.6), we actually get more than twice as much isopropyl chloride (55%) than we would expect if the 1° and 2° hydrogen atoms were equally reactive (25%). Clearly, then, 2° hydrogen atoms are more reactive than 1° hydrogen atoms.

In the case of isobutane, we get almost four times as much tert-butyl chloride (37%) as we would get (10%) if the 1° and 3° hydrogen atoms were equally reactive.

The order of reactivity of the hydrogens then must be

\[
3° > 2° > 1°
\]

10.13 The hydrogen atoms of these molecules are all equivalent. Replacing any one of them yields the same product.

$$\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}$$

We can minimize the amounts of more highly chlorinated products formed by using a large excess of the cyclopropane or cyclobutane. (And we can recover the unreacted cyclopropane or cyclobutane after the reaction is over.)

10.14 (a) $$\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\end{align*}$$

(b) $$\begin{align*}
\text{CH}_3\text{C} & \quad \text{CH}_3\text{C} \\
\text{CH}_3\text{C} & \quad \text{CH}_3\text{C} \\
\end{align*}$$

(c) $$\begin{align*}
\text{CH}_3 & \\
\end{align*}$$

10.15 At lower temperatures, isomer distribution accurately reflects the inherent reactivities of the hydrogens of the alkanes. As the temperature is raised, chlorine atoms become more reactive, and hence less discriminating. If the temperature is high enough, hydrogens are replaced by chlorine on a purely statistical basis.
None of the fractions would show optical activity. Fractions (b), (d), and (f) are racemic forms; all others contain achiral molecules.

Ions likely to be formed are the molecular ion (MT†), M†-Br, and others. The MT† peak would be accompanied by M†+2 and M†+4 peaks due to the isotopes of bromine. The natural abundance of 79Br is 50.5% and the natural abundance of 81Br is 49.5%. Thus, the MT† peak (where both bromines are 79Br) has probability (.505)(.505) = .255, the M†+2 peak (one 79Br and one 81Br) has probability 2(.495)(.505) = .500, and the probability of the M†+4 peak (where both bromine atoms are 81Br) is (.495)(.495) = .245. Thus, the M†, M†+2, and M†+4 peaks will have an intensity ratio of approximately 1:2:1, respectively. (This calculation does not take into account the contribution of 13C, 3H, and other isotopes.) The M†-Br peak would also be accompanied by an M†-Br+2 peak.

10.18 (a) No, the only fractions that would contain chiral molecules (as enantiomers) would be those containing 1-chloro-2-methylbutane and the one containing 2-chloro-3-methylbutane. These fractions would not show optical activity, however, because they would contain racemic forms of the enantiomers.

(b) Yes, the fractions containing 1-chloro-2-methylbutane and the one containing 2-chloro-3-methylbutane.

(c) Yes, each fraction from the distillation could be identified on the basis of 1H NMR spectroscopy. The signals related to the carbons where the chlorine atom is bonded would be sufficient to distinguish them. The protons at C1 of 1-chloro-2-methylbutane would be a doublet due to splitting from the single hydrogen at C2. There would be no proton signal for C2 of 2-chloro-3-methylbutane since there are no hydrogens bonded at C2 in this compound; however, there would be a strong singlet for the six hydrogens of the geminal methyl groups. The protons at C2 of 2-chloro-3-methylbutane would approximately be a pentet, due to combined splitting from the three hydrogens at C1 and the single hydrogen at C3. The protons at C1 of 1-chloro-3-methylbutane would be a triplet due to splitting by the two hydrogens at C2.

10.19 Chain-Initiating Step

\[ \text{CH}_3 \quad \text{heat} \rightarrow \text{Cl}^+ \]
10.21 (a) Five

(b) Five. None of the fractions would be a racemic form.

(c) The fractions containing A, D, and E. The fraction containing B and C would be optically inactive. (B contains no stereocentre and C is a meso compound.)

10.22 (a) Oxygen-oxygen bonds are especially weak, that is,

\[
\begin{align*}
\text{HO–OH} & \quad \Delta H^\circ = 213 \text{ kJ mol}^{-1} \\
\text{CH}_3\text{CH}_2\text{O–OCH}_3 & \quad \Delta H^\circ = 184 \text{ kJ mol}^{-1}
\end{align*}
\]

This means that a peroxide will dissociate into radicals at a relatively low temperature.

\[
\begin{align*}
\text{RO–OR} \quad & \text{100–200°C} \rightarrow 2 \text{RO}^* \\
\text{Oxygen-hydrogen single bonds, on the other hand, are very strong. (For HO–H, } \Delta H^\circ & = 498 \text{ kJ mol}^{-1}\text{.) This means that reactions like the following will be highly exothermic.}
\end{align*}
\]

\[
\begin{align*}
\text{RO}^* + \text{R–H} & \rightarrow \text{RO–H} + \text{R}^* \\
\text{Chain Initiation}
\end{align*}
\]

(b) Step 1 \[\text{(CH}_3\text{)}_3\text{CO–OC(CH}_3\text{)}_3 \xrightarrow{\text{heat}} 2 \text{(CH}_3\text{)}_3\text{CO}^*\]

Step 2 \[\text{(CH}_3\text{)}_3\text{CO}^* + \text{R–H} \rightarrow (\text{CH}_3\text{)}_3\text{COH} + \text{R}^*\]

Step 3 \[\text{R}^* + \text{Cl–Cl} \rightarrow \text{R–Cl} + \text{Cl}^*\]

Step 4 \[\text{Cl}^* + \text{R–H} \rightarrow \text{H–Cl} + \text{R}^*\]

10.23 CH\text{C}CH\text{C}CH\text{C} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \quad \text{CH}_2^* \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^* 

3° \quad (2°) \quad (3°) \quad (1°)

10.24 (1) \[\text{Cl}_2 \rightarrow 2 \text{Cl}^* \quad \Delta H^\circ = +243 \text{ kJ mol}^{-1}\]

(2) \[\text{Cl}^* + \text{CH}_4 \rightarrow \text{CH}_3\text{Cl} + \text{H}^* \quad \Delta H^\circ = +85.8 \text{ kJ mol}^{-1}\]

(3) \[\text{H}^* + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}^* \quad \Delta H^\circ = -188 \text{ kJ mol}^{-1}\]

This mechanism is highly unlikely to compete with one given in Section 10.4 because step (2) of this mechanism is highly endothermic (\(\Delta H^\circ = +85.8 \text{ kJ mol}^{-1}\)). This means that the energy of activation for this step, a chain-propagating step, will have to be larger than +85.8 kJ mol\(^{-1}\). Notice in Section 10.50 that neither of the chain-propagating steps for the mechanism given in Section 10.4 has an energy of activation greater than +15.9 kJ mol\(^{-1}\). The alternative mechanism given in this problem, consequently, will proceed at a rate that is very much slower than the one given in Section 10.4 and will, for all practical purposes, not compete with it at all.

10.25 (a) \[\text{CH}_3\text{CH}_3 \xrightarrow{\text{Br}_2, \text{heat, light}} \text{CH}_2\text{CH}_2\text{Br \ NaI (S}_2\text{O}_2\text{)} \rightarrow \text{CH}_3\text{CH}_2\text{I}\]

(b) \[\text{CH}_3\text{CH}_2\text{Br \ NaOH \ (S}_2\text{O}_2\text{)} \rightarrow \text{CH}_3\text{CH}_2\text{OH \ Na} \rightarrow \text{CH}_3\text{CH}_2\text{O}^- + \text{Na}^+\]

(c) \[\text{CH}_3\text{CHCH}_2\text{CH}_3 \xrightarrow{\text{Br}_2, \text{heat, light}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{NaOH \ (E}_2\text{)} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{	ext{heat (E}_2\text{)}} \text{CH}_3\text{C}_2\text{CH}_3 \xrightarrow{\text{HBr, ROOR, heat, light}} \text{CH}_3\text{CH}_{3}\]

(d) \[\text{CH}_3\text{C}_2\text{CH}_3 \xrightarrow{\text{Br}_2, \text{heat, light}} \text{CH}_3\text{C}_2\text{CH}_3 \xrightarrow{\text{NaOH \ (E}_2\text{)} \rightarrow \text{CH}_3\text{C}_2\text{CH}_3 \xrightarrow{\text{heat (E}_2\text{)}} \text{CH}_3\text{C}_2\text{CH}_3 \xrightarrow{\text{HBr, ROOR, heat, light}} \text{CH}_3\text{C}_2\text{CH}_3 \]

(e) \[\text{CH}_4 \xrightarrow{\text{Br}_2, \text{heat, light}} \text{CH}_3\text{Br}\]

\[
\begin{align*}
\text{HC} & \rightarrow 1) \text{NaH} \rightarrow \text{HC}–\text{O–CH}_3 \quad 2) \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{C} & \rightarrow \text{C}–\text{CH}_3 \quad 1) \text{NaH} \rightarrow \text{CH}_3\text{C} & \rightarrow \text{C}–\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{HC} & \rightarrow 1) \text{NaH} \rightarrow \text{HC}–\text{O–CH}_3 \quad 2) \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{C} & \rightarrow \text{C}–\text{CH}_3 \quad 1) \text{NaH} \rightarrow \text{CH}_3\text{C} & \rightarrow \text{C}–\text{CH}_3
\end{align*}
\]
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(f) \[
\text{HC} = \text{CH} \quad 1) \text{NaNH}_2 \\
2) \text{CH}_3\text{CH}_2\text{Br} \\
\text{[from part (a)]} \\
\text{H}_2\text{Ni,B} \\
\text{or} \\
\text{H}_2\text{, Lindlar's catalyst}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2\text{, Lindlar's catalyst} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 \\
\text{H}_2\text{Ni,B} & \rightarrow \text{HA, H}_2\text{O} \\
\text{CH}_3\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 \\
\text{and} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(g) \[
\text{CH}_3\text{CH}_2\text{Br} + \text{Na}^+ \rightarrow \text{N}_2\text{N}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{N}_2\text{N}_2
\]

10.26 Chlorine atoms are electronegative and abstract hydrogens according to their "electron richness." The electronegative fluorine atom reduces electron density in proportion to its proximity to the different CH groups. The CH group is the least reactive site because the bond dissociation energy for a CH group is greater than that for a CH3 group.

10.27 Besides direct H- abstraction from C5 there would be many H- abstractions from the three methyl groups, leading to:

\[
\begin{align*}
\text{HO}^- + \text{HO}^- & \rightarrow \text{HO}^- + \text{HO}^- \\
\text{dimerization} & \rightarrow \text{HO}^- + \text{HO}^- \\
\end{align*}
\]

Any of these radicals could then, besides directly attacking chlorine, intramolecularly abstract H- from C5 (analogous to the "back biting" that explains branching during alkene radical polymerization).

10.28 Use the single-bond dissociation energies of Table 10.1:

Table 10.1 Single-bond homolytic dissociation energies \(\text{DH}^\circ\) at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\text{A} : \text{B} \rightarrow \text{A}^- + \text{B}^-)</th>
<th>(\text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>435</td>
<td>(CH3)2CH-Br</td>
</tr>
<tr>
<td>D-D</td>
<td>444</td>
<td>(CH3)2CH-I</td>
</tr>
<tr>
<td>F-F</td>
<td>159</td>
<td>(CH3)2CH-OH</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>243</td>
<td>(CH3)2CH-OCH3</td>
</tr>
<tr>
<td>Br-Br</td>
<td>192</td>
<td>(CH3)2CHCH2-H</td>
</tr>
<tr>
<td>I-I</td>
<td>151</td>
<td>(CH3)2C=I</td>
</tr>
<tr>
<td>H-F</td>
<td>569</td>
<td>(CH3)2C-Cl</td>
</tr>
<tr>
<td>H-Cl</td>
<td>431</td>
<td>(CH3)2C-Br</td>
</tr>
<tr>
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<td>(CH3)2C-I</td>
</tr>
<tr>
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</tr>
<tr>
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<td>435</td>
<td>(CH3)2C-OCH3</td>
</tr>
<tr>
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<td>452</td>
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<td>349</td>
<td>CH3CH2CH2-H</td>
</tr>
<tr>
<td>CH3-Br</td>
<td>293</td>
<td>CH3CH2CH-H</td>
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<td>CH3H</td>
</tr>
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<td>CH3-OH</td>
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<td>HC=CH-H</td>
</tr>
<tr>
<td>CH3-OCH3</td>
<td>335</td>
<td>CH3=CH3</td>
</tr>
<tr>
<td>CH3-CH2-H</td>
<td>410</td>
<td>CH3CH=CH2</td>
</tr>
<tr>
<td>CH3-CH2-F</td>
<td>444</td>
<td>CH3CH2CH3</td>
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<td>CH3-CH2-Cl</td>
<td>341</td>
<td>CH3CH2CH2Cl</td>
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<td>CH3-CH2-Br</td>
<td>289</td>
<td>(CH3)2C=CH2</td>
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<tr>
<td>CH3-CH2-I</td>
<td>224</td>
<td>(CH3)2C-OCH3</td>
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<td>CH3CH2-CHO</td>
<td>339</td>
<td>(CH3)2CO-O(CH3)</td>
</tr>
</tbody>
</table>
QUIZ

10.1 On the basis of Table 10.1, what is the order of decreasing stability of the radicals, 
\[ \text{HC} \equiv \text{C} \cdot > \text{CH} = \text{CH} \cdot > \text{CH} = \text{CHCH}_2 \cdot ? \]
(a) \[ \text{HC} \equiv \text{C} \cdot > \text{CH} = \text{CH} \cdot > \text{CH} = \text{CHCH}_2 \cdot \]
(b) \[ \text{CH} = \text{CH} \cdot > \text{HC} \equiv \text{C} \cdot > \text{CH} = \text{CHCH}_2 \cdot \]
(c) \[ \text{CH} = \text{CHCH}_2 \cdot > \text{HC} \equiv \text{C} \cdot > \text{CH} = \text{CHCH}_2 \cdot \]
(d) \[ \text{CH} = \text{CHCH}_2 \cdot > \text{CH} = \text{CH} \cdot > \text{HC} \equiv \text{C} \cdot \]
(e) \[ \text{CH} = \text{CH} \cdot > \text{CH} = \text{CHCH}_2 \cdot > \text{HC} \equiv \text{C} \cdot \]

10.2 In the radical chlorination of methane, one propagation step is shown as 
\[ \text{Cl} \cdot + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \]
Why do we eliminate the possibility that this step goes as shown below? 
\[ \text{Cl} \cdot + \text{CH}_4 \rightarrow \text{CH}_3 \text{Cl} + \text{H} \]
(a) Because in the next propagation step, \( \text{H} \) would have to react with \( \text{Cl} \) to form \( \text{Cl}^- \) and \( \text{HCl} \); this reaction is not feasible.
(b) Because this alternative step has a more endothermic \( \Delta H^\circ \) than the first.
(c) Because free hydrogen atoms cannot exist.
(d) Because this alternative step is not consistent with the high photochemical efficiency of this reaction.

10.3 Pure (S)-\( \text{CH}_3\text{CH}_2\text{CHBrCH}_3 \) is subjected to monobromination to form several isomers of \( \text{C}_4\text{H}_8\text{Br} \). Which of the following is not produced?

(a) \[
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{Br} \\
\text{CH}_3
\end{array}
\]
(b) \[
\begin{array}{c}
\text{CH}_2 \\
\text{H} \\
\text{Br} \\
\text{CH}_3
\end{array}
\]
(c) \[
\begin{array}{c}
\text{CH}_3 \\
\text{Br} \\
\text{H} \\
\text{CH}_3
\end{array}
\]
(d) \[
\begin{array}{c}
\text{CH}_3\text{CH}_2\text{CHBrCH}_3 \\
\text{CH}_3
\end{array}
\]
(e) \[
\begin{array}{c}
\text{CH}_3\text{CH}_2\text{CHBrCH}_3 \\
\text{CH}_3\text{CHBrCH}_3
\end{array}
\]

10.4 Using the data of Table 10.1, calculate the heat of reaction, \( \Delta H^\circ \), of the reaction, 
\[ \text{CH}_3\text{CH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{HBr} \]
(a) \( 52.3 \text{ kJ mol}^{-1} \) (b) \( -52.3 \text{ kJ mol}^{-1} \) (c) \( 1257 \text{ kJ mol}^{-1} \)
(d) \( -1257 \text{ kJ mol}^{-1} \) (e) \( -244.8 \text{ kJ mol}^{-1} \)

10.5 Which gas-phase reaction would have \( E_{\text{act}} = 0? \)
(a) \[ \text{CH}_3 \cdot + (\text{CH}_3)_2\text{C} - \rightarrow \text{CH}_4 + (\text{CH}_3)_2\text{C} \cdot \]
(b) \[ \text{CH}_3 \cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{CH}_2 \cdot \]
(c) \[ \text{CH}_3\text{CH} \cdot + \text{CH}_3\text{CH} \cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 \]
(d) \[ \text{Br} \cdot + \text{H} - \text{Cl} \rightarrow \text{H} - \text{Br} + \text{Cl} \cdot \]
(e) \[ \text{Br} \cdot + \text{H} - \text{I} \rightarrow \text{H} - \text{Br} + \text{I} \cdot \]

10.6 What is the most stable radical that would be formed in the following reaction?
\[ \text{CH}_3 \cdot + \text{CH}_3\text{CH}_2\text{CHCH}_3 \rightarrow \square + \text{HCl} \]

10.7 The reaction of 2-methylbutane with chlorine would yield a total of _____ different monochloro products (including stereoisomers).

10.8 For which reaction would the transition state most resemble the products?
(a) \[ \text{CH}_4 \cdot + \text{F} \cdot \rightarrow \text{CH}_3 \cdot + \text{HF} \]
(b) \[ \text{CH}_4 \cdot + \text{Cl} \cdot \rightarrow \text{CH}_3 \cdot + \text{HCl} \]
(c) \[ \text{CH}_4 \cdot + \text{Br} \cdot \rightarrow \text{CH}_3 \cdot + \text{HBr} \]
(d) \[ \text{CH}_4 \cdot + \text{I} \cdot \rightarrow \text{CH}_3 \cdot + \text{HI} \]
A SPECIAL TOPIC
Chain-Growth Polymers

A.1 Head-to-tail polymerization leads to a more stable radical on the growing polymer chain. In head-to-tail coupling, the radical is 2° (actually 2° benzylic, and as we shall see in Section 15.12A this makes it even more stable). In head-to-head coupling, the radical is 1°.

A.2 (a) \[ R^+ + \text{CH}_2=\text{CH} \rightarrow \text{CH}_2=\text{CH}^+ \]

(from initiator) Monomer

\[ \text{CH}_3=\text{CH} \]

(b) \[ R^+ + \text{CH}_2=\text{CCl}_2 \rightarrow \text{CH}_2=\text{CCl}_2^+ \]

(from initiator) Monomer

\[ \text{CH}_3=\text{CCl}_2 \]

A.3 In the cationic polymerization of isobutylene (see text), the growing polymer chain has a stable 3° carbocation at the end. In the cationic polymerization of ethene, for example, the intermediates would be much less stable 1° cations.

\[ \text{H}^+ + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2=\text{CH}_2^+ \]

1° Carbocation

With vinyl chloride and acrylonitrile, the cations at the end of the growing chain would be destabilized by electron-withdrawing groups.

\[ \text{H}^+ + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2=\text{CH}_2^+ \]

\[ \text{CH}_2=\text{CCl}_2^+ \]

\[ \text{CH}_2=\text{CN}^+ \]

A.4 \[ \text{HO} + \text{CH}_2=\text{C} \rightarrow \text{HO-CH}_2=\text{C} \]

CO,CH, \rightarrow \text{etc.}

A.5 (a) Atactic polystyrene (Ph = C₆H₅)

Syndiotactic polystyrene (Ph = C₆H₅)

Isotactic polystyrene (Ph = C₆H₅)

(b) The solution of isotactic polystyrene.
ALCOHOLS AND ETHERS

SOLUTIONS TO PROBLEMS

11.1 These names mix two systems of nomenclature (radicofunctional and substitutive; see Section 4.3F). The proper names are: isopropyl alcohol (radicofunctional) or 2-propanol (substitutive), and tert-buty1 alcohol (radicofunctional) and 2-methyl-2-propanol (substitutive). Names with mixed systems of nomenclature should not be used.

11.2 (a) 1-Propanol
   (Propyl alcohol)
   2-Propanol
   (Isopropyl alcohol)
   Methoxyethane
   (Ethyl methyl ether)
   (b) 1-Butanol
       (Butyl alcohol)
       2-Methyl-1-propanol
       (Isobutyl alcohol)
       (sec-Butyl alcohol)
       2-Butanol
       2-Methyl-2-propanol
       (tert-Butyl alcohol)

11.3 1-Methoxypropane
      (Methyl propyl ether)
      Ethoxyethane
      (Diethyl ether)
      (Isopropyl methyl ether)

11.4 (a) CH₃CH₂OH  (b) CH₃CHCH₃  (c) CH₃C=OH  (d) CH₃CH₂CH₂OH

11.5 A rearrangement takes place.

11.6 (a) CH₃C=CH₂ THF-H₂O  CH₃COCH₂HgOAc  NaBH₄  OH⁻  CH₃C=CH₂
       (b) CH₃CH=CH₂ THF-H₂O  CH₃COCH₂HgOAc  NaBH₄  OH⁻  CH₃CHCH₃
       (c) CH₃C=CHCH₃ THF-H₂O  CH₃COCH₂HgOAc  NaBH₄  OH⁻  CH₃CCH₂CH₃

11.7 (a) C≡C  + HgOCOCF₃  →  RO·  H⁺  RO⁺  HgOCOCF₃
       (b) CH₃C=CH₂ THF-H₂O  CH₃COCH₂HgOAc  NaBH₄  OH⁻  demercuration

11.8 (a) CH₃C=CH₂  + Hg + CF₃COO⁻  →  CH₃C=CH₂CH₂HgOAc  NaBH₄  OH⁻  demercuration
**11.8**

(a) \(3\text{CH}_2\text{CH}=	ext{CH}_2 \xrightarrow{\text{THF}: \text{BH}_3} (\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B} \)

(b) \(3\text{CH}_2\text{C}=	ext{CH}_2 \xrightarrow{\text{THF}: \text{BH}_3} \text{CH}_3 (\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B} \)

(c) \(3\text{CH}_2\text{CH}==\text{CH}_3 \xrightarrow{\text{THF}: \text{BH}_3} (\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B} \)

(d) \(3\text{C}_2\text{H}_6 \xrightarrow{\text{THF}: \text{BH}_3} \text{syn addition} \quad \text{anti Markovnikov} \)

**11.9**

\(\text{CH}_3\text{C}==\text{CH}_2 \xrightarrow{\text{THF}: \text{BH}_3} \left(\text{CH}_3\text{CH}==\text{CH}_2\right)_2\text{BH} \)

**11.10**

(a) \(\text{CH}_3\text{C}_2\text{H}_4\text{C}==\text{CH}_2 \xrightarrow{(1) \text{THF}: \text{BH}_3 \quad (2) \text{H}_2\text{O}, \text{OH}} \left(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}\right) \)

(b) \(\text{CH}_3\text{C}_2\text{H}_4\text{C}==\text{CH}_2 \xrightarrow{(1) \text{THF}: \text{BH}_3 \quad (2) \text{H}_2\text{O}, \text{OH}} \left(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\right) \)

(c) \(\text{CH}_3\text{C}_2\text{H}_4\text{C}==\text{CH}_2 \xrightarrow{(1) \text{THF}: \text{BH}_3 \quad (2) \text{H}_2\text{O}, \text{OH}} (\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})_3 \)

(d) \(\text{CH}_3\text{C}_2\text{H}_4\text{C}==\text{CH}_2 \xrightarrow{(1) \text{THF}: \text{BH}_3 \quad (2) \text{H}_2\text{O}, \text{OH}} (\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})_3 \)

**11.11**

(a) \(3\text{CH}_2\text{CH}==\text{CH}_2 \xrightarrow{\text{THF}: \text{BH}_3} (\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{B} \)

(b) \(3\text{CH}_2\text{CH}==\text{CH}_2 \xrightarrow{\text{THF}: \text{BH}_3} (\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{B} \)

**11.12**

(a) \(\text{CH}_3\text{CH}_2\text{OH} + \text{NaNH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{ONa} + \text{NH}_3 \)

(b) \(\text{CH}_3\text{CH}_2\text{OH} + \text{HC}==\text{CHNa} \rightarrow \text{CH}_3\text{CH}_2\text{ONa} + \text{HC}==\text{CH} \)

(c) \(\text{CH}_3\text{CH}_2\text{OH} + \text{NaOAc} \rightarrow \text{CH}_3\text{CH}_2\text{ONa} + \text{HOAc} \)

**11.13** Use an alcohol containing labeled oxygen. If all of the label appears in the sulfonate ester, then one can conclude that the alcohol C-O bond does not break during the reaction:

\(\text{R}==\text{O}-\text{H} + \text{R}^\prime==\text{SO}_2\text{Cl} \overset{\text{base (-HCl)}}{\longrightarrow} \text{R}==\text{O}-\text{SO}_2\text{R}^\prime \)

**11.14**

(a) \(\text{H}_3\text{C}-\text{SO}_2\text{OH} \xrightarrow{\text{PCl}_3 (-\text{POCl}_3, -\text{HCl})} \text{H}_3\text{C}-\text{SO}_2\text{Cl} \)

(b) \(\text{CH}_3\text{OH} \xrightarrow{\text{base (-HCl)}} \text{H}_3\text{C}-\text{SO}_2\text{OCH}_3 \)
(b) \( \text{CH}_3\text{SO}_2\text{OH} \xrightarrow{\text{PCL}_3} \text{CH}_3\text{SO}_2\text{Cl} \xrightarrow{\text{base} (-\text{HCl})} \) 
\( \text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}(-\text{CH}_3)_2 \)

(c) \( \text{CH}_3\text{SO}_2\text{Cl} \xrightarrow{\text{base} (-\text{HCl})} \text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}(-\text{CH}_3)_2 \)

11.15 (a) \( \text{H}_2\text{C}=\text{C}—\text{OH} + \text{TsCl} \xrightarrow{\text{retention} (-\text{HCl})} \text{H}_2\text{C}=\text{C}—\text{OTs} \)
\( \text{H}_2\text{C}_2 \)
(R)-2-Butanol

(b) \( \text{HO} + \text{H}_2\text{C}=\text{C}—\text{OTs} \xrightarrow{\text{inversion} S_n2} \text{HO}—\text{C—CH}_3 + \text{OTs} \)

(c) \( \text{cis-4-Methyl-cyclohexanol} \xrightarrow{T_{\text{TsCl}}} \text{trans-1-Chloro-4-methylcyclohexane} \)

11.16 (a) Tertiary alcohols react faster than secondary alcohols because they form more stable carbanions; that is, 3° rather than 2°.

\( \text{CH}_3—\text{C—CH}_3 \xrightarrow{\text{CT}} \text{CH}_3—\text{C—Cl} \)

(b) \( \text{CH}_3\text{OH} \) reacts faster than 1° alcohols because it offers less hindrance to \( S_n2 \) attack. (Recall that \( \text{CH}_3\text{OH} \) and 1° alcohols must react through an \( S_n1 \) mechanism.)

11.17
\( \text{CH}_3\text{CHCHCH}_3 + \text{HBr} \xrightarrow{+ \text{OH}_2^-} \text{CH}_3\text{CHCHCH}_3 + \text{Br}^- \)

\( \text{CH}_3\text{CHCHCH}_3 \xleftarrow{\text{Br}^-} \text{CH}_3\text{CHCHCH}_3 \xleftarrow{\text{H}_2\text{O} \text{hydride shift}} \text{CH}_3\text{CHCHCH}_3 \)

11.18 (a) \( \text{CH}_3—\text{C—OH} \xrightarrow{R—H} \text{CH}_3—\text{C—OH} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3—\text{C—OH} \xrightarrow{R—\text{OH}} \text{CH}_3—\text{C—OH} \)

This reaction succeeds because a 3° carbanion is much more stable than a 1° carbanion. Consequently, mixing the 1° alcohol and \( \text{H}_2\text{SO}_4 \) does not lead to formation of appreciable amounts of a 1° carbanion. However, when the 3° alcohol is added, it is rapidly converted to a 3° carbanion, which then reacts with the 1° alcohol that is present in the mixture.

11.19 (a) (1) \( \text{CH}_3\text{CHO}^+ \xrightarrow{\text{L}} \text{CH}_3—\text{C—L} \xrightarrow{\text{S_n2}} \text{CH}_3\text{CHO}—\text{CH}_3 + \text{L}^- + \text{Na}^+ \)
(\( L = \text{X}, \text{OSO}_2\text{R}, \) or \( \text{OSO}_2\text{OR} \))

(2) \( \text{CH}_3\text{O}^- + \text{CH}_3—\text{C—L} \xrightarrow{\text{S_n2}} \text{CH}_3\text{O}—\text{CH}_3 + \text{L}^- \)
(\( L = \text{X}, \text{OSO}_2\text{R}, \) or \( \text{OSO}_2\text{OR} \))

(b) Both methods involve \( S_n2 \) reactions. Therefore, method (1) is better because substitution takes place at an unhindered methyl carbon atom. In method (2) where substitution must take place at a relatively hindered secondary carbon atom, the reaction would be accompanied by considerable elimination.

11.20 Reaction of the alcohol with \( K \) and then of the resulting salt with \( \text{C}_6\text{H}_5\text{Br} \) does not break bonds to the stereocenter, and these reactions therefore occur with retention of configuration at the stereocenter.

Reaction of the tosylate, \( \text{C}_6\text{H}_5\text{CH}(-\text{CH}_3)_2 \), with \( \text{C}_6\text{H}_5\text{OH} \) in \( \text{K}_2\text{CO}_3 \) solution, however, is an \( S_n2 \) reaction that takes place at the stereocenter and thus it occurs with inversion at the stereocenter.

11.21 \( \text{Cl—CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{OH}^-} \text{Cl—CH}_2\text{CH}_2\text{OH} \xrightarrow{+ \text{H}_2\text{O}} \text{Cl—CH}_2\text{CH}_2\text{O} + \text{H}_2\text{O} \)
11.22 (a) \( HO^- + HOCH_2CH_2Cl \rightarrow H_2O + O-CH_2CH_2Cl \rightarrow HOC\cdotCH_2 + Cl^- \)

(b) The \( -O^- \) group must displace the \( Cl^- \) from the backside.

\[
\text{trans-2-Chlorocyclohexanol}
\]

Backside attack is not possible with the cis isomer (below); therefore, it does not form an epoxide.

\[
\text{cis-2-Chlorocyclohexanol}
\]

11.23 (a) \( CH_2=CHCH_3 \xrightarrow{H^+} CH_2=CHCH_3 \xrightarrow{R-OH} CH_2=CHCH_3CH_3 \xrightarrow{H^+} CH_2=CHCH_3CH_3 \)

(b) The \( \text{tert}- \)butyl group is easily removed because, in acid, it is easily converted to a relatively stable, tertiary carbocation.

(c) \( CH_2=CHCH_3CH_2OH \xrightarrow{H^+} CH_2=CHCH_3CH_2OH \xrightarrow{H^+} CH_2=CHCH_3CH_2OH \)

11.24 (a) \( CH_3O\cdotCHCH_2CH_2CH_3 + HI \rightarrow I^- + CH_3O\cdotCHCH_2CH_2CH_3 \)

11.25 (a) \( H_2C=CH_2 \rightarrow H_2C=CH_2 \xrightarrow{CH_2CH_2^+} CH_3CCH_2OCH_3 \)

(b) An analogous reaction yields ethyl cellosolve, \( HOCH_2CH_2OCH_2CH_3 \).

(c) \( H_2C=CH_2 \xrightarrow{H^+} CH_2=CHCH_2^+ \xrightarrow{H^+} CH_2=CHCH_2^+ \)

(d) \( H_2C=CH_2 \xrightarrow{CH_2=CHCH_2=CH_2^+} CH_2=CHCH_2=CH_2 \)

(e) \( H_2C=CH_2 \xrightarrow{CH_2=CHCH_2=CH_2=CH_2^+} CH_2=CHCH_2=CH_2 \)

11.26 The reaction is an \( S_{N}2 \) reaction, and thus nucleophilic attack takes place much more rapidly at the primary carbon atom than at the more hindered secondary carbon atom.
Ethoxide ion attacks the epoxide ring at the primary carbon because it is less hindered, and the following reactions take place.

\[
\text{Cl}^-\text{CH}\rightarrow\text{Cl}^-\text{CH}_2\text{CH}^-\text{CH}_2\text{OC}_2\text{H}_5 \\
\rightarrow\text{H}_2\text{C}^-\text{CH}^-\text{CH}_2\text{OC}_2\text{H}_5
\]

11.28

\[
\text{H}_2\text{O}^+ + \text{H}_2\text{O} \leftrightarrow \text{H}_4\text{O}^+ \\
\downarrow \text{H}^+ \\
\downarrow \text{H}_2\text{O}^+ \\
\text{H}_2\text{O}^+ + \text{H}_2\text{O} \leftrightarrow \text{H}_4\text{O}^+
\]

11.29

\[
\begin{align*}
\text{Na}^+\text{CN}^- & \leftrightarrow \text{Na}^+\text{Cl}^- \\
\text{R}_2\text{N}^+\text{Cl}^- & \leftrightarrow \text{R}_2\text{N}^+\text{CN}^-
\end{align*}
\]

Aqueous phase

\[
\begin{align*}
\text{R}_2\text{N}^+\text{Cl}^- + \text{CH}_3\text{(CH}_2)_2\text{CN} & \leftrightarrow \text{R}_2\text{N}^+\text{CN}^- + \text{CH}_3\text{(CH}_2)_2\text{Cl} \\
\text{Organic phase (decane)}
\end{align*}
\]

11.30

(a) 3,3-Dimethyl-1-butanol
(b) 4-Penten-2-ol
(c) 2-Methyl-1,4-butanediol
(d) 2-Phenylethanol
(e) 1-Methyl-2-cyclopenten-1-ol
(f) cis-3-Methylcyclohexanol

11.31

(a) 11.32

11.33

(a) \( \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 \xrightarrow{\text{THF}:\text{BH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{B} \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{OH}^-/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}^-,\text{COOH}/(\text{CH}_3)\text{COH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \)

(d) \( \text{HBr} / \text{RGO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

(e) \( \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 \xrightarrow{\text{H}_3\text{B} / \text{P-2}} \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 \)

(f) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{OH}^-/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

11.34

(a) \( 3 \text{CH}_3\text{CH}_2\text{CH}_3 + \text{PBr}_3 \rightarrow 3 \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{H}_3\text{P}_2 \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{CH}_3\text{CH}_2\text{COH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{HBr}/\text{no peroxides}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \)
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(c) See (b) above.

(d) **CH_{3}CH=CH** \[\xrightarrow{H_{2}, NiB (P-2)}\] **CH_{3}CH=CH_{2}** \[\xrightarrow{HBr (no peroxides)}\] **CH_{3}CH_{2}CH=CH_{2}**

11.35 (a) **CH_{3}OH** + **SOCl_{2}** \[\rightarrow\] **ClCH_{2}CH_{2}Cl** + **SO_{2}** + **HCl**

(b) **CH_{3}** + **HCl** \[\rightarrow\] **CH_{3}Cl**

(c) **CH_{3}** \[\xrightarrow{HBr (no peroxides)}\] **BrCH_{3}

(d) **CH_{3}** \[\xrightarrow{(1) THF: BH_{3} (2) H_{2}O_{2}}\] **CH_{3}CH=CH_{2}** + enantiomer

(e) **CH_{3}Br** \[\xrightarrow{BuOK + BuOH}\] **CH_{3}CH=CH_{2}** \[\xrightarrow{(1) THF: BH_{3} (2) H_{2}O_{2}}\] **CH_{3}CH_{2}OH**

11.36 (a) **CH_{3}CH_{2}CH_{2}ONa** Sodium butoxide

(b) **CH_{3}CH_{2}CH_{2}OCH_{2}CH_{2}CH_{3}** Butyl propyl ether

(c) **CH_{3}SO_{2}OCH_{2}CH_{2}CH_{3}** Butyl mesylate

(d) **H_{2}C-\xrightarrow{SO_{2}OCH_{2}CH_{2}CH_{3}} CH_{3}** Butyl tosylate

(e) **CH_{3}OCH_{2}CH_{2}CH_{3}** 1-Methoxybutane

(f) **CH_{3}CHCH_{3}** sec-Butyl iodide

(g) **CH_{3}CHCH_{3}** sec-Butyl chloride

(h) same as (g)

(i) **H_{3}C-\xrightarrow{H} CH_{3}** mainly, trans-2-butene

(j) **CH_{3}CHCH_{3}** sec-Butyl bromide

(k) **CH_{3}CH_{2}CHOH-\xrightarrow{Si-C(CH_{3})_{3}} CH_{3}** sec-Butyl tert-butyldimethylsilyl ether

(l) **CH_{3}CHCH_{3}** 2-Butanal

11.38 (a) **CH_{3}Br + CH_{3}CH_{3}**  

(b) **CH_{3}C-Br + CH_{3}CH_{2}Br** (2 molar equivalents)
11.39 $\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \\
3^* \text{Carbocation is more stable}$

11.40 (a) $\text{CH}_2=\text{C}-\text{CH} = \text{CH}_2 + \text{THF-BH}_3 \rightarrow (\text{CH}_2=\text{C}-\text{CH} = \text{CH}_2)_2\text{B}$

(b) $\text{CH}_3\text{CH}=\text{CH}_2 + \text{THF-BH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

(c) $\text{CH}-\text{CH} = \text{CH} = \text{CH}_2$ (1) THF-BH$_3$ (2) $\text{H}_2\text{O}_2$OH,$\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

(d) $\text{C}_3\text{H}_5\text{H} \rightarrow \text{C}_3\text{H}_5\text{H} + \text{HA}$

11.41 (a) $\text{H}_2\text{C}=\text{C}-\text{CH} = \text{CH}_2$ (b) $\text{H}_2\text{C}=\text{C}-\text{CH} = \text{CH}_2$ (c) $\text{H}_2\text{C}=\text{C}-\text{CH} = \text{CH}_2$

11.42 (a) $\text{CH}_3\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2$ (b) $\text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{CH}=\text{CH}_2\text{Na} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (c) $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2\text{Br}$

11.43 (a) $\text{CH}_2=\text{C}-\text{CH}_2\text{Br} + \text{HC}-\text{OOH} \rightarrow \text{H}_2\text{C}=\text{C}-\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{C}=\text{C}-\text{CH}_2\text{Br} + \text{enantiomer}$

(b) The trans product because the Cl$^-$ attacks anti to the epoxide and an inversion of configuration occurs.
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11.44

(a) $\text{CH}_2\text{=CH}_2 \xrightarrow{\text{NaNH}_2, \text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

(b) $\text{CH}_2\text{C}=\text{CH}_2 \xrightarrow{\text{H}_2\text{O}, \text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

(c) $\text{H}_2\text{C}==\text{CCH}_3 \xrightarrow{\text{NaBH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

(d) $\text{CH}_2\text{C}=\text{CH}_2 \xrightarrow{\text{H}_2\text{O}, \text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

11.45

(a) $\text{CH}_3\text{C}=\text{CH}_2 \xrightarrow{(1) \text{THF}:\text{BH}_3, (2) \text{H}_2\text{O}, \text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

(b) $\text{CH}_3\text{C}=\text{CH}_2 \xrightarrow{(1) \text{THF}:\text{BH}_3, (2) \text{H}_2\text{O}, \text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

(c) $\text{CH}_3\text{C}=\text{CH}_2 \xrightarrow{\text{H}_2\text{O}, \text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

(d) $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{NaOH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

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(a) $\text{CH}_3\text{C}=\text{CH}_2 \xrightarrow{\text{Hg(OAc)}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{HgOAc}$

(b) $\text{CH}_3\text{C}=\text{CH}_2 \xrightarrow{\text{NaBH}_3, \text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}$

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(a) $\text{CH}_3\text{CH}==\text{CCH}_3 \xrightarrow{(1) \text{Hg(OAc)}_2, (2) \text{NaBH}_3/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}$

(b) Diastereomers

(c) $\text{CH}_3\text{CH}==\text{CCH}_3 \xrightarrow{(1) \text{Hg(OAc)}_2, (2) \text{NaBH}_3/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}$

(d) $\text{CH}_3\text{CH}==\text{CCH}_3 \xrightarrow{(1) \text{Hg(OAc)}_2, (2) \text{NaBH}_3/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}$

(e) $\text{CH}_3\text{CH}==\text{CCH}_3 \xrightarrow{(1) \text{Hg(OAc)}_2, (2) \text{NaBH}_3/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}$

(f) $\text{CH}_3\text{CH}==\text{CCH}_3 \xrightarrow{(1) \text{Hg(OAc)}_2, (2) \text{NaBH}_3/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}$

(g) Enantiomers
The reactions proceed through the formation of bromonium ions identical to those formed in the bromination of trans- and cis-2-butenes (see Section 8.7A).

\[ \text{Attack at the other carbon atom of the bromonium ion gives the same product.} \]

\[ 
\text{meso-2,3-Dibromobutane}
\]

\[ 
\text{A and B are enantiomers}
\]

\[ \text{A, C, and D are all diastereomers} \]

\[ \text{B, C, and D are all diastereomers} \]

\[ \text{C is meso} \]

\[ \text{D is meso} \]

**QUIZ**

11.1 Which set of reagents would effect the conversion.

- (a) \( \text{BH}_3\text{THF, then H}_2\text{O}_2/\text{OH}^- \)
- (b) \( \text{H}_2\text{O}/\text{Hg(OAc)}_2, \text{THF, then NaBH}_3/\text{OH}^- \)
- (c) \( \text{H}_3\text{O}^+, \text{H}_2\text{O, heat} \)
- (d) More than one of these
- (e) None of these

11.2 Which of the reagents in item 11.1 would effect the conversion.

- (a) \( \text{BH}_3\text{THF, then H}_2\text{O}_2/\text{OH}^- \)
- (b) \( \text{H}_2\text{O}/\text{Hg(OAc)}_2, \text{THF, then NaBH}_3/\text{OH}^- \)
- (c) \( \text{H}_3\text{O}^+, \text{H}_2\text{O, heat} \)
- (d) More than one of these
- (e) None of these
12.1 (a) \( \text{H-C-O-H} \)  
\( \begin{align*} 3 \text{H} &= -3 \\ 1 \text{O} &= +1 \\ \text{Total} &= -2 \quad \text{oxidation state of C} \end{align*} \)

(b) \( \text{CH}_3\text{OH} \)  
\( \begin{align*} 2 \text{H} &= -2 \\ 1 \text{O} &= +2 \\ \text{Total} &= 0 \quad \text{oxidation state of C} \end{align*} \)

(c) A change from \(-2\) to \(0\)

(d) An oxidation, since the oxidation state increases

(e) A reduction from \(+6\) to \(+3\)

12.2 (a) \( \text{H-C-C-OH} \)  
\( \begin{align*} 3 \text{H} &= -3 \\ \text{Total} &= -1 \end{align*} \)

(b) \( \text{H-C-O-H} \)  
\( \begin{align*} 1 \text{H} &= -1 \\ \text{Total} &= -2 \quad \text{oxidation state of C} \end{align*} \)
(b) Only the carbon atom of the \(-\text{CH}_2\text{OH}\) group of ethanol undergoes a change in oxidation state. The oxidation state of the carbon atom in the \(\text{CH}_3\)\(-\) group remains unchanged.

\[
\begin{align*}
\text{H}_3\text{C}-\text{CH}_2-\text{OH} + \text{H}_2 & \rightarrow \text{H}_3\text{C}-\text{CH}_2-\text{OH}
\end{align*}
\]

12.3 (a) If we consider the hydrogenation of ethene as an example, we find that the oxidation state of carbon decreases. Thus, because the reaction involves the addition of hydrogen, it is both an addition reaction and a reduction.

\[
\begin{align*}
\text{H}_2\text{C}=\text{C}-\text{H} + \text{H}_2 & \rightarrow \text{H}_3\text{C}-\text{CH}_2-\text{OH}
\end{align*}
\]

(b) The hydrogenation of acetaldehyde is not only an addition reaction, but it is also a reduction because the carbon atom of the \(\text{C}=\text{O}\) group goes from \(+1\) to \(-1\) oxidation state. The reverse reaction (the dehydrogenation of ethanol) is not only an elimination reaction, but also an oxidation.

### Ion-Electron Half-Reaction Method for Balancing Organic Oxidation–Reduction Equations

Only two simple rules are needed:

**Rule 1** Electrons \((e^-)\) together with protons \((\text{H}^+)\) are arbitrarily considered the reducing agents in the half-reaction for the reduction of the oxidizing agent. Ion charges are balanced by adding electrons to the left-hand side. (If the reaction is run in neutral or basic solution, add an equal number of \(\text{OH}^-\) ions to both sides of the balanced half-reaction to neutralize the \(\text{H}^+\), and show the resulting \(\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}\).

**Rule 2** Water \((\text{H}_2\text{O})\) is arbitrarily taken as the formal source of oxygen for the oxidation of the organic compound, producing product, protons, and electrons on the right-hand side. (Again, use \(\text{OH}^-\) to neutralize \(\text{H}^+\) in the balanced half-reaction in neutral or basic media.)

### EXAMPLE 1

Write a balanced equation for the oxidation of \(\text{RCH}_2\text{OH}\) to \(\text{RCO}_2\text{H}\) by \(\text{MnO}_4^-\) in acid solution.

Reduction half-reaction:

\[
\text{Cr}_2\text{O}_7^{2-} + \text{H}^+ + e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Balancing atoms and charges:

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Oxidation half-reaction:

\[
\text{RCH}_2\text{OH} + \text{H}_2\text{O} = \text{RCO}_2\text{H} + 4\text{H}^+ + 4e^{-}
\]

The least common multiple of a 6-electron uptake in the reduction step and a 4-electron loss in the oxidation step is 12, so we multiply the first half-reaction by 2 and the second by 3, and add:

\[
3\text{RCH}_2\text{OH} + 3\text{H}_2\text{O} + 2\text{Cr}_2\text{O}_7^{2-} + 28\text{H}^+ = 3\text{RCO}_2\text{H} + 12\text{H}^+ + 4\text{Cr}^{3+} + 14\text{H}_2\text{O}
\]

Canceling common terms, we get:

\[
3\text{RCH}_2\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ = 3\text{RCO}_2\text{H} + 4\text{Cr}^{3+} + 11\text{H}_2\text{O}
\]

This shows that the oxidation of 3 mol of a primary alcohol to a carboxylic acid requires 2 mol of dichromate.

### EXAMPLE 2

Write a balanced equation for the oxidation of styrene to benzoate ion and carbonate ion by \(\text{MnO}_4^-\) in alkaline solution.

Reduction:

\[
\text{MnO}_4^- + 4\text{H}^+ + 3e^- = \text{MnO}_2 + 2\text{H}_2\text{O} \text{ (in acid)}
\]

Since this reaction is carried out in basic solution, we must add 4 \(\text{OH}^-\) to neutralize the \(4\text{H}^+\) on the left side, and, of course, 4 \(\text{OH}^-\) to the right side to maintain a balanced equation.

\[
\text{MnO}_4^- + 4\text{H}^+ + 4\text{OH}^- + 3e^- = \text{MnO}_2 + 2\text{H}_2\text{O} + 4\text{OH}^- \\
\text{or. } \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- = \text{MnO}_2 + 4\text{OH}^- \\
\]

Oxidation:

\[
\text{ArCH} = \text{CH}_2 + \text{H}_2\text{O} = \text{ArCO}_2^- + \text{CO}_3^{2-} + 13\text{H}^+ + 10e^- \\
\]

We add 13 \(\text{OH}^-\) to each side to neutralize the \(\text{H}^+\) on the right side.

\[
\text{ArCH} = \text{CH}_2 + 5\text{H}_2\text{O} + 13\text{OH}^- = \text{ArCO}_2^- + \text{CO}_3^{2-} + 13\text{H}_2\text{O} + 10e^- \\
\]
The least common multiple is 30, so we multiply the reduction half-reaction by 10 and the oxidation half-reaction by 3 and add:

\[
3ArCH=CH_2 + 39 OH^- + 10MnO_4^- + 20H_2O = 3ArCO_2^- + 3CO_2^2^- + 24H_2O + 10MnO_4^- + 40 OH^- 
\]

Canceling:

\[
3ArCH=CH_2 + 10MnO_4^- = 3ArCO_2^- + 3CO_2^2^- + 4H_2O + 10MnO_4^- + OH^- 
\]

**SAMPLE PROBLEMS**

Using the ion-electron half-reaction method, write balanced equations for the following oxidation reactions.

(a) Cyclohexene + \( \text{MnO}_4^- \) + \( \text{H}^+ \) \xrightarrow{\text{redox}} \( \text{HO}_2\text{C(CH}_2\text{)}_2\text{CO}_2 \text{H} + \text{Mn}^{2+} + \text{H}_2\text{O} \)

(b) Cyclopentene + \( \text{MnO}_4^- \) + \( \text{H}_2\text{O} \) \xrightarrow{\text{redox}} \( \text{cis-1,2-cyclopentanediol} + \text{MnO}_2 + \text{OH}^- \)

(c) Cyclopentanol + \( \text{HNO}_3 \) \xrightarrow{\text{redox}} \( \text{HO}_2\text{C(CH}_2\text{)}_3\text{CO}_2 \text{H} + \text{NO}_2 + \text{H}_2\text{O} \)

(d) 1,2,3-CyclohexanetrioI + \( \text{HIO}_3 \) \xrightarrow{\text{redox}} \( \text{OCH(CH}_2\text{)}_3\text{CHO} + \text{HCO}_2\text{H} + \text{HIO}_3 \)

**SOLUTIONS TO SAMPLE PROBLEMS**

(a) Reduction:

\[
\text{MnO}_4^- + 8 \text{H}^+ + 5 e^- = \text{Mn}^{2+} + 4 \text{H}_2\text{O} 
\]

Oxidation:

\[
\text{HO}_2\text{C(CH}_2\text{)}_2\text{CH}_2\text{CO}_2\text{H} + 8 \text{H}^+ + 8 e^- = 8 \text{MnO}_4^- + 32 \text{H}_2\text{O} 
\]

(b) Reduction:

\[
\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 e^- = \text{MnO}_4^- + 4 \text{OH}^- 
\]

Oxidation:

\[
\text{HO}_2\text{C(CH}_2\text{)}_2\text{CO}_2\text{H} + 2 \text{OH}^- = 2 \text{MnO}_4^- + 8 \text{OH}^+ + 6 e^- 
\]

Adding and cancelling:

\[
3 \text{HO}_2\text{C(CH}_2\text{)}_2\text{CO}_2\text{H} + 6 \text{OH}^- = 3 \text{ HO}_2\text{C(CH}_2\text{)}_2\text{CO}_2\text{H} + 6 \text{OH}^- 
\]

(c) Reduction:

\[
\text{HNO}_3 + \text{H}^+ + e^- = \text{NO}_2 + \text{H}_2\text{O} 
\]

Oxidation:

\[
\text{HO}_2\text{C(CH}_2\text{)}_2\text{CO}_2\text{H} + 3 \text{H}_2\text{O} = 8 \text{H}_2\text{CO}_2\text{H} + 8 \text{OH}^- + 8 e^- 
\]

Adding and cancelling:

\[
8 \text{HO}_2\text{C(CH}_2\text{)}_2\text{CO}_2\text{H} + 8 \text{H}_2\text{O} = 8 \text{NO}_2 + 8 \text{H}_2\text{O} 
\]

(d) Reduction:

\[
\text{HIO}_3 + 2 \text{H}^+ + 2 e^- = \text{HIO}_3 + \text{H}_2\text{O} 
\]
12.4 (a) LiAlH₄
(b) LiAlH₄
(c) NaBH₄

12.5 (a) \( \text{NH}^+\text{CrO}_3\text{Cl}^-\text{(PCC)/CH}_2\text{Cl}_2 \)
(b) KMnO₄, OH⁻, H₂O, heat; then H₂O⁺
(c) H₂CIO₄/acetone
(d) (1) O₃ (2) Zn, HOAc

12.6 (a) \( \delta^-\delta^+ \)
Stronger base
Stronger acid
\( \text{C}_6\text{H}_5\text{Li} + \text{H}_2\text{OH} \rightarrow \text{C}_6\text{H}_5 + \text{LiOH} \)
Weaker acid
Weaker base

(b) \( \delta^-\delta^+ \)
Stronger base
Stronger acid
\( \text{C}_6\text{H}_5\text{Li} + \text{H}_2\text{OEt} \rightarrow \text{C}_6\text{H}_5 + \text{LiOEt} \)
Weaker acid
Weaker base

12.7 \( \text{C}_6\text{H}_5\text{Br} \underset{\text{Mg, EtO}}{\rightarrow} \text{C}_6\text{H}_4\text{Br} \stackrel{\text{MgBr Cl}}{\longrightarrow} \text{C}_6\text{H}_4\text{D} \)

12.8 \( \text{C}_6\text{H}_5\text{MgBr} + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{C}_6\text{H}_5\text{OH} \)

12.9 (a) (1) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{H} + \text{CH}_3\text{MgI} \)

(1) ether (2) NH₄⁺ \( \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{H} \)

(b) (1) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{H} + \text{CH}_3\text{MgI} \)

(1) ether (2) NH₄⁺ \( \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{H} \)

(c) \( \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + 2 \text{CH}_3\text{MgI} \)

(1) ether (2) NH₄⁺ \( \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \)
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12.11 (a) \( \text{CH}_2\text{CH}_2\text{OH} + \text{(CH}_3\text{)}_2\text{C} = \text{CH}_2 \)
(b) \( \text{CH}_2\text{CH}_2\text{CN} \)
(c) \( \text{(CH}_3\text{)}_2\text{C} = \text{CH}_2 \)
(d) \( \text{CH}_2\text{CH}_2\text{OCH}_3 + \text{(CH}_3\text{)}_2\text{C} = \text{CH}_2 \)
(e) \( \text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 \)
(f) \( \text{CH}_2\text{CH}_2\text{CHCH}_3 \)
(g) \( \text{CH}_2\text{CH}_2\text{CHCH}_3\text{CH} = \text{CH}_2 \)
(h) \( \text{CH}_2\text{CH}_2\text{CHCH}_3\text{CH}_2\text{OH} \)
(i) \( \text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)
(j) \( \text{CH}_2\text{CH}_2\text{CH}_3 \)
(k) \( \text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2\text{C} = \text{CH}_2 \)

12.12 (a) \( \text{CH}_3\text{CH}_3 \)
(b) \( \text{CH}_3\text{CH}_3\text{D} \)
(c) \( \text{C}_2\text{H}_5\text{CHCHCH}_3 \)
(d) \( \text{C}_2\text{H}_5\text{C} = \text{CH}_2 \)
(e) \( \text{C}_2\text{H}_5\text{C} = \text{CHCH}_3 \)
(f) \( \text{C}_2\text{H}_5\text{C} = \text{CHCH}_3 \)
(g) \( \text{CH}_3\text{CH}_3 + \text{CH}_2\text{C} = \text{CHCH}_3 \)
(h) \( \text{CH}_3\text{CH}_3 + \text{MgBr} \)
12.13 (a) \((\text{CH}_3)_2\text{CHCHCH}_2\text{CH}_3\) (b) \((\text{CH}_3)_2\text{CCH}_3\text{CH}_2\text{CH}_3\) (c) \(\text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{C} \equiv \text{C} - \text{CH}_3\) (d) \(\text{CH}_3\text{CH}_2\text{CH}_3\) (e) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2\) (f) \(\text{CH}_3\text{CH}_2\text{CH}_2\) (g) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\) (h) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\) (i) \(\text{CH}_3\text{CH}_2\text{D}\)

Note: This variation of the Corey-Posner, Whitesides-House synthesis is stereo-specific.

12.14 (a) LiAlH_4 (b) NaBH_4 (c) LiAlH_4

12.15 (a) \(3\) \((\text{CH}_3)_2\text{CHOH} + \text{Pb} \rightarrow (\text{CH}_3)_2\text{CHBr} + \text{H}_3\text{PO}_3\) (b) \((\text{CH}_3)_2\text{CHBr} + \text{Mg} \xrightarrow{\text{ether}} (\text{CH}_3)_2\text{CHMgBr}\) (c) \((\text{CH}_3)_2\text{CHBr}\) [from part (a)]

12.16 (a) \(\delta^+ \xrightarrow{\delta^-} \text{CH}_2\text{Li} + \text{H} \equiv \text{C} \equiv \text{C} - \text{CH}_3 \rightarrow \text{CH}_4 + \delta^+ \delta^- \text{Li} : \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3\) (b) \(\text{CH}_2\text{Li} + \text{C} \equiv \text{C} \equiv \text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{Li} : \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3\) (c) \(\text{CH}_3\text{CH}_2\text{C} \equiv \text{C} - \text{O} \xrightarrow{\text{Na} + \text{H}} \text{CH}_3\text{CH}_2\text{C} \equiv \text{C} - \text{O} \xrightarrow{\text{Na} + \text{H}} \text{CH}_3\text{CH}_2\text{C} \equiv \text{C} - \text{O} \text{SO}_2\text{CH}_3\) (d) \(\text{CH}_3\text{CH}_2\text{C} \equiv \text{C} - \text{O} \text{SO}_2\text{CH}_3\) (e) \(\text{CH}_3\text{CH}_2\text{CHCH}_3\) (f) \(\text{CH}_3\text{CH}_2\text{OSO}_2\text{CH}_3\)
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12.19 (a) Partial Analysis

\[
\begin{align*}
\text{CH}_3\text{CHCC}_6\text{H}_5 & \rightarrow \text{CH}_3\text{CHCHC}_6\text{H}_5 \rightarrow \text{CH}_3\text{CH} + \text{C}_6\text{H}_5\text{MgBr} \\
\text{Synthesis} \\
\text{CH}_3\text{CHCH}_2\text{OH} \xrightarrow{\text{PCC}} \text{CH}_3\text{CHCH}_2\text{CH}_3 \xrightarrow{\text{MgBr}} \text{CH}_3\text{CHCHC}_6\text{H}_5 \xrightarrow{\text{H}_2\text{CrO}_4} \text{CH}_3\text{CHCC}_6\text{H}_5 \\
\end{align*}
\]

(b) Partial Analysis

\[
\begin{align*}
\text{CH}_3\text{CH} & \rightarrow 2\text{CH}_3\text{CH}_2\text{MgBr} \\
\text{Synthesis} \\
\text{CH}_3\text{CHCH}_2\text{OH} \xrightarrow{\text{PBr}} \text{CH}_3\text{CHCH}_2\text{Br} \xrightarrow{\text{Mg, EtO}} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\
& \xrightarrow{(1) \text{CH}_2\text{CH}_2\text{COCH}_3} \text{CH}_3\text{CHCH}_2\text{CH}_3 \xrightarrow{(2) \text{NH}_4^+} \text{CH}_3\text{CHCH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\
\end{align*}
\]

(c) Partial Analysis

\[
\begin{align*}
\text{CH}_3 & \rightarrow \text{CH}_3 \xrightarrow{\text{MgBr}} \text{CH}_3 \xrightarrow{\text{H}_2\text{CrO}_4} \text{CH}_3 \\
\text{Synthesis} \\
\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}} \text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{Mg, EtO}} \text{CH}_2\text{CH}_2\text{CH}_3 \\
& \xrightarrow{(1) \text{CH}_2\text{CH}_2\text{COCH}_3} \text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{(2) \text{NH}_4^+} \text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(d) Partial Analysis

\[
\begin{align*}
\text{CH}_3 & \rightarrow \text{CH}_3 \xrightarrow{\text{H}_2\text{CrO}_4} \text{CH}_3 \\
\text{Synthesis} \\
\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{CH}_2\text{CH}_2\text{CHO} \\
& \xrightarrow{\text{Mg, EtO}} \text{CH}_2\text{CH}_2\text{CH}_3 \\
& \xrightarrow{(1) \text{CH}_2\text{CH}_2\text{COCH}_3} \text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{(2) \text{H}_2\text{O}^+} \text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(e) Partial Analysis

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{Mg, EtO}} \text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{Synthesis} \\
\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PBr}} \text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{Mg, EtO}} \text{CH}_2\text{CH}_2\text{CH}_3 \\
& \xrightarrow{(1) \text{CH}_2\text{CH}_2\text{COCH}_3} \text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{(2) \text{NH}_4^+} \text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

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(f) Partial Analysis
\[
\begin{align*}
\text{OH} + \text{CH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_2\text{CH}\text{CH}_2\text{MgBr} \\
\text{Synthesis} \quad \text{OH} + \text{H}_2\text{O} & \rightarrow \text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

(g) Partial Analysis
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3\text{C} &= \text{CH}_2\text{CH}_2\text{CH}_3 + \text{BrMgCH}_2\text{CH}_2\text{CH}_3 \\
\text{Synthesis} \quad \text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{PCC, Et}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

(h) Partial Analysis
\[
\begin{align*}
\text{Br} + \text{CH}_3\text{CH}_2\text{C}_6\text{H}_5 & \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{CH}_3\text{CH}_2\text{C}_6\text{H}_5 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

Synthesis
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

12.20 Analysis
\[
\begin{align*}
\text{C}_6\text{H}_5\text{OH} & \rightarrow \text{C}_6\text{H}_5\text{Mg}^2\text{Br} + \text{CO}_2 \\
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

Synthesis
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]

12.21 The starting compound is a cyclic ester. Addition of two molar equivalents of CH_3MgI will (after acidification) furnish the desired product.
12.22 Analysis

\[
\text{CH}_3\text{CH}_2\text{C}+\text{C}==\text{CH} \rightarrow \text{CH}_3\text{CH}==\text{CH}_3 + \text{Na}^+ \cdot \text{C}==\text{CH}
\]

Synthesis

\[
\text{HC}==\text{CH} \xrightarrow{\text{NaH, liq.} \text{NH}_3} \text{HC}==\text{C}^+:\text{Na}^+ \xrightarrow{(1) \text{CH}_3\text{CH}_2\text{CH}_3} \text{CH}_3\text{CH}==\text{CH}_3 + \text{Na}^+ \cdot \text{C}==\text{CH}
\]

12.23 The three- and four-membered rings are strained, and so they open on reaction with \(\text{RMgX}\) or \(\text{RLi}\). THF possesses an essentially unstrained ring and hence is far more resistant to attack by an organometallic compound.

12.24 (a) \(\text{RMgX} + \text{C}_2\text{H}_5\text{O}-\text{C}^--\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_5\text{O}^+ \cdot \text{C}^--\text{C}_2\text{H}_3\]

(b) \(\text{RMgX} + \text{H}^+\text{C}^--\text{C}_2\text{H}_3 \rightarrow \text{H}^+\text{C}^--\text{C}_2\text{H}_3\)

12.25 Before converting the reactant to a Grignard reagent it is first necessary to mask the alcohol, such as by converting it to a tert-butylidimethylsilyl ether. After the Grignard reaction is over the protecting group is removed.

12.26 2-Phenylethanol, 1,2-diphenylethanol, and 1,1-diphenylethanol are distinct from diphenylacetic acid and benzyl phenylacetate in that they do not have carbonyl groups. IR spectroscopy can be used to segregate these compounds into two groups according to those that do or do not exhibit carbonyl absorptions.

\(^1\text{H} \text{NMR} \) can differentiate among all of the compounds. In the case of the alcohols, in the \(^1\text{H} \text{NMR} \) spectrum of 2-phenylethanol there will be two triplets of equal integral value, whereas for 1,2-diphenylethanol there will be a doublet and a triplet in a 2:1 area ratio. The triplet will be downfield of the doublet. 1,1-Diphenylethanol will exhibit a singlet for the unsplitted methyl hydrogens.

The broadband proton-decoupled \(^1\text{C} \text{NMR} \) spectrum of 2-phenylethanol should show 6 signals (assuming no overlap), four of which are in the chemical shift region for aromatic carbons. 1,2-Diphenylethanol should exhibit 10 signals (assuming no overlap), 8 of which are in the aromatic region. 1,1-Diphenylethanol should show 6 signals (assuming no overlap), four of which would be in the aromatic region. The DEPT \(^1\text{C} \text{NMR} \) spectra would give direct evidence as to the number of attached hydrogens on each carbon.

Regarding the carbonyl compounds, both diphenylacetic acid and benzyl phenylacetate will show carbonyl absorptions in the IR, but only the former will also have a hydroxyl absorption. The \(^1\text{H} \text{NMR} \) spectrum of diphenylacetic acid should show a broad absorption for the carboxylic acid hydrogen and a sharp singlet for the unsplitted hydrogens at C2. Their integral values should be the same, and approximately one tenth the integral value of the signals in the aromatic region. Benzyl phenylacetate will exhibit two singlets, one for each of the unsplitted CH3 groups. These signals will have an area ratio of 1:5 with respect to the signal for the 10 aromatic hydrogens. The broadband \(^1\text{H} \text{decoupled} \) \(^1\text{C} \text{NMR} \) spectrum for diphenylacetic acid should show four aromatic carbon signals, whereas that for benzyl phenylacetate (assuming no overlapping signals) would show 10 signals in the aromatic carbon region. Aside from the carbonyl and aromatic carbon signals, benzyl phenylacetate would show two additional signals, whereas diphenylacetic acid would show only one. DEPT \(^1\text{C} \text{NMR} \) spectra for these two compounds would also distinguish them directly.
12.27 It makes it impossible to distinguish between aldehyde and ketone type sugars (aldoses and ketoses) that had been components of the saccharide. Also, because the R groups of these sugars contain stereocenters, reduction of the ketone carbonyl will be stereoselective. This will complicate the determination of the ratio of sugars differing in configurational at C2.

12.28 The IR indicates the presence of OH and absence of C=O and C=O. The MS indicates a molecular weight of 116 amu and confirms the presence of hydroxyl. The reaction data indicate X contains 2 protons per molecule that are acidic enough to react with a Grignard reagent, meaning two hydroxyl groups per molecule. (This analytical procedure, the Zerewitinoff determination, was routinely done before the advent of NMR.) Thus X has a partial structure like:

\[ \text{C}_5\text{H}_2\text{O(OH)}_2 \]

with one ring, or

\[ \text{C}_4\text{H}_6\text{O(OH)}_2 \]

with two rings, or (less likely)

\[ \text{C}_3\text{H}_5\text{O(OH)}_2 \]

with three rings.

QUIZ

12.1 Which of the following could be employed to transform ethanol into \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)?

(a) Ethanol + HBr, then Mg/diethyl ether, then \( \text{H}_3\text{O}^+ \)

(b) Ethanol + HBr, then Mg/diethyl ether, then \( \text{HCl} \), then \( \text{H}_3\text{O}^+ \)

(c) Ethanol + \( \text{H}_2\text{SO}_4/140^\circ \text{C} \)

(d) Ethanol + \( \text{Na} \), then \( \text{HCl} \), then \( \text{H}_3\text{O}^+ \)

(e) Ethanol + \( \text{H}_2\text{SO}_4/180^\circ \text{C} \), then \( \text{H}_3\text{C}-\text{COCH}_3 \)

12.2 The principal product(s) formed when 1 mol of methylmagnesium iodide reacts with 1 mol of \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \).

(a) \( \text{CH}_4 + \text{CH}_3\text{CH}_2\text{CH}_2\text{OMgI} \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 \)

(d) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 \)

(e) None of the above
ANSWERS TO FIRST REVIEW PROBLEM SET

1. (a) \[
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\]  
\[+\text{H}^+ \xrightarrow{\text{CH}_3} \]  
\[\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]  
\[\text{mechanism shift} \]  
\[\begin{array}{c}
\text{CH} \\
\text{CH}_3
\end{array}
\]  
\[\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]  
\[\text{2° Carbocation} \]  
(b) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]  
\[\xrightarrow{\text{Br}^-\text{Br}^-} \]  
\[\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]  
\[\xrightarrow{\text{Br}^-} \]  
\[\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]  
\[\text{2° Carbocation} \]  
(c) The enantiomer of the product given would be formed in an equimolar amount via the following reaction:

\[
\begin{array}{c}
\text{Cl} \\
\text{Br}
\end{array}
\]  
\[\xrightarrow{\text{Br}^-} \]  
\[\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\]  
\[\text{The cis-1, 2-dibromocyclopentane would be formed as a racemic form via the reaction of the bromonium ion with a bromide ion:} \]  
\[
\begin{array}{c}
\text{Br}^+ \\
\text{Br}^-
\end{array}
\]  
\[\xrightarrow{\text{Br}^-} \]  
\[\begin{array}{c}
\text{Br}^+ \\
\text{Br}^-\text{Br}^-
\end{array}
\]  
\[\text{Racemic trans-1,2-dibromocyclopentane} \]  

2. (a) \[
\begin{array}{c}
\text{CHCl}_3
\end{array}
\]  
(b) The cis isomer  
(c) \[
\begin{array}{c}
\text{CH}_2\text{Cl}
\end{array}
\]  
3. This indicates that the bonds in BF₃ are geometrically arranged so as to cancel each other's polarities in contrast to the case of NF₃. This, together with other evidence, indicates that BF₃ has trigonal planar structure and NF₃ has trigonal pyramidal structure.

4. (a) sp³  
(b) They are much smaller (60°) than the expected 109.5°.  
(c) That the bent bonds in cyclopropane, like compressed springs, contain stored energy that is available to assist in reactions that open the 3-membered ring.

5. All of these differences can be explained by the contribution to the CH₂=CHCl molecule made by the following A and B resonance structures:

\[\text{A} \]  
\[\text{B} \]  
(a) Because of the contribution made to the hybrid by B, the C-Cl bond of CH₂=CH-Cl has some double-bond character and is, therefore, shorter than the "pure" single bond of CH₂CH₂-Cl.  
(b) The contribution made to the hybrid by B imparts some single-bond character to the carbon-carbon double bond of CH₂=CH-Cl, causing it to be longer than the "pure" double bond of CH₂=CH₂.  
(c) Electronegativity differences would cause a carbon-chlorine bond to be polarized as follows:

\[\begin{array}{c}
\text{C} \\
\text{Cl}
\end{array}\]  
\[\delta^+ \delta^- \]  

And, trans-2-bromocyclopentanol (the bromohydrin) would be formed (as a racemic form) via the reaction of the bromonium ion with water.

\[
\begin{array}{c}
\text{Br}^+ \\
\text{H}_2\text{O}
\end{array}
\]  
\[\xrightarrow{\text{H}^+} \]  
\[\begin{array}{c}
\text{OH}^+ \\
\text{H}_2\text{O}
\end{array}
\]  
\[\xrightarrow{\text{Br}^-} \]  
\[\begin{array}{c}
\text{Br}^- \\
\text{OH}^+
\end{array}
\]  
\[\text{Racemic trans-2-bromocyclopentanol} \]
And this effect accounts, almost entirely, for the dipole moment of CH₂CH₂Cl.

\[
\delta^+ \delta^- \quad \mu = 2.05 \text{ D}
\]

With CH₂=CH-Cl, however, the resonance contribution of B tends to oppose the polarization of the C-Cl bond caused by electronegativity differences. That is, the resonance effect partially cancels the electronegativity effect causing the dipole moment to be smaller.

6 A = CH₃(CH₂)₃CH₂C≡CH
   B = CH₃(CH₂)₃CH₂C≡CNa
   C = CH₃(CH₂)₃CH₂C≡C(CH₂)₃CH₃
   Muscalure = CH₃(CH₂)₃CH₂C≡C(CH₂)₃CH₃

(E)-2,3-Diphenyl-2-butene  (Z)-2,3-Diphenyl-2-butene

Because catalytic hydrogenation is a syn addition, catalytic hydrogenation of the (Z) isomer would yield a meso compound.

\[
\begin{align*}
\text{H₂}/\text{Pd} & \quad \text{H₂}/\text{Pd} \\
\text{(Z)} & \quad \text{(by addition at one face)} \\
\text{A meso compound} & \quad \text{(by addition at the other face)}
\end{align*}
\]

Syn addition of hydrogen to the (E) isomer would yield a racemic form:

8 From the molecular formula of A and of its hydrogenation product B, we can conclude that A has two rings and a double bond. (B has two rings.)
From the product of strong oxidation with KMnO₄ and its stereochemistry (i.e., compound C), we can deduce the structure of A.

\[
\begin{array}{c}
\text{KMnO}_4, \text{OH}^+, \text{heat} \\
(2) \text{H}_2\text{O}^+
\end{array}
\]

Compound B is bicyclo[2.2.1]heptane and C is a glycol.

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\text{(1) } \text{KMnO}_4, \text{OH}^+, \text{heat} & \quad \text{(2) } \text{H}_2\text{O}^+
\end{align*}
\]

Notice that C is also a meso compound.
ANSWERS TO FIRST REVIEW PROBLEM SET

9 (a) CH₂C≡CH $\xrightarrow{NaNH_2, liq. NH_3}$ CH₂C≡CNa $\xrightarrow{CH_3}$ CH₂C≡CH₃

(b) CH₂C≡CCH₃
\[ \text{[from (a)]} \]

(c) CH₂C≡CCH₃
\[ \text{[from (a)]} \]

(d) CH₂C≡CH $\xrightarrow{H_2, Ni,B(P-2)}$ CH₃CH=CH₂ $\xrightarrow{NBS, light 25^\circ}$ BrCH₂CH=CH₂

CH₄I $\xrightarrow{Li, Et_2O}$ CH₃Li $\xrightarrow{CuI}$ (CH₃)₂CuLi

or

CH₂C≡CH $\xrightarrow{(1) NaNH_2, \text{liq. NH}_3}$ (2) CH₃Br $\xrightarrow{NaNi(BP-2)}$ CH₃C≡CH₃ $\xrightarrow{CH₃CH=CH₂}$ BrCH₂CH=CH₂

CH₃CH₂CH=CH₂ $\xrightarrow{\text{ tert-ButOH, tert-ButOH, heat}}$ CH₃CH₂CHCH₃

(c) CH₃CH₂CH=CH₂ $\xrightarrow{\text{NBS, CCl₄}}$ CH₃CH₂CH₂CH₂Br

\[ \text{[from (d)]} \]

(f) CH₃CH₂CH=CH₂ $\xrightarrow{\text{HBr, ROOR}}$ CH₃CH₂CH₂CH₂Br

\[ \text{[from (d)]} \]

(g) CH₃CH=CHCH₃ $\xrightarrow{\text{HBr, no peroxides}}$ CH₃CH=CHCH₃

\[ \text{[from (b) or (c)]} \]

or

CH₃CH=CHCH₃ $\xrightarrow{\text{HBr, no peroxides}}$ CH₃CH=CHCH₃

\[ \text{[from (d)]} \]

(h) H₂C=CH $\xrightarrow{\text{Br₂, CCl₄}}$ (anti addition)

\[ \text{[from (c)]} \]

(i) H₂C=CH + H₂C=CH $\xrightarrow{\text{Br₂, CCl₄}}$ (anti addition)

\[ \text{[from (b)]} \]

(j) H₂C=CH $\xrightarrow{\text{OxO, (2) NaHSO₃}}$ (syn addition)

\[ \text{[from (b)]} \]

(k) H₂C≡CCH₃ $\xrightarrow{\text{HBr, Br', CH₃COOH, heat}}$ CH₂C≡CBr

\[ \text{[from (c)]} \]

10 CH₃CH₂CH₂CH₃ $\xrightarrow{\text{Br₂, hv, heat}}$ CH₃C₂H₃CH₂Br

(a) CH₃CH₂CH₂CH₃ $\xrightarrow{\text{CH₃CH₂OH, heat}}$ CH₃C≡CHCH₃

\[ \text{[from (a)]} \]

(b) CH₃C≡CHCH₃ $\xrightarrow{\text{H₂O, H₂O}}$ CH₃C≡CHCH₃

\[ \text{[from (a)]} \]
212  ANSWERS TO FIRST REVIEW PROBLEM SET

(c) $\text{CH}_3\text{C}≡\text{CHCH}_3 \xrightarrow{(1) \text{THF, BH}_3, \text{H}_2\text{O}, \text{HCl}} \text{CH}_3\text{CHCHCH}_3$

(d) $\text{CH}_3\text{CHCH}≡\text{CH}_2 \xrightarrow{\text{Br}_2, \text{CCl}_4} \text{CH}_3\text{CHCHCHCH}_2\text{Br} \xrightarrow{1 \text{ NaNa}_2, \text{H}_2\text{O}, \text{heat}} \text{CH}_3\text{CHCHCH}_3$

(e) $\text{CH}_3\text{CHCH}≡\text{CH}_2 \xrightarrow{\text{HBr, ROOR, heat}} \text{CH}_3\text{CHCHCH}_2\text{Br}$

(f) $\text{CH}_3\text{CHCH}≡\text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_3\text{CHCHCH}_2\text{Cl}$

(g) $\text{CH}_3\text{C}≡\text{CHCH}_3 \xrightarrow{\text{HCl}} \text{CH}_3\text{CHCHCH}_2\text{Cl}$

(h) $\text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{Br} \xrightarrow{\text{NaI, acetone, SN}_2} \text{CH}_3\text{CHCHCH}_2\text{I}$

(i) $\text{CH}_3\text{C}≡\text{CHCH}_3 \xrightarrow{(1) \text{O}, \text{Zn, HOAc}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}$

(j) $\text{CH}_3\text{CHCH}≡\text{CH}_2 \xrightarrow{(1) \text{O}, \text{Zn, HOAc}} \text{CH}_3\text{CHCHCH}_2\text{OH} + \text{CH}_3\text{CHOH}$

11

$\text{CH}_3\text{CCH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2, \text{heat}} \text{CH}_3\text{CHCHCH}_3$ + $\text{CH}_3\text{CCHCH}_2\text{Cl}$

B cannot undergo dehydrohalogenation because it has no $\beta$-hydrogen; however, C and D can, as shown next.

12

$\text{CH}_3\text{C}≡\text{CHCH}_3 \xrightarrow{\text{H}_2\text{B, Pt}} \text{CH}_3\text{CHCH}_2\text{CH}_3$

No IR absorption in 2200–2300 cm$^{-1}$ region.

(a meso compound)
13. The eliminations are anti eliminations, requiring an anti periplanar arrangement of the bromine atoms.

\[ \text{meso-2,3-Dibromobutane} \]

\[ \text{trans-2-Butene} \]

\[ \text{(2S,3S)-2,3-Dibromobutane} \]

\[ \text{cis-2-Butene} \]

\[ \text{(2R,3R)-2,3-Dibromobutane} \]

\[ \text{cis-2-Butene} \]

14. The eliminations are anti eliminations, requiring an anti periplanar arrangement of the \(-\text{H}\) and \(-\text{Br}\).

\[ \text{meso-1,2-Dibromo-1,2-diphenylethane} \]

\[ \text{(E)-1-Bromo-1,2-diphenylethane} \]

\[ \text{(2R,3R)-1,2-Dibromo-1,2-diphenylethane} \]

\[ \text{(Z)-1-Bromo-1,2-diphenylethane} \]

(2S,3S)-1,2-Dibromo-1,2-diphenylethane will also give (Z)-1-bromo-1,2-diphenylethane in an anti elimination.

15. In all the following structures, notice that the large tert-butyl group is equatorial.

(a) \[ \text{ bromine addition is anti; cf. Section 8.7} \]

\[ \text{+ enantiomer as a racemic form} \]

(b) \[ \text{syn hydroxylation; cf. Section 8.10} \]

\[ \text{+ enantiomer as a racemic form} \]

(c) \[ \text{anti hydroxylation; cf. Section 11.19} \]

\[ \text{+ enantiomer as a racemic form} \]

(d) \[ \text{syn and anti Markovnikov addition of } \text{—H and } \text{—OH; cf. Section 11.7} \]

\[ \text{+ enantiomer as a racemic form} \]

(e) \[ \text{Markovnikov addition of } \text{—H and } \text{—OH; cf. Section 11.4} \]

\[ \text{+ enantiomer as a racemic form} \]

(f) \[ \text{anti addition of } \text{—Br and } \text{—OH, with } \text{—Br and } \text{—OH placement resulting from the more stable partial carbocation in the intermediate bromonium ion; cf. Section 8.8} \]

\[ \text{+ enantiomer as a racemic form} \]
(g) \[ \text{enantiomer as a racemic form} \]

(h) \[ \text{enantiomer as a racemic form} \]

(i) \[ \text{(syn addition of deuterium; cf. Section 7.14)} \]

(j) \[ \text{(syn, anti Markovnikov addition of -D and -B, with -B being replaced by -T where T stands; cf. Section 11.7)} \]

16 \[ A = \text{CH}_3\text{C} = \text{CHCH}_2\text{CH}_3 \quad B = \left(\frac{\text{CH}_3\text{C}}{\text{CH}_3\text{CCH}_2\text{CH}_3}\right)_{\text{BH}} = \text{CH}_3\text{CCHCH}_2\text{CH}_3 \quad C = \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_3 \quad \text{OH} \]

17 (a) The following products are diastereomers. They would have different boiling points and would be in separate fractions. Each fraction would be optically active.

(b) Only one product is formed. It is achiral, and, therefore, it would not be optically active.

(c) Two diastereomeric products are formed. Two fractions would be obtained. Each fraction would be optically active.

(d) One optically active compound is produced.

(e) Two diastereomeric products are formed. Two fractions would be obtained. Each fraction would be optically active.
Two diastereomeric products are formed. Two fractions would be obtained. Each fraction would be optically active.

\[ \text{Diastereomers} \]

\[ \begin{align*}
\text{(1) } & \text{ } \text{ (optically active)} \\
\text{(2) } & \text{ } \text{ (optically active)} \\
\end{align*} \]

\( m/z 120 = M^+ \)
\( 105 = M^+ - J(\text{CH}_3) = C_6H_5-\text{CHCH}_3 \)
\( 77 = M^+ - 43(\text{i-Pr}) = C_6H_5+ \)

\( \delta 7.2-7.6 \quad \text{5 ring protons} \)
\( 2.95 \quad \text{CH of isopropyl group} \)
\( 1.29 \quad \text{equivalent CH}_3 \text{s of isopropyl group} \)

C\(_4\)H\(_9\)O has IHDD = 2
IR absorption indicates C=O
\( ^13C \text{ NMR spectrum for X is consistent with structure} \)
(b) Isomer 9 is slow to react in an E2 reaction because in its more stable conformation (see following structure) all the chlorine atoms are equatorial and an anti periplanar transition state cannot be achieved. All other isomers 1-8 can have an -Cl axial and thus achieve an anti periplanar transition state.

(a) CH₃CHCH₂CH₃ → H₂CH₂CH₂F + FCH₂CH₃

\[ \begin{array}{c}
\text{Enantiomers} \\
(\text{obtained in one fraction as an optically inactive racemic form})
\end{array} \]

1 + 2

3 + 4 + 5 + 6

(achiral and, therefore, optically inactive)

Enantiomers
(achiral and, therefore, optically inactive)

(b) Four fractions. The enantiomeric pairs would not be separated by fractional distillation because enantiomers have the same boiling points.

(c) All of the fractions would be optically inactive.

(d) The fraction containing 1 and 2 and the fraction containing 4 and 5.

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\[ \begin{array}{c}
\text{(R)}-2\text{-Fluorobutane} \\
(\text{optically active}) \\
\text{1} \\
(\text{achiral and, therefore, optically inactive}) \\
\text{2} \\
\text{3} \\
(\text{optically active}) \\
\text{4} \\
(\text{optically active}) \\
\text{5} \\
(\text{meso compound (optically inactive)}) \\
\text{6} \\
(\text{optically active})
\end{array} \]

(b) Five. Compounds 3 and 4 are diastereomers. All others are constitutional isomers of each other.

(c) See above.

24

Each of the two structures just given has a plane of symmetry (indicated by the dashed line), and, therefore, each is a meso compound. The two structures are not superposable one on the other, therefore, they represent molecules of different compounds and are diastereomers.
25 Only a proton or deuteron anti to the bromine can be eliminated; that is, the two groups undergoing elimination (H and Br or D and Br) must lie in an anti periplanar arrangement. The two conformations of erythro-2-bromobutane-3-d in which a proton or deuteron is anti periplanar to the bromine are I and II.

\[
\begin{align*}
\text{H}_2\text{C} & \text{C} \quad \text{Br} \quad \text{CH}_3 & \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H}_2\text{C} & \text{C} \quad \text{Br} \quad \text{CH}_3 & \quad \text{D} \quad \text{D} \quad \text{D} \quad \text{D}
\end{align*}
\]

Conformation I can undergo loss of HBr to yield cis-2-butene-2-d. Conformation II can undergo loss of DBr to yield trans-2-butene.

13 CONJUGATED UNSATURATED SYSTEMS

SOLUTIONS TO PROBLEMS

13.1 (a) \( ^{14}\text{CH}_2=\text{CHCH}_2\text{X} \) and \( \text{CH}_2=\text{CH}^{14}\text{CH}_2\text{X} \)

(b) The reaction proceeds through the resonance-stabilized radical.

\[ ^{14}\text{CH}_2=\text{CH} \quad \leftrightarrow \quad ^{14}\text{CH}_2=\text{CH} \]

Thus, attack on \( X \) can occur by the carbon atom at either end of the chain since these atoms are equivalent.

(c) 50:50 because attack at the two ends of the chain is equally probable.

13.2 (a) \( \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \)

(b) We know that the allylic cation is almost as stable as a tertiary carbocation. Here we find not only the resonance stabilization of an allylic cation but also the additional stabilization that arises from contributor D in which the plus charge is on a secondary carbon atom.

(c) \( \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \quad \leftrightarrow \quad \text{CH}_3=\text{CH} \)

Thus, attack on the chlorine will occur at the two positive centers shown in structure F.

13.3 (a) \( \text{CH}_3=\text{C} \quad \leftrightarrow \quad \text{CH}_3=\text{C} \)

(b) \( \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \quad \leftrightarrow \quad \text{CH}_2=\text{CH} \)

CH_2=CH-CH=CH=CH_2
13.4 (a) CH₃C=CH:CH the positive charge is on a tertiary carbon atom rather than a primary one (rule 8).

(b) CH₃:CH=CH because the positive charge is on a secondary carbon atom rather than a primary one (rule 8).

(c) CH₃N(CH₃)₂ because all atoms have a complete octet (rule 8b), and there are more covalent bonds (rule 8a).

(d) CH₃C-OH because it has no charge separation (rule 8c).

(e) CH₂=CH:CH=CH because the radical is on a secondary carbon atom rather than a primary one (rule 8).

(f) :NH₂-C≡N because it has no charge separation (rule 8c).

13.5 In resonance structures, the positions of the nuclei must remain the same for all structures (rule 2). The keto and enol forms shown differ not only in the positions of their electrons, but also in the position of one of the hydrogen atoms. In the enol form, it is attached to an oxygen atom; in the keto form, it has been moved so that it is attached to a carbon atom.

13.6 (a) cis-1,3-Pentadiene, trans-2,4-hexadiene, cis-trans-2,4-hexadiene, and 1,3-cyclohexadiene are conjugated dienes.

(b) 1,4-Cyclohexadiene and 1,4-pentadiene are isolated dienes.

(c) 1-Penten-4-yne is an isolated enyne.

13.7 The formula, C₄H₆, tells us that A and B have six hydrogen atoms less than an alkane. This unsaturation may be due to three double bonds, one triple bond and one double bond, or combinations of two double bonds and a ring, or one triple bond and a ring. Since both A and B react with 2 mol of H₂ to yield cyclohexene, they are either cyclohexene or cyclohexadiene. The absorption maximum of 256 nm for A tells us that it is conjugated. Compound B, with no absorption maximum beyond 300 nm, possesses isolated double bonds. We can rule out cyclohexyne because of ring strain caused by the requirement of linearity of the —C≡C— system. Therefore, A is 1,3-cyclohexadiene; B is 1,4-cyclohexadiene.

13.8 All three compounds have an unbranched five-carbon chain, because the product of hydrogenation is unbranched pentane. The formula, C₅H₈, suggests that they have one double bond and one triple bond. Compounds D, E, and F must differ, therefore, in the way the multiple bonds are distributed in the chain. Compounds E and F have a terminal —C≡CH (IR absorption at ~3300 cm⁻¹). The UV absorption maximum near 250 nm for D and E suggests that in these compounds, the multiple bonds are conjugated. The structures are

13.9 (a) Recall that 1,2 and 1,4 addition refer to the conjugated system itself and not the entire carbon chain. CH₃CH₂CH =CHCH₂ and CH₃CH₂CH =CHCH₂Cl

(b) The most stable cation is a hybrid of equivalent forms:

CH₃CH=CHCH₂Cl CH₃CH=CHCH₂Cl

Thus, 1,4 and 1,2 addition yield the same product.

CH₃CH=CHCH₂Cl
13.10 Addition of the proton gives the resonance hybrid.

(a) \( \text{CH}_3\text{CH}=\text{CH} \cdots \text{CH}=\text{CH}_2 \)
(b) \( \text{CH}_2=\text{CH} \cdots \text{CH} \cdots \text{CH}=\text{CH}_2 \)

The inductive effect of the methyl group in I stabilizes the positive charge on the adjacent carbon. Such stabilization of the positive charge does not occur in II. Because I contributes more heavily to the resonance hybrid than does II, C2 bears a greater positive charge and reacts faster with the bromide ion.

(b) In the 1,4-addition product, the double bond is more highly substituted than in the 1,2-addition product; hence it is the more stable alkene.

13.11 (a), (c)

(b) \( \pi \)-Electron interaction occurs here.

13.12 (a) \( \text{H}_2\text{C} \cdots \text{CH} \cdots \text{CH}_3 \) + \( \text{H}_2\text{C} \cdots \text{CH}_3 \)
(b) \( \text{H}_3\text{C} \cdots \text{CH} \cdots \text{COCH}_3 \)
(c) \( \text{H}_3\text{C} \cdots \text{CH} \cdots \text{CO} \) (major product) + \( \text{H}_3\text{C} \cdots \text{CH} \cdots \text{CO} \) (minor product)

13.13 Use the trans diester because the stereochemistry is retained in the adduct.

13.14 \( \text{C} \cdots \text{H}_2\text{OCH}_3 \) + \( \text{C} \cdots \text{H}_2\text{OCH}_3 \)

13.15 

(Or, in each case, the other face of the dienophile could present itself to the diene, resulting in the respective enantiomer.)

13.16 (a) \( \text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \) \( \text{(CH}_3\text{)_2CO} \rightarrow \text{CH}_2=\text{CH} \cdots \text{CH}=\text{CH}_2 \)
(b) \( \text{HOCCH}_2\text{CH}_2\text{CH}_2\text{OH} \) \( \text{(CH}_3\text{)_2CO} \rightarrow \text{CH}_2=\text{CH} \cdots \text{CH}=\text{CH}_2 \)
(c) \( \text{CH}_2=\text{CH} \cdots \text{CH}_2\text{OH} \) \( \text{(CH}_3\text{)_2CO} \rightarrow \text{CH}_2=\text{CH} \cdots \text{CH}=\text{CH}_2 \)
(d) \( \text{CH}_2=\text{CH} \cdots \text{CH}_2\text{Cl} \) \( \text{(CH}_3\text{)_2CO} \rightarrow \text{CH}_2=\text{CH} \cdots \text{CH}=\text{CH}_2 \)
(e) \( \text{CH}_2=\text{CH} \cdots \text{CH}_2\text{Cl} \) \( \text{(CH}_3\text{)_2CO} \rightarrow \text{CH}_2=\text{CH} \cdots \text{CH}=\text{CH}_2 \)
(f) \( \text{CH}_2=\text{CH} \cdots \text{CH}_2\text{OH} \) \( \text{(CH}_3\text{)_2CO} \rightarrow \text{CH}_2=\text{CH} \cdots \text{CH}=\text{CH}_2 \)
(g) \( \text{CH}_2=\text{CH} \cdots \text{C} \cdots \text{CH}_2 \) + \( \text{H}_2 \) \( \text{Ni}_2\text{B [P2]} \rightarrow \text{CH}_2=\text{CH} \cdots \text{CH}=\text{CH}_2 \)

13.17 \( \text{CH}_2=\text{C} \cdots \text{C} \cdots \text{CH}=\text{CH}_2 \)
13.18 (a) Cl–CH=CH=CH₂ + Cl–CH₂–CH=CH₂–Cl

(b) CH₂=CH–CH=CH₂

(c) CH₂=CH–CH=CH₂

(d) CH₃–CH₂=CH–CH₃

(e) Cl–CH₂=CH–CH=CH₂ + Cl–CH₂–CH=CH₂–OH

(f) 4 CO₂ (Note: KMnO₄ oxidizes HO₂C–CO₂H to 2 CO₂)

(g) CH₃–CH=CH₂ + CH₃–CH=CH₂–OH

13.19 (a) CH=CH–CH₂–CH₃ + NBS

(b) CH₂=CH–CH=CH₂ + NBS

Note: In the second step, both allylic halides undergo elimination of HBr to yield 1,3-butadiene; therefore, separating the mixture produced in the first step is unnecessary. The BrCH₂CH=CHCH₃ undergoes a 1,4 elimination (the opposite of a 1,4 addition).

Here again both products undergo elimination of HBr to yield 1,3-pentadiene.
13.21 Various IR, $^1$H NMR, $^{13}$C NMR, and MS features could be used to differentiate the members of any of these pairs. IR absorptions can be used to indicate whether double or triple bonds are present in a given molecule, or whether a hydroxyl group or halogen is present. Chemical shifts in the proton and carbon NMR spectra indicated can also be used to indicate the hybridization state of carbon atoms. The number of signals in the proton or carbon NMR spectrum for a given compound can suggest whether there is symmetry to the structure or not. Splitting patterns in the proton spectra can give detailed information about the connectivity of atoms. Mass spectra will indicate molecular weight differences when the molecular ions are present. Fragmentation patterns can indicate specific aspects of molecular structure characteristic to one member of a pair or another. UV would distinguish members of a pair where one is conjugated and the other is not. Consult tables with representative spectral information to predict specific aspects of the spectra for each compound.

13.22 (a) Because a highly resonance-stabilized radical is formed:

\[ \text{CH}_2=\text{CH}-\text{CH}-\text{CH}=\text{CH}_2 \quad \text{CH}_2=\text{CH}-\text{CH}-\text{CH}-\text{CH}_2 \quad \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_2 \]

(b) Because the carbanion is more stable:

\[ \text{CH}_2=\text{CH}-\text{CH}-\text{CH}=\text{CH}_2 \quad \text{CH}_2=\text{CH}-\text{CH}-\text{CH}=\text{CH}_2 \quad \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \]

That is, we can write more resonance structures of nearly equal energies.

13.23

\[ \text{CH}_3 \quad \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \quad \text{HCl} \rightarrow \left[ \begin{array}{c} \text{CH}_3 \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \text{CH}_2=\text{C}=\text{CH}_2 \end{array} \right] \]

\[ \text{I} \]

\[ \text{II} \]

The resonance hybrid, I, has the positive charge, in part, on the tertiary carbon atom; in II, the positive charge is on primary and secondary carbon atoms only. Therefore, hybrid I is more stable and will be the intermediate carbocation. A 1,4 addition to I gives

\[ \text{CH}_3 \quad \text{CH}_2=\text{C}=\text{CH}-\text{CH}_2=\text{Cl} \]

The endo adduct is less stable than the exo, but is produced at a faster rate at 25°C. At 90°C the Diels-Alder reaction becomes reversible; an equilibrium is established, and the more stable exo adduct predominates.
13.29 Conjugated unsaturated systems

13.30 (a) Norbornadiene

(b) Norbornadiene

13.31 Chlordan

Note: The other double bond is less reactive because of the presence of the two chlorine substituents.

13.32 Conjugated unsaturated systems

13.33 Protonation of the alcohol and loss of water lead to an allylic cation that can react with a chloride ion at either Cl1 or Cl3.

\[
\text{CH}_2\text{CH}=\text{CHCH}_2\text{OH} \xrightarrow{\text{H}^+} \text{CH}_2\text{CH}=\text{CHCH}_2\text{O}^+\xrightarrow{\text{H}_2\text{O}} \text{CH}_2\text{CH}=\text{CHCH}_2\text{Cl} + \text{CH}_2\text{CHCH}=\text{CH}_2
\]

13.34 (1) \(\text{CH}_2\text{CH}==\text{CHCH}_2 + \text{Cl}_2 \rightarrow \text{ClCH}_2\text{CH}==\text{CHCH}_2\)

(2) \(\text{ClCH}_2\text{CH}==\text{CHCH}_2 + \text{Cl}_2 \rightarrow \text{ClCH}_2\text{CH}==\text{CHCH}_2\text{Cl} + \text{ClCH}_2\text{CHCH}=\text{CH}_2\text{Cl}
\]

13.35 A six-membered ring cannot accommodate a triple bond because of the strain that would be introduced.

13.36 Too highly strained
13.36 The products are CH₂CH₃CH₂CHCH=CH₂ and CH₂CH₂CH =CHCH₂Br (cis and trans). They are formed from an allylic radical in the following way:

\[ \text{Br}_2 \rightarrow 2 \text{Br}^- \quad \text{(from NBS)} \]
\[ \text{Br}^- + \text{CH}_2\text{CH}_2\text{CHCH} = \text{CH}_2 \rightarrow \text{CH}_2\text{CH}_2\text{CHCH} = \text{CH}_2 + \text{HBr} \]
\[ \delta^+ \delta^- \quad \text{CH}_2\text{CH}_2\text{CH} = \text{CH} \rightarrow \text{CH}_2\text{CH}_2\text{CHCH} = \text{CH}_2 + \text{Br}^- \]
\[ + \text{CH}_2\text{CH}_2\text{CH} = \text{CHCH}_2\text{Br} \quad \text{(cis and trans)} \]

13.37 (a) The same carbocation (a resonance hybrid) is produced in the dissociation step:

(b) Structure I contributes more than II to the resonance hybrid of the carbocation (rule 8). Therefore, the hybrid carbocation has a larger partial positive charge on the tertiary carbon atom than on the primary carbon atom. Reaction of the carbocation with water will therefore occur more frequently at the tertiary carbon atom.

13.38 (a) Propyne. (b) Base (\(\text{I}^-\)) removes a proton, leaving the anion whose resonance structures are shown:

\[ \text{CH}_2\text{C} = \text{CH}_2 + \cdot \text{I} \quad \text{\xrightarrow{\text{H}^+}} \quad \text{H}^+ \text{I} \quad \text{H} \text{I} \]

13.39 The first crystalline solid is the Diels-Alder adduct below, mp 125°C.

On melting, this adduct undergoes a reverse Diels-Alder reaction, yielding furan (which vaporizes) and maleic anhydride, mp 50°C.

13.40 (a) \(\text{b} + \text{enantiomer} \quad \text{(b) } \text{c} + \text{enantiomer} \quad \text{(c) } \text{d} + \text{enantiomer} \quad \text{(d) } \text{e} + \text{enantiomer} \)

13.41 The product formed when butyl bromide undergoes elimination is 1-buten, a simple monosubstituted alkene. When 4-bromo-1-butene undergoes elimination, the product is 1,3-butadiene, a conjugated diene, and therefore, a more stable product. The transition states leading to the products reflect the relative stabilities of the products. Since the transition state leading to 1,3-butadiene has the lower free energy of activation of the two, the elimination reaction of 4-bromo-1-butene will occur more rapidly.
13.42 The diene portion of the molecule is locked into an s-trans conformation. It cannot, therefore, achieve the s-cis conformation necessary for a Diels-Alder reaction.

13.43 CH$_3$OCH =CHCH=CHCH$_3$

*13.44 Ph

13.45 (a) Br

*13.45 (b) Br

(c) See above

QUIZ

13.1 Give the 1,4-addition product of the following reaction:
CH$_2$CH=CHCH=CHCH$_3$ + HCl

(a) CH$_3$CH=CHCH=CHCH$_3$
(b) CH$_2$CH$\text{CH}$CH=CHCH$_3$
(c) CH$_3$CH=CHCH=CHCH$_3$
(d) CH$_2$CH$\text{CH}$CH=CHCH$_3$
(e) CH$_2$CH=CHCH=CHCH$_3$

13.2 Which diene and dienophile could be used to synthesize the following compound?

(a) [\text{H}] + [\text{H}CN]H  (b) [\text{H}] + [\text{H}CN]H  (c) [\text{H}] + [\text{H}CN]H  (d) [\text{H}] + [\text{H}CN]H  (e) [\text{H}] + [\text{H}CN]H

13.3 Which reagent(s) could be used to carry out the following reaction?

\[
\begin{array}{c}
\text{NK} \\
\text{Br}
\end{array}
\]

(a) NBS/CCl$_4$  (b) NBS/CCl$_4$, then Br$_2$/hv  
(c) Br$_2$/hv, then (CH$_3$)$_2$CO/(CH$_3$)$_2$COH, then NBS/CCl$_4$  
(d) (CH$_3$)$_2$CO/(CH$_3$)$_2$COH, then NBS/CCl$_4$

13.4 Which of the following structures does not contribute to the hybrid for the carbocation formed when 4-chloro-2-pentene ionizes in an S$_{N}$1 reaction?

(a) CH$_2$CH=CHCH=CHCH$_3$  (b) CH$_2$CH=CHCH=CHCH$_3$  (c) CH$_2$CH=CHCH=CHCH$_3$  (d) All of these contribute to the resonance hybrid.

13.5 Which of the following resonance structures accounts at least in part for the lack of S$_{N}$2 reactivity of vinyl chloride?

(a) CH$_2$=CH-Cl  (b) \text{CH$_3$}=-C=CH$_2$  (c) Neither  (d) Both
### SUMMARY OF REACTIONS BY TYPE

#### CHAPTERS 1–13

#### I. SUBSTITUTION REACTIONS

<table>
<thead>
<tr>
<th>Type</th>
<th>Stereochemical Result</th>
<th>Favoring Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 6</td>
<td>inversion</td>
<td>1°, 2°, benzylic (1° or 2°), or allylic (1° or 2°) leaving group (e.g., halide, tosylate, mesylate); strong nucleophile; polar aprotic solvent</td>
</tr>
<tr>
<td>Section 6</td>
<td>racemization</td>
<td>3°, benzylic (e.g., halide, tosylate, mesylate); or allylic leaving group</td>
</tr>
</tbody>
</table>

#### II. ELIMINATION REACTIONS

<table>
<thead>
<tr>
<th>Type</th>
<th>Stereochemical/Regiochemical Result</th>
<th>Favoring Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 6</td>
<td>elimination to form the most substituted alkene (Zaitsev elimination) with small bases</td>
<td>strong base (e.g., NaOMe/EtOH, KOH/EtOH, tert-BuOK/tert-BuOH); formation of the less substituted alkene with use of a bulky base (e.g., tert-BuOK/tert-BuOH); heat</td>
</tr>
<tr>
<td>Section 7.6</td>
<td>formation of most substituted alkene; may occur with carbocation rearrangement</td>
<td>weak base; heat</td>
</tr>
<tr>
<td>Section 7.7</td>
<td>formation of most substituted alkene; may occur with carbocation rearrangement</td>
<td>catalytic acid (H+, e.g., covaH2SO4, H3PO4); heat</td>
</tr>
</tbody>
</table>

#### III. MECHANISTIC SUMMARY OF ALKENE AND ALKyne ADDITION REACTIONS

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Stereochemical Result</th>
<th>Regiochemical Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkenes</td>
<td>syn</td>
<td>anti</td>
</tr>
<tr>
<td>H2, Pt, Pd or Ni</td>
<td>* X2/CCL4</td>
<td>* H2O, H+ (hydration)</td>
</tr>
<tr>
<td>RCO2H (e.g., MMPP)</td>
<td>(i) RCO2H, (ii) H2O* or OH*</td>
<td>* addition of other alkenes</td>
</tr>
<tr>
<td>H2O2 OH*</td>
<td>(Section 11.17)</td>
<td>(Section 10.7)</td>
</tr>
<tr>
<td>* (i) THF:BH3 (ii) H2O2 OH*</td>
<td>* X2/ROH</td>
<td>* addition of other alkenes</td>
</tr>
</tbody>
</table>

*Shares mechanistic themes with other reactions denoted by the same symbol.*
IV. ALKENE AND ALKYN E CLEAVAGE WITH OXIDATION

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Reactant</th>
<th>Product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) KMnO_4/OH^-; heat; (ii) H_2O^+</td>
<td>tetrasubstituted alkene</td>
<td>two ketones</td>
</tr>
<tr>
<td>(Section 8.11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) O_3, (ii) Zn, HOAc</td>
<td>trisubstituted alkene</td>
<td>one ketone, one carboxylic acid</td>
</tr>
<tr>
<td>(Section 8.11A)</td>
<td></td>
<td>one carboxylic acid and CO_2</td>
</tr>
<tr>
<td>Alkenes</td>
<td>monosubstituted alkene</td>
<td>one ketone, one aldehyde</td>
</tr>
<tr>
<td>Alkynes</td>
<td></td>
<td>one aldehyde and formaldehyde</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Reactant</th>
<th>Product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) KMnO_4/OH^-; heat; (ii) H_2O^+</td>
<td>terminal alkylne</td>
<td>a carboxylic acid and formic acid</td>
</tr>
<tr>
<td>(Section 8.14)</td>
<td>internal alkylne</td>
<td>two carboxylic acids</td>
</tr>
<tr>
<td>(i) O_3, (ii) Zn, HOAc</td>
<td>terminal alkylne</td>
<td>a carboxylic acid and formic acid</td>
</tr>
<tr>
<td>(Section 8.14)</td>
<td>internal alkylne</td>
<td>two carboxylic acids</td>
</tr>
</tbody>
</table>

V. CARBON—CARBON BOND-FORMING REACTIONS

(a) Alkylation of alkynide anions (with 1° alkyl halides, epoxides, and aldehydes or ketones) (Sections 4.18C, 4.20B, 7.12 and 12.8D)
(b) Grignard reaction (with aldehydes and ketones, or epoxides) (Sections 12.7B, C, and 12.8)
(c) Reactions of lithium dialkylcuprates (Corey-House, Posner-Whitesides reaction) (Section 12.9)
(d) Carbocation addition to alkenes (e.g., polymerization) (Special Topic A)
(e) Diels-Alder reaction (Section 13.11)
(f) Addition of a carbene to an alkene (Section 8.9)

VI. REDUCTIONS/OXIDATIONS (NOT INCLUDING ALKENES/ALKYNES)

(a) 2 R—X (w/Zn/H^+) → 2 R—H + ZnX_2 (Section 4.18B)
(b) Lithium aluminium hydride (LiAlH_3) and sodium borohydride (NaBH_4) reduction of carbonyl compounds (Section 12.3)
(c) Oxidation of alcohols with chromic acid, pyridinium chlorochromate (PCC), or hot potassium permanganate (Section 12.4)

VII. MISCELLANEOUS

(a) R—CO—R + PCl_3 → R—CICO—R → alkynes (Section 7.10)
(b) R—COOH + SOCl_2 or PCl_3 → R—COCl → acyl chlorides for Friedel-Crafts reactions, esters, amides, etc. (Sections 15.7 and 18.5)
(c) Terminal alkynes + NaNH_2 in NH_3 → alkynide anions (Sections 4.18C, 12.8D)
(d) R—OH + TsCl or MsCl (with pyridine) → R—OTs or R—OMs (Section 11.10)
(e) R—OH + Na (or NaNH_2) → R—O^+Na^+ + H_2 (or NH_3) (Sections 6.16B, 11.15B)

VIII. CHEMICAL TESTS

(a) Alkenes/Alkynes: Br_2/CCl_4 (Section 8.6)
(b) Rings/Unsaturation/etc.: Index of Hydrogen Deficiency (Section 7.16)
(c) Position of Unsaturation: KMnO_4 (Section 8.11); O_3 (Section 8.11A)
REACTIONS OF AROMATIC COMPOUNDS

SOLUTIONS TO PROBLEMS

15.1

15.2 The rate is dependent on the concentration of NO₂⁺ ion formed from protonated nitric acid.

\[
\text{H-O-NO}_2 + \text{HA} \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}^+ + \text{A}^- \\
\text{(where HA = HNO}_3 \text{ or HOSO}_2\text{H)}
\]

Because H₂SO₃ (HOSO₂H) is a stronger acid, a mixture of it and HNO₃ will contain a higher concentration of protonated nitric acid than will nitric acid alone.

That is, the reaction,

\[
\text{H-O-NO}_2 + \text{HOSO}_2\text{H} \rightarrow \text{H-O-NO}_2 + \text{HSO}_4^-
\]

produces more protonated nitric acid than the reaction,

\[
\text{H-O-NO}_2 + \text{H-O-NO}_2 \rightarrow \text{H-O-NO}_2 + \text{NO}_3^-
\]

15.3

Step 1

\[
\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{F} \leftrightarrow \text{CH}_2\text{CHCH}_3 + \text{F}^-
\]

Step 2

\[
\text{CH}_3 + \text{H}_2\text{C}=\text{CH}_3 \leftrightarrow \text{CH}_3\text{CCH}_3
\]

Step 3

\[
\text{CH}_3\text{CHH}_3 + \text{F}^- \rightarrow \text{CH}_3\text{CCH}_3 + \text{HF}
\]

15.4

\[
\text{CH}_3\text{C}=\text{O}-\text{CCH}_3 + \text{AlCl}_3 \rightarrow \text{CH}_3\text{C}=\text{O}\text{AlCl}_3
\]

\[
\text{CH}_3\text{C}=\text{O} + \text{CH}_3\text{C}-\text{AlCl}_3
\]

15.5 The carbocation formed by the action of AlCl₃ on neopentyl chloride is primary. This carbocation rearranges to the more stable tertiary carbocation before it can react with the benzene ring:

\[
\text{CH}_3\text{C}=\text{CHCH}_2\text{CH}_3 + \text{AlCl}_3 \rightarrow \text{AlCl}_4^- + \text{CH}_3\text{C}=\text{CHCH}_2\text{+} \rightarrow \text{CH}_3\text{C}=\text{CHCH}_2\text{CH}_3
\]

15.6 CH₃CH₂CH₂OH + BF₃ \leftrightarrow CH₃CH₂CH₂⁺ + HOBF₃

The propyl cation can rearrange into an isopropyl cation:

\[
\text{CH}_3\text{CHCH}_3^+ + \text{hydride shift} \rightarrow \text{CH}_3^\text{CHCH}_3
\]
Both carbocations can then attack the ring.

15.7 (a) \[ \text{CH}_2\text{CH}_2\text{CH}_2\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl} \]  
Zn(Hg) \[ \text{HCl} \text{ reflux} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

15.8 If the methyl group had no directive effect on the incoming electrophile, we would expect to obtain the products in purely statistical amounts. Since there are two ortho hydrogen atoms, two meta hydrogen atoms, and one para hydrogen, we would expect to get 40% ortho (2/5), 40% meta (2/5), and 20% para (1/5). Thus, we would expect that only 60% of the mixture of mononitrotoluenes would have the nitro group in the ortho or para position. And we would expect to obtain 40% of \( m \)-nitrotoluene. In actuality, we get 96% of combined \( o \) and \( p \)-nitrotoluene and only 4% \( m \)-nitrotoluene. This shows the ortho-para directive effect of the methyl group.

15.9 (a) \[ \text{CH}_3 \rightarrow \text{SO}_3 \text{H} \]  
(b) \[ \text{CH}_3 \rightarrow \text{HNO}_3 \text{H}_2\text{SO}_4 \]  
(c) \[ \text{CH}_3 \rightarrow \text{Br} \text{FeBr}_3 \]  
(d) \[ \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{COC}_\text{OH} + \]
15.10 As the following structures show, attack at the ortho and para positions of phenol leads to arenium ions that are more stable (than the one resulting from meta attack) because they are hybrids of four resonance structures, one of which is relatively stable. Only three resonance structures are possible for the meta arenium ion, and none is relatively stable.

**Ortho attack**

\[
\begin{align*}
\text{Br}^+ + \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{C}_6\text{H}_4\text{BrOH}^- \\
\text{C}_6\text{H}_4\text{BrOH}^- & \leftrightarrow \text{C}_6\text{H}_5\text{Br}^- + \text{H}^+ \\
\end{align*}
\]

Relatively stable

**Meta attack**

\[
\begin{align*}
\text{Br}^+ + \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{C}_6\text{H}_4\text{BrOH}^- \\
\text{C}_6\text{H}_4\text{BrOH}^- & \leftrightarrow \text{C}_6\text{H}_5\text{Br}^- + \text{H}^+ \\
\end{align*}
\]

Relatively stable

**Para attack**

\[
\begin{align*}
\text{Br}^+ + \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{C}_6\text{H}_4\text{BrOH}^- \\
\text{C}_6\text{H}_4\text{BrOH}^- & \leftrightarrow \text{C}_6\text{H}_5\text{Br}^- + \text{H}^+ \\
\end{align*}
\]

Relatively stable

15.11 (a) The atom (an oxygen atom) attached to the benzene ring has an unshared electron pair that it can donate to the arenium ions formed from ortho and para attack, stabilizing them. (The arenium ions are analogous to the previous answer with a \(-\text{COCH}_3\) group replacing the \(-\text{H}\)).

(b) Structures such as the following compete with the benzene ring for the oxygen electrons, making them less available to the benzene ring.

\[
\begin{align*}
\text{O}^\text{CH}^- & \leftrightarrow \text{C}_6\text{H}_5\text{Br}^- + \text{H}^+ \\
\end{align*}
\]

This effect makes the benzene ring of phenyl acetate less electron rich and, therefore, less reactive.

(c) Because the acetamido group has an unshared electron pair on the nitrogen atom that it can donate to the benzene ring it is an ortho-para director.

(d) Structures such as the following compete with the benzene ring for the nitrogen electrons, making them less available to the benzene ring.

15.12 The electron-withdrawing inductive effect of the chlorine of chloroethene makes its double bond less electron rich than that of ethene. This causes the rate of reaction of chloroethene with an electrophile (i.e., a proton) to be slower than the corresponding reaction of ethene.

When chloroethene adds a proton, the orientation is governed by a resonance effect. In theory, two carbocations can form:

\[
\begin{align*}
\text{Cl}^-\text{CH}^-\text{CH}_2 + \text{H}^+ \rightarrow \text{Cl}^-\text{CH}^-\text{CH}_2^+ \\
I & \text{ (less stable)} \\
\text{Cl}^-\text{CH}^-\text{CH}_2^+ \rightarrow \text{Cl}^-\text{CH}^-\text{CH}_2 + \text{H}^+ \\
II & \text{ (more stable)} \\
\end{align*}
\]

Carbocation II is more stable than I because of the resonance contribution of the extra structure just shown in which the chlorine atom donates an electron pair (see Section 15.11D).
REACTIONS OF AROMATIC COMPOUNDS

15.13 Ortho attack

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{Br}^+ \\
\text{CH}_2\text{CH}_2 & \quad \text{Br} \\
\text{CH}_3\text{CH}_3 & \quad \text{Br} \\
\text{CH}_3\text{CH}_3 & \quad \text{Br} \\
\end{align*}
\]

Para attack

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{Br}^+ \\
\text{CH}_2\text{CH}_2 & \quad \text{Br} \\
\text{CH}_3\text{CH}_3 & \quad \text{Br} \\
\text{CH}_3\text{CH}_3 & \quad \text{Br} \\
\end{align*}
\]

Relatively stable

15.14 The phenyl group, as the following resonance structures show, can act as an electron-releasing group and can stabilize the areniun ions formed from ortho and para attack.

Ortho attack

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{NO}_2^+ \\
\text{CH}_2\text{CH}_2 & \quad \text{NO}_2 \\
\text{CH}_3\text{CH}_3 & \quad \text{NO}_2 \\
\text{CH}_3\text{CH}_3 & \quad \text{NO}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{NO}_2 \\
\text{H} & \quad \text{NO}_2 \\
\text{H} & \quad \text{NO}_2 \\
\text{H} & \quad \text{NO}_2 \\
\end{align*}
\]

Relatively stable

15.15

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{CH} & \quad \text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{CH}_3 & \quad \text{CH} & \quad \text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{CH}_3 & \quad \text{CH} & \quad \text{CH}_3\text{CH}_3 \\
\end{align*}
\]

leads to 1-chloro-1-phenylpropane

leads to 2-chloro-1-phenylpropane

leads to 1-chloro-3-phenylpropane

The major product is 1-chloro-1-phenylpropane because I is the most stable radical. It is a benzylic radical and therefore is stabilized by resonance.
The addition of hydrogen bromide to 1-phenylpropene in the presence of peroxides is a chain mechanism analogous to the one we discussed when we described anti-Markovnikov addition in Section 10.9. The step that determines the orientation of the reaction is the first chain-propagating step. Bromine attacks the second carbon atom of the chain because by doing so the reaction produces a more stable benzylic radical. Had the bromine atom attacked the double bond in the opposite way, a less stable secondary radical would have been formed.

\[
\text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \text{Br}^- \rightarrow \text{C}_6\text{H}_5\text{CH}-\text{CHCH}_3 \text{Br}^- \quad \text{A secondary radical}
\]

(b) Hydrogen bromide addition in the absence of peroxides.

\[
\text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \text{HBr} \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \text{Br}^- \quad \text{A benzylic cation}
\]

\[
\text{C}_6\text{H}_5\text{CHCH}_3 + \text{H}^- \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \text{Br}^-\quad \text{A secondary cation}
\]

The mechanism for the addition of hydrogen bromide to 1-phenylpropene in the presence of peroxides is a chain mechanism analogous to the one we discussed when we described anti-Markovnikov addition in Section 10.9. The step that determines the orientation of the reaction is the first chain-propagating step. Bromine attacks the second carbon atom of the chain because by doing so the reaction produces a more stable benzylic radical. Had the bromine atom attacked the double bond in the opposite way, a less stable secondary radical would have been formed.

(a) Hydrogen bromide addition in the presence of peroxides.

**Chain Initiation**

1. \( \text{R} + \cdot \text{O} - \text{O} - \text{R} \rightarrow 2 \cdot \text{R}^- \)
2. \( \cdot \text{R}^- + \cdot \text{H}^- \text{Br} \rightarrow \cdot \text{R}^- \cdot \text{H}^- + \text{Br}^- \)
3. \( \cdot \text{Br}^- + \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 \text{Br}^- \quad \text{A benzylic radical} \)

**Chain Propagation**

4. \( \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \cdot \text{Br}^- \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \text{Br}^- \quad 2\text{-Bromo-1-phenylpropane} \)

(b) Hydrogen bromide addition in the absence of peroxides.

\[
\text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \cdot \text{H}^- \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \cdot \text{Br}^- \quad \text{A benzylic cation}
\]

\[
\text{C}_6\text{H}_5\text{CHCH}_3 + \cdot \text{H}^- \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCH}_3 + \text{Br}^-\quad \text{A secondary cation}
\]

15.18 (a) \( \text{Cl} \text{C}_6\text{H}_5\text{CHCH}_3 \) because the more stable carbocation intermediate is the benzylic carbocation, \( \text{Cl} \text{C}_6\text{H}_5\text{CHCH}_3 \), which then reacts with a chloride ion.

(b) \( \text{OH} \text{C}_6\text{H}_5\text{CHCH}_3 \) because the more stable intermediate is a benzylic cation, which then reacts with \( \text{H}_2\text{O} \).
15.19 (a) The first method would fail because introducing the chlorine substituent first would introduce an ortho-para directing group. Consequently, the subsequent Friedel-Crafts reaction would not then take place at the desired meta position. The second method would fail for essentially the same reasons. Introducing the ethyl group first would introduce an ortho-para director, and subsequent ring chlorination would not then take place at the desired meta position.

(b) If we introduce an acetyl group first, which we later convert to an ethyl group, we install a meta director. This allows us to put the chlorine atom in the desired position. Conversion of the acetyl group to an ethyl group is then carried out using the Clemmensen reduction.

\[ \text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{COCl} \]

15.20 (a) In concentrated base and ethanol (a relatively nonpolar solvent), the \( S_N2 \) reaction is favored. Thus, the rate depends on the concentration of both the alkyl halide and NaOCH₂H₂. Since no carbocation is formed, the only product is CH₃CH=CHCH₂OCH₃CH₃

(b) When the concentration of C₂H₅O⁻ ion is small or zero, the reaction occurs through the \( S_N1 \) mechanism. The carbocation that is produced in the first step of the \( S_N1 \) mechanism is a resonance hybrid.

\[ \text{CH}_3\text{CH}=\text{CHCH}_3 \text{Cl} \rightarrow \left[ \text{CH}_3\text{CH}=\text{CHCH}_3 \right]^+ + \text{Cl}^- \]

This ion reacts with the nucleophile (C₂H₅O⁻ or C₂H₅OH) to produce two isomeric ethers

\[ \text{CH}_3\text{CH}=\text{CHCH}_2\text{OCH}_3 \text{CH}_3 \quad \text{and} \quad \text{CH}_3\text{CHCH}=\text{CH}_2 \]

15.21 (a) In concentrated base and ethanol (a relatively nonpolar solvent), the \( S_N2 \) reaction is favored. Thus, the rate depends on the concentration of both the alkyl halide and NaOCH₂H₂. Since no carbocation is formed, the only product is

\[ \text{CH}_3\text{CH}=\text{CHCH}_2\text{OCH}_3\text{CH}_3 \]

(b) When the concentration of C₂H₅O⁻ ion is small or zero, the reaction occurs through the \( S_N1 \) mechanism. The carbocation that is produced in the first step of the \( S_N1 \) mechanism is a resonance hybrid.

\[ \text{CH}_3\text{CH}=\text{CHCH}_3 \text{Cl} \rightarrow \left[ \text{CH}_3\text{CH}=\text{CHCH}_3 \right]^+ + \text{Cl}^- \]

This ion reacts with the nucleophile (C₂H₅O⁻ or C₂H₅OH) to produce two isomeric ethers

\[ \text{CH}_3\text{CH}=\text{CHCH}_2\text{OCH}_3\text{CH}_3 \quad \text{and} \quad \text{CH}_3\text{CHCH}=\text{CH}_2 \]

15.22 (a) The carbocation that is produced in the \( S_N1 \) reaction is exceptionally stable because one resonance contributor is not only allylic but also tertiary.

\[ \text{CH}_3\text{Cl} \xrightarrow{\text{S}_N1} \left[ \text{CH}_3\text{C}=\text{CHCH}_3 \right] \xrightarrow{\text{CH}_3\text{H}} \left[ \text{CH}_3\text{C}=\text{CHCH}_3 \right] \]

(b) \( \text{CH}_3\text{C}=\text{CHCH}_3 \text{OH} + \text{CH}_3\text{C}=\text{CHCH}_3 \text{OH} \)

15.23 Compounds that undergo reactions by an \( S_N1 \) path must be capable of forming relatively stable carbocations. Primary halides of the type ROCH₂X form carbocations that are stabilized by resonance:

\[ \text{R}+\text{O}^-=\text{CH}_2 \quad \leftrightarrow \quad \text{R}-\text{O}^-=\text{CH}_2 \]

15.24 The relative rates are in the order of the relative stabilities of the carbocations:

\[ \text{C}_2\text{H}_5\text{CH}_3 < \text{C}_2\text{H}_5\text{CHCH}_3 < \text{(C}_2\text{H}_5)_2\text{CH} < \text{(C}_2\text{H}_5)_3\text{CH} \]

The solvolysis reaction involves a carbocation intermediate.

15.25

15.26 (a)
REATIONS OF AROMATIC COMPOUNDS

15.27 (a) \( \text{benzene} + \text{NH}_2\text{COCH}_3 \rightarrow \text{NHCOCH}_3 \) (mainly)
(b) \( \text{benzene} + \text{NO}_2 \)
(c) \( \text{NO}_2 \)
(d) \( \text{ClOO} \)
(e) \( \text{OH} \)
(f) \( \text{H} \)

15.28 (a) \( \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_3 \)
(b) \( \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_3 \)
(c) \( \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_2\text{CH}_3 \)
(d) \( \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_2\text{CH}_3 \), Br

15.29 (a) \( \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_3 + \text{CH}_3\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_3 \)
(b) \( \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_3 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CHCH}_2\text{CH}_3 \)
(c) \( \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_3 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CHCH}_2\text{CH}_3 \)

(Note: The use of Cl-CH\(_2\)CH\(_2\)CH\(_3\) in a Friedel-Crafts synthesis gives mainly the rearranged product, isopropylbenzene.)
REACTIONS OF AROMATIC COMPOUNDS

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(f) \[ \text{C}_6\text{H}_5 + \text{Cl}_2 \rightarrow \text{Cl}_2\text{C}_6\text{H}_5 \]

(g) \[ \text{C}_6\text{H}_5 + \text{HNO}_3 \rightarrow \text{HNO}_2\text{C}_6\text{H}_5 \quad (\text{syn addition}) \]

(h) \[ \text{C}_6\text{H}_5 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{Br} \]

(i) \[ \text{C}_6\text{H}_5 + \text{Br}_2 \rightarrow \text{Br} \text{C}_6\text{H}_5 \quad (\text{ortho}) \]

(k) \[ \text{C}_6\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} \quad (\text{separate}) \]

H_2O/H_2SO_4, heat
REATIONS OF AROMATIC COMPOUNDS

(h) \[ \text{CH} = \text{CH}_2 \] 
(1) THF, HBr 
(2) CH\(_2\)CO\(_2\)D
\[ \text{CH}_2\text{CH}_2\text{D} \]

(i) \[ \text{CH} = \text{CH}_2 \] 
HBr, peroxides
\[ \text{CH}_2\text{CH}_3\text{Br} \]

(j) \[ \text{CH}_2\text{CH}_2\text{Br} \] 
NaI
\[ \text{CH}_2\text{CH}_2\text{I} \]

(k) \[ \text{CH}_2\text{CH}_2\text{Br} \] 
CN\(^-\)
\[ \text{CH}_2\text{CH}_2\text{CN} \]

(l) \[ \text{CH} = \text{CH}_2 \] 
Pd, N\(_2\)
\[ \text{CHDCH}_2\text{D} \]

(m) \[ + \] 
heat
\[ \text{CH}_3\text{CH}_3 \]

(n) \[ \text{CH}_3\text{CH}_2\text{OH} \] 
NaH
\[ \text{CH}_2\text{CH}_2\text{ONa} \]
\[ \text{CH}_2\text{CH}_2\text{OCH}_3 \]

15.31 (a) \[ \text{CH}_3 \] 
KMnO\(_4\), H\(_2\)SO\(_4\) 
heat
\[ \text{CO}_2\text{H} \]

(b) \[ \text{CH}_3 \] 
Cl, FeCl\(_3\)
\[ \text{COCH}_3 \]

(c) \[ \text{CH}_3 \] 
HNO\(_3\), H\(_2\)SO\(_4\) 
\[ \text{CH}_3 \text{Br} \text{NO}_2 \]

(d) \[ \text{CH}_3 \] 
Br, FeBr\(_3\)
\[ \text{CO}_2\text{H} \]

(e) \[ \text{Cl}_2 \] 
(excess) light
\[ \text{CH}_3 \text{Cl} \]

(f) \[ \text{CH}_3 \] 
Cl, CH\(_2\)CH\(_3\) 
AlCl\(_3\)
\[ \text{CH}_3\text{CHCH}_3 \]

(g) \[ \text{Cl} \text{CHCH}_3 \] 
AlCl\(_3\)
\[ \text{CH}_3\text{CHCH}_3 \]

(h) \[ \text{CH}_3 \] 
HNO\(_3\) (excess) 
H\(_2\)SO\(_4\)
\[ \text{CH}_3\text{NO}_3 \]
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(i) \[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{SO}_3, \text{H}_2\text{SO}_4, \text{heat}} (\text{separate}) \\
\text{CH}_3 & \xrightarrow{(1) \text{Kmno}_4, \text{OH}^-, \text{heat}} \xrightarrow{(2) \text{H}_2\text{O}^+} \\
\text{COOH} & \\
\text{NO}_2 & \xrightarrow{(1) \text{HNO}_2, \text{H}_2\text{SO}_4, \text{heat}} \xrightarrow{(2) \text{H}_2\text{O}^+} \\
\text{Cl} & \\
\end{align*}
\]

(ii) \[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{Cl}_2, \text{FeCl}_3, \text{heat}} \xrightarrow{(1) \text{H}^+} \xrightarrow{(2) \text{OH}^-} \\
\end{align*}
\]

(iii) \[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{Cl}^-, \text{CCH}_2\text{CH}_2\text{CH}_3} \xrightarrow{\text{AlCl}_3} \xrightarrow{\text{Zn(Hg)}}, \text{HCl} \\
\text{C} & \xrightarrow{\text{O}} \text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

(i) \[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{SO}_3, \text{H}_2\text{SO}_4, \text{heat}} (\text{minor product}) \\
\text{CH}_3 & \xrightarrow{(1) \text{H}_2\text{O}/\text{H}_2\text{SO}_4, \text{heat}} \xrightarrow{(2) \text{OH}^-} \\
\end{align*}
\]

15.32 (a) Step (2) will fail because a Friedel-Crafts reaction will not take place on a ring that bears an -NO₂ group (or any meta director).

(b) The last step will first brominate the double bond.

15.33 (a) Step (2) will fail because a Friedel-Crafts reaction will not take place on a ring that bears an -NO₂ group (or any meta director).
### REACTIONS OF AROMATIC COMPOUNDS

**15.32** (a) 


**15.33** (a) Step (2) will fail because a Friedel-Crafts reaction will not take place on a ring that bears an -NO₂ group (or any meta director).

(b) The last step will first brominate the double bond.
15.34 (a) Electrophilic aromatic substitution will take place as follows:

(b) The ring directly attached to the oxygen atom is activated toward electrophilic attack because the oxygen atom can donate an unshared electron pair to it and stabilize the intermediate arenium ion when attack occurs at the ortho or para position.

15.35 (a) 

(b) 

(c) 

15.36 

15.37 This problem serves as another illustration of the use of a sulfonic acid group as a blocking group in a synthetic sequence. Here we are able to bring about nitration between two meta substituents.

15.38 

15.39 (a) (1) 

(b) 1,2 Addition.

(c) Yes. The carbocation given is a hybrid of secondary allylic and benzylic contributors and is therefore more stable than any other possibility; for example,
(d) Since the reaction produces only the more stable isomer—that is, the one in which the double bond is conjugated with the benzene ring—the reaction is likely to be under equilibrium control:

\[
\begin{align*}
\text{More stable isomer} & \quad \text{Not formed} \\
\end{align*}
\]

15.40

\[
\begin{align*}
\text{Toluene} + \text{succinic anhydride} & \rightarrow \text{Zn(Hg)} \\
(C_8H_8O_2) + \text{HCl} & \rightarrow \text{A} \\
(C_8H_8O_2) + \text{AlCl}_3 & \rightarrow \text{B} \\
& \rightarrow \text{C} \\
& \rightarrow \text{D} \\
& \rightarrow \text{E} \\
& \rightarrow \text{F} \\
& \rightarrow \text{G} \\
& \rightarrow \text{H} \\
\end{align*}
\]

15.41

\[
\begin{align*}
\text{CH}_3 + \text{HNO}_3 & \rightarrow \text{CH}_3 \text{NO}_2 \\
\text{CH}_3 \text{NO}_2 & \rightarrow \text{CH}_2 \text{OH} \\
\text{CH}_2 \text{OH} & \rightarrow \text{H}_2 \text{O} \\
\end{align*}
\]

15.42 (a) \[\text{HA} \rightarrow \text{B} \rightarrow \text{H} \]

(b) \[\text{HA} \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{H} \]

15.43 (a) \[\text{Zn(Hg)} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{E} \rightarrow \text{F} \rightarrow \text{G} \rightarrow \text{H} \]

(b) \[\text{NaBH}_4 \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{E} \rightarrow \text{F} \rightarrow \text{G} \rightarrow \text{H} \]
15.44 (a) Large ortho substituents prevent the two rings from becoming coplanar and prevent rotation about the single bond that connects them. If the correct substitution patterns are present, the molecule as a whole will be chiral. Thus, enantiomeric forms are possible even though the molecules do not have a stereocenter. The compound with 2-NO₂, 6-CO₂H, 2'-NO₂, 6'-CO₂H is an example.

These molecules are nonsuperposable mirror images and, thus, are enantiomers.

(b) Yes

(c) This molecule has a plane of symmetry.

The plane of the page is a plane of symmetry.

15.45 (a) A B C

15.46

15.47 (a and b) The tert-butyl group is easily introduced by any of the variations of the Friedel-Crafts alkylation reaction, and, because of the stability of the tert-butyl cation, it is easily removed under acidic conditions.

(c) In contrast to the -SO₂H group often used as a blocking group, -CH₃ activates the ring to further electrophilic substitution.

15.48 At the lower temperature, the reaction is kinetically controlled, and the usual ofp directive effects of the -CH₃ group are observed. At higher temperatures, the reaction is thermodynamically controlled. At reaction times long enough for equilibrium to be reached, the most stable isomer, m-toluenesulfonic acid, is the principal product.

15.49 The evidence indicates that the mechanistic step in which the C-H bond is broken is not rate determining. (In the case cited, it makes no difference kinetically if a C-H or C-D bond is broken in electrophilic aromatic substitution.) This evidence is consistent with the two-step mechanism given in Section 15.2. The step in which the aromatic compound reacts with the electrophile (NO₂⁺) is the slow rate-determining step. Proton (or deuteron) loss from the arenium ion to return to an aromatic system is a rapid step and has no effect on the overall rate.
15.50 (a) \( \text{C}_6\text{H}_5\text{CH}_3\text{Br} \xrightarrow{\text{NaCN}} \text{DMF} \xrightarrow{(-\text{NaBr})} \text{C}_6\text{H}_5\text{CH}_2\text{CN} \)

(b) \( \text{C}_6\text{H}_5\text{CH}_3\text{Br} \xrightarrow{\text{CH}_3\text{OH}} \text{CH}_3\text{OH} \xrightarrow{\text{CH}_3\text{OH}} \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_3 \)

(c) \( \text{C}_6\text{H}_5\text{CH}_3\text{Br} \xrightarrow{\text{CH}_2\text{CO}_2\text{Na}} \text{CH}_2\text{CO}_2\text{Na} \xrightarrow{\text{CH}_2\text{CO}_2\text{Na}} \text{C}_6\text{H}_5\text{CH}_2\text{OCOCH}_3 \)

(d) \( \text{C}_6\text{H}_5\text{CH}_3\text{Br} \xrightarrow{\text{NaI}} \text{NaI} \xrightarrow{\text{acetone}} \text{C}_6\text{H}_5\text{CH}_2\text{I} \)

(e) \( \text{CH}_2=\text{CHCH}_3\text{Br} \xrightarrow{\text{NaOH} \xrightarrow{\text{acetone}} \text{NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{N}_3 \)

(f) \( \text{CH}_2=\text{CHCH}_3\text{Br} \xrightarrow{\text{NaOH} \xrightarrow{\text{acetone}} \text{NaOH}} \text{CH}_2=\text{CHCH}_2\text{CH} \)

15.51 \( A = \) [Chemical structure]

\( \xrightarrow{+\text{BrOH}} \)

\[ \begin{align*}
A & = \text{BrCH}_2\text{CH}_3 \\
B & = \text{BrCH} = \text{CHCH}_3 \\
C & = \text{CH}_3 \\
\end{align*} \]

15.52 \( (\text{C}_6\text{H}_5)_3\text{C} \xrightarrow{+\text{H}_{2}} (\text{C}_6\text{H}_5)_3\text{C} \xrightarrow{+\text{H}_2\text{O}} (\text{C}_6\text{H}_5)_3\text{C}^\text{*} \xrightarrow{+\text{EtOH}} \text{C}_6\text{H}_5\text{C} \)

Very stable carbocation

15.53 (a) \( \text{CH}_3\text{CH} = \text{CHCH}_3\text{Br} \) would be the most reactive in an \( S_2\text{2} \) reaction because it is a 1° allylic halide. There would, therefore, be less steric hindrance to the attacking nucleophile.

(b) \( \text{CH}_3\text{CH} = \text{CHCH}_3\text{Br} \) would be the most reactive in an \( S_2\text{1} \) reaction because it is a 3° allylic halide. The carbocation formed in the rate-determining step, being both 3° and allylic, would be the most stable.

15.54 The final product is \( p\)-nitroaniline. (The reactions are \( \text{Section 15.14} \).) The presence of six signals in the \( ^{13}\text{C} \) NMR spectrum confirms that the substitution in the final product is \( ortho \) and not \( para \). A final product with \( para \) substitution (i.e., \( p\)-nitroaniline) would have given only four signals in the \( ^{13}\text{C} \) NMR spectrum.

15.55 \( \text{CH}_2\text{OHCOHCH}_2\text{OH} \) (Glycerol) After sodium borohydride reduction of the aldehyde, ozonolysis oxidatively degrades the aromatic ring, leaving only the polyhydroxy side chain. Water is an alternative to HOAc used to work up ozonolysis reactions.
15.4 Complete the following syntheses.

(a) \[
\begin{align*}
&\text{CH}_3 \quad \text{A} \quad \text{CH}_3 \\
&\text{HNO}_3 \quad \text{H}_2\text{SO}_4
\end{align*}
\]

(b) \[
\begin{align*}
&\text{CH}_3 \quad \text{C} \quad \text{CH}_3 \\
&\text{HNO}_3 \quad \text{H}_2\text{SO}_4
\end{align*}
\]

Solutions to Problems

16.1 (a) \[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
&\text{CH}_3\text{CH}_2\text{CHCH}_3 \\
&\text{CH}_3\text{CH}=\text{CH}_2
\end{align*}
\]

(b) \[
\begin{align*}
&\text{CH}_3\text{CH}=\text{CH}_2 \quad \text{C} \quad \text{CH}_3 \\
&\text{HNO}_3 \quad \text{H}_2\text{SO}_4
\end{align*}
\]

3-Methyl-2-butanone

2-Methylbutanal

3-Methylbutanal
16.2 (a) 1-Pentanol, because its molecules form hydrogen bonds to each other.
(b) 2-Pentanol, because its molecules form hydrogen bonds to each other.
(c) Pentanal, because its molecules are more polar.
(d) 2-Phenylethanol, because its molecules form hydrogen bonds to each other.
(e) Benzyl alcohol because its molecules form hydrogen bonds to each other.

16.3 (a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{CH}_3\text{CH}_2\text{CH}_3 \)
(b) \( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{LiAlH}(\text{OC}(\text{CH}_3)_3)_2, \text{diethyl ether}} \text{CH}_3\text{CH}_2\text{CH}_3 \)

16.4 (a) An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.
(b) An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.
(c) An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.
(d) An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.
(e) An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.
(f) An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.
(g) An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.

16.5 (a) The nucleophile is the negatively charged carbon of the Grignard reagent acting as a carbamion.
(b) The magnesium portion of the Grignard reagent acts as a Lewis acid and accepts an electron pair of the carbonyl oxygen. This acid-base interaction makes the carbonyl carbon even more positive and, therefore, even more susceptible to nucleophilic attack.

(c) The product that forms initially (above) is a magnesium derivative of an alcohol.
(d) On addition of water, the organic product that forms is an alcohol.

16.6 The nucleophile is a hydride ion.

16.7 An image showing a series of chemical reactions involving nucleophilic addition to the carbonyl group.
16.8 Acid-Catalyzed Reaction

$$\text{CH}_2\text{C} = \text{CH}_2 + \text{H}^+ \rightarrow \text{CH}_2\text{C} = \text{CH}_2 \rightarrow \text{CH}_2\text{C} = \text{CH}_2 + \text{H}_2\text{O}$$

Base-Catalyzed Reaction

$$\text{CH}_2\text{C} = \text{CH}_2 + \text{OH}^- \rightarrow \text{CH}_2\text{C} = \text{CH}_2 + \text{H}_2\text{O}$$

16.9 Acetal group

Sucrose

16.10

16.11

Sucrose

16.12

Sucrose

16.13 (a)

$$\text{A} \xrightarrow{\text{H}^+} \text{B}$$

$$\text{2CH}_2\text{MgI} \rightarrow \text{C}$$
(b) Addition would take place at the ketone group as well as at the ester group. The product (after hydrolysis) would be.

\[
\text{HOCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

Tetrahydropyranyl ethers are acetals; thus, they are stable in aqueous base and hydrolyze readily in aqueous acid.

(c) HOCH₃CH₂CH₂CH₂Cl

16.14 (a)

16.15 (a) \( \text{C}_8\text{H}_8\text{O} + \text{HSCH}_2\text{CH}_2\text{SH} \) BF₃ →

(b) \( \text{C}_8\text{H}_8\text{O} + \text{HSCH}_2\text{CH}_2\text{SH} \) BF₃ →

16.16 (b) Raney Ni

Raney Ni

\( \text{CH}_3\text{CH}_3\text{Ni} + \text{NiS} \)

16.17 (b) Raney Ni

Raney Ni

\( \text{CH}_3\text{CH}_3\text{Ni} + \text{NiS} \)

16.18 (b) Raney Ni

Raney Ni

\( \text{CH}_3\text{CH}_3\text{Ni} + \text{NiS} \)
ALDEHYDES AND KETONES I. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

16.16 (a) CH$_3$CH$_2$ $\rightarrow$ HCN $\rightarrow$ OH $\rightarrow$ HCl $\rightarrow$ H$_2$O reflux $\rightarrow$ OH $\rightarrow$ CH$_3$CHCO$_2$H

(b) $\text{A racemic form}$

16.17 (a) CH$_3$I $\rightarrow$ (1) (C$_6$H$_5$)$_3$P $\rightarrow$ iCH$_2$ $\rightarrow$ p(C$_6$H$_5$)$_3$ $\rightarrow$ C$_6$H$_5$C=CH$_2$

(b) CH$_3$CH$_2$Br $\rightarrow$ (1) (C$_6$H$_5$)$_3$P $\rightarrow$ CH$_3$CH$_2$ $\rightarrow$ p(C$_6$H$_5$)$_3$ $\rightarrow$ C$_6$H$_5$C=CH$_2$

(c) iCH$_2$ $\rightarrow$ p(C$_6$H$_5$)$_3$ $\rightarrow$ from part (a)

(d) $\text{[from part (a)]}$

(e) CH$_3$CH$_2$CH$_2$I $\rightarrow$ (1) (C$_6$H$_5$)$_3$P $\rightarrow$ CH$_3$CH$_2$CH$_2$ $\rightarrow$ p(C$_6$H$_5$)$_3$ $\rightarrow$ C$_6$H$_5$C=CHCH$_3$

(f) CH$_3$=CH$_2$I $\rightarrow$ (1) (C$_6$H$_5$)$_3$P $\rightarrow$ CH$_3$=CH$_2$ $\rightarrow$ p(C$_6$H$_5$)$_3$ $\rightarrow$ C$_6$H$_5$C=CHCH$_3$

(g) C$_2$H$_5$I $\rightarrow$ (1) (C$_6$H$_5$)$_3$P $\rightarrow$ C$_2$H$_5$ $\rightarrow$ p(C$_6$H$_5$)$_3$ $\rightarrow$ C$_6$H$_5$C=CHC$_2$H$_5$

16.18 (C$_6$H$_5$)$_3$P$^+$ + CH$_3$CO$_2$CH$_2$CH$_3$ $\rightarrow$ CH$_3$CO$_2$CH$_2$H $\rightarrow$ (C$_6$H$_5$)$_3$P$^+$

16.19 (a) (CH$_3$)$_2$C=O + BrCH$_2$CO$_2$CH$_2$CH$_3$ $\rightarrow$ BrCH$_2$CO$_2$CH$_2$H $\rightarrow$ (CH$_3$)$_2$C=O

(b) $\text{[from part (a)]}$

(c) CH$_3$CH$_2$I + BrCH$_2$CO$_2$CH$_2$CH$_3$ $\rightarrow$ BrCH$_2$CO$_2$CH$_2$H $\rightarrow$ (C$_6$H$_5$)$_3$P$^+$
ALDEHYDES AND KETONES I. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

16.21 The product is a lactone, formed as follows:

![Lactone Formation Diagram]

16.22 \( \text{CH}_3\text{C}—\text{O—CHCH}_3 \) The isopropyl group has a greater migratory aptitude than the methyl group. The mechanism is as follows:

![Mechanism Diagram]

16.23 (a) \( \text{HCHO} \) Methanal
(b) \( \text{CH}_3\text{CHO} \) Ethanal
(c) \( \text{C}_6\text{H}_5\text{CH}_2\text{CHO} \) Phenylethanal
(d) \( \text{CH}_3\text{COCH}_3 \) Propanone
(e) \( \text{CH}_3\text{COCH}_2\text{CH}_3 \) Butanone
(f) \( \text{CH}_3\text{COC}_6\text{H}_5 \) 1-Phenylethanone or methyl phenyl ketone
(g) \( \text{C}_6\text{H}_5\text{COCH}_3 \) Diphenylmethanone or diphenyl ketone
(h) \( \text{CHO} \) 2-Hydroxybenzaldehyde or \( \alpha \)-hydroxybenzaldehyde
(i) \( \text{CHO} \) 4-Hydroxy-3-methoxybenzaldehyde
(j) \( \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 \) 3-Pentanone

16.24 (a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)
(b) \( \text{CH}_3\text{CH}_2\text{CHOHCH}_3 \)
(c) \( \text{CH}_3\text{CH}_2\text{CH}_3 \)
(d) \( \text{CH}_3\text{CH}_2\text{CHOHCH}_3 \)
(e) \( \text{CH}_3\text{CH}_2\text{CH}_3 \)
(f) \( \text{CH}_3\text{CH}_2\text{CH}_3 \)
(g) \( \text{CH}_3\text{CH}_2\text{CH}_3 \)
(h) \( \text{CH}_3\text{CH}_2\text{CH}_3 \)
(i) \( \text{CH}_3\text{CH}_2\text{CH}_3 \)
(j) \( \text{CH}_3\text{CH}_2\text{CH}_3 \)
(k) \( \text{CH}_3\text{CH}_2\text{COOH} \)
(l) \( \text{CH}_3\text{CH}_2\text{COOH} \)
(m) \( \text{CH}_3\text{CH}_2\text{COOH} \)
(n) \( \text{CH}_3\text{CH}_2\text{COOH} \)
(o) \( \text{CH}_3\text{CH}_2\text{COOH} \)
(p) \( \text{CH}_3\text{CH}_2\text{COOH} \)

16.25 (a) \( \text{CH}_3\text{CHOHCH}_3 \)
(b) \( \text{CH}_3\text{CHOHCH}_3 \)
(c) \( \text{CH}_3\text{CHOHCH}_3 \)
(d) \( \text{CH}_3\text{CHOHCH}_3 \)
(e) \( \text{CH}_3\text{CHOHCH}_3 \)
(f) \( \text{CH}_3\text{CHOHCH}_3 \)
(g) \( \text{CH}_3\text{CHOHCH}_3 \)
(h) \( \text{CH}_3\text{CHOHCH}_3 \)
(i) \( \text{CH}_3\text{CHOHCH}_3 \)
(j) \( \text{CH}_3\text{CHOHCH}_3 \)
(k) \( \text{CH}_3\text{CHOHCH}_3 \)
(l) \( \text{CH}_3\text{CHOHCH}_3 \)
(m) \( \text{CH}_3\text{CHOHCH}_3 \)
(n) \( \text{CH}_3\text{CHOHCH}_3 \)
(o) \( \text{CH}_3\text{CHOHCH}_3 \)
(p) \( \text{CH}_3\text{CHOHCH}_3 \)

2-Methyl-3-pentanone
2,4-Dimethyl-3-pentanone
5-Nonanone
4-Heptanone
3-Phenyl-2-propenal

(k) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)
(l) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)
(m) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)
(n) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)
(o) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)

2-Methyl-3-pentanone
2,4-Dimethyl-3-pentanone
5-Nonanone
4-Heptanone
3-Phenyl-2-propenal
ALDEHYDES AND KETONES I. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

16.26 (a)  

16.27 (a)  

16.28 (a)  

(b)  

(c)  

(e)  

(f)  

(g)  

(h)  

(i)  

(j)  

(k)  

(l)  

(m)  

(n)  

(o)  

(p)  

(q)  

(r)  

(s)  

(t)  

(u)  

(v)  

(w)  

(x)  

(y)  

(z)
300 ALDEHYDES AND KETONES I. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

16.29 (a) \( \text{PhCHO} + \text{CH}_2\text{Cl}_2 \xrightarrow{\text{AlCl}_3} \text{PhCH}_2\text{Cl} \)

(b) \( \text{PhCHO} + \text{CH}_2\text{CH}_2\text{CuLi} \rightarrow \text{PhCH}_2\text{Li} \)

(c) \( \text{PhC≡N} + \text{CH}_2\text{CH}_2\text{Li} \xrightarrow{2 \text{H}_2\text{O}} \text{PhCH}_2\text{Li} \)

(d) \( \text{PhCHO} + \text{CH}_2\text{CH}_2\text{MgBr} \xrightarrow{2 \text{H}_2\text{O}} \text{PhCH}_2\text{CH}_2\text{OH} \)

16.30 (a) \( \text{PhCH}_2\text{OH} \xrightarrow{\text{PCC}} \text{PhCH} = \text{H} \)

(b) \( \text{PhCH} = \text{OH} \xrightarrow{\text{SOCl}_2} \text{PhCH} = \text{Cl} \xrightarrow{\text{LiAlH}_4} \text{PhCH} = \text{H} \)

(c) \( \text{PhC≡CH} \xrightarrow{1 \text{KMnO}_4, \text{OH}} \text{PhC} = \text{OCH}_2 \xrightarrow{\text{as in (b)}} \text{PhCH} = \text{H} \)

(d) \( \text{PhCH} = \text{CH}_2 \xrightarrow{1 \text{KMnO}_4, \text{OH}} \text{PhC} = \text{OCH}_2 \xrightarrow{\text{as in (b)}} \text{PhCH} = \text{H} \)

(e) \( \text{PhOCH}_3 \xrightarrow{1 \text{H}_2\text{AlB} \text{Me}_2\text{H}, \text{hexane, } -78^\circ\text{C}} \text{PhCH} = \text{H} \xrightarrow{2 \text{H}_2\text{O}} \text{PhCH} = \text{H} \)

(f) \( \text{PhC≡N} \xrightarrow{1 \text{H}_2\text{AlB} \text{Me}_2\text{H}, \text{hexane, } -78^\circ\text{C}} \text{PhCH} = \text{H} \xrightarrow{2 \text{H}_2\text{O}} \text{PhCH} = \text{H} \)
ALDEHYDES AND KETONES I. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

16.31

\[
\begin{align*}
\text{CH}_3\text{CHO} & \xrightarrow{\text{H}_2\text{C}=\text{O}, \text{acetone}} \text{A} \\
& \xrightarrow{(1) \text{CH}_3\text{MgI}, (2) \text{NH}_2^-} \text{B} \\
& \xrightarrow{\text{H}^+} \text{heat} \\
\text{C} & \xrightarrow{(1) \text{O}_3, (2) \text{Zn}, \text{HgAc}} \text{D} \\
& \xrightarrow{(1) \text{AgO}, \text{OH}^-} \text{OH} \\
& \xrightarrow{(2) \text{H}^+} \\
\text{E} & \xrightarrow{\text{heat}} \text{O} \\
\text{CH}_3\text{CH} & \xrightarrow{\text{BrCH}_2\text{CO}_2\text{Et}, \text{Zn}} \text{H}_2\text{O}' \\
& \xrightarrow{\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}, \text{H}_2\text{O}' \text{heat}} \text{K} \\
& \xrightarrow{(1) \text{DBAL-H}, (2) \text{H}_2\text{O}'} \\
\text{CH}_3\text{CH}\text{CH} & \xrightarrow{\text{H}_2\text{Pt}} \text{L} \\
\end{align*}
\]

The compound C\textsubscript{7}H\textsubscript{6}O\textsubscript{2} is 3,4-dihydroxybenzaldehyde. The reaction involves hydrolysis of the acetal of formaldehyde.

16.32

\[
\begin{align*}
\text{CHO} & \xrightarrow{\text{H}^+ \text{heat}} \text{OH} \\
& \xrightarrow{\text{H}_2\text{O}' \text{heat}} \text{M} \\
\end{align*}
\]

16.33

\[
\begin{align*}
\text{CHO} & \xrightarrow{\text{OH} \text{H}_2\text{O}' \text{heat}} \text{OH} \\
& \xrightarrow{\text{H}_2\text{O}' \text{heat}} \\
\end{align*}
\]

16.34 (a)

\[
\begin{align*}
\text{CHO} & \xrightarrow{\text{Me}_3\text{Si}, \text{Et}_2\text{O}} \text{OH} \\
& \xrightarrow{(1) \text{CH}_3\text{CHO}, (2) \text{H}_2\text{O}'} \\
\end{align*}
\]

(b)

\[
\begin{align*}
\text{CHO} & \xrightarrow{\text{LiAlH}_4, \text{then H}_2\text{O}} \text{OH} \\
& \xrightarrow{\text{PCC}, \text{CH}_2\text{Cl}_2} \\
\end{align*}
\]

16.35

\[
\begin{align*}
\text{B} & \xrightarrow{(1) \text{CH}_3\text{CHO}, (2) \text{H}_2\text{O}' \text{H}_2\text{O}} \text{C} \\
& \xrightarrow{(1) \text{CH}_3\text{CHO}, (2) \text{H}_2\text{O}' \text{H}_2\text{O}} \text{D} \quad \text{(acetal)} \\
\end{align*}
\]

16.36 (a) (CH\textsubscript{3})\textsubscript{2}\text{SO}, \text{NaOH} \text{or CH}_3\text{J}, \text{NaOH} \\
(b) \text{PCC}/\text{CH}_2\text{Cl}_2 \\
(c) \text{Zn, BrCHCO}_2\text{Et, then H}_2\text{O}' \\
(d) \text{LiAlH}_4, \text{then H}_2\text{O} \quad \text{Intermediate is CH}_3\text{O} \xrightarrow{\text{H}_2\text{O}} \text{CHO}
ALDEHYDES AND KETONES I. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

16.37 \[ CH_2=CHCH_2OH \xrightarrow{\text{PCC/CHCl}_2} CH_2=CHCH = \xrightarrow{\text{H}^+} CH_2=CH-CH=CH_2 \] 

The product would be racemic as no chiral reagents were used.

16.38 \[ \text{(R)-3-Phenyl-2-pentanone} \xrightarrow{\text{NaBH}_3} \begin{array}{c} \text{(R)} \\ \text{(S)} \end{array} \text{Diastereomers} \]

16.39 \[ \text{BrCH}(_2)\text{CH}(_2)\text{CH}_2\text{Br} \xrightarrow{(1) 2\text{C}_6\text{H}_5\text{P}} \xrightarrow{(2) \text{RLi}} \begin{array}{c} \text{(a) C}_6\text{H}_5\text{CH}(_2)\text{CH}(_2)\text{CH}_2\text{CH}(_2)\text{CH}(_2)\text{H} \\ \text{(b) C}_6\text{H}_5\text{CH}(_2)\text{CH}(_2)\text{CH}_2\text{CH}(_2)\text{CH}(_2)\text{H} \end{array} \]

16.40
(a) \( \text{Ag(NH}_3\text{)}_2^+\text{OH}^- \) (positive test with benzaldehyde)
(b) \( \text{Ag(NH}_3\text{)}_2^+\text{OH}^- \) (positive test with hexanal)
(c) Concentrated \( \text{H}_2\text{SO}_4 \) (2-hexanone is soluble)
(d) \( \text{CrO}_3 \) in \( \text{H}_2\text{SO}_4 \) (positive test with 2-hexan)al
(e) \( \text{Br}_2 \) in \( \text{CCl}_4 \) (decolorization with \( \text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5 \))
(f) \( \text{Ag(NH}_3\text{)}_2^+\text{OH}^- \) (positive test with pentanal)
(g) \( \text{Br}_2 \) in \( \text{CCl}_4 \) (immediate decolorization occurs with enol form)
(h) \( \text{Ag(NH}_3\text{)}_2^+\text{OH}^- \) (positive test with cyclic hemiacetal)

16.41 Compound W is

[Diagram: singlet \( \delta 3.4 \) IR peak near \( 1715 \text{ cm}^{-1} \)]

Compound X is

[Diagram: triplet \( \delta 2.5 \) triplet \( \delta 3.1 \)]

16.42 Each \( ^1\text{H} \) NMR spectrum (Figs. 16.4 and 16.5) has a five-hydrogen peak near \( \delta 7.2 \), suggesting the Y and Z each has a \( \text{C}_6\text{H}_5^- \) group. The IR spectrum of each compound shows a strong peak near \( 1710 \text{ cm}^{-1} \). This absorption indicates that each compound has a \( \text{C} = \text{O} \) group not adjacent to the phenyl group. We have, therefore, the following pieces.

If we subtract the atoms of these pieces from the molecular formula,

\[ \text{C}_6\text{H}_5\text{O} = \text{C}_6\text{H}_5\text{C} = \text{C}_6\text{H}_5 + \text{C} = \text{O} \]

We are left with \( \text{C}_6\text{H}_7 \)

In the \( ^1\text{H} \) NMR spectrum of Y, we see an ethyl group (triplet, \( \delta 1.0 \) (3H) and quartet, \( \delta 2.45 \) (2H)) and an unsplit \( -\text{CH}_2^- \) group (singlet, \( \delta 3.7 \) (2H)). This means that Y must be

\[ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

1-Phenyl-2-butanone

In the \( ^1\text{H} \) NMR spectrum of Z, we see an unsplit \( -\text{CH}_2^- \) group (singlet, \( \delta 2.1 \) (3H)) and two triplets at \( \delta 2.7 \) and 2.9. This means Z must be

\[ \text{CH}_2\text{CH}_2\text{CCH}_3 \]

4-Phenyl-2-butanone
16.43 That compound A forms a phenylhydrazone, gives a negative Tollens' test, and gives an IR band near 1710 cm\(^{-1}\) indicates that A is a ketone. The \(^{13}\)C spectrum of A contains only four signals indicating that A has a high degree of symmetry. The information from the DEPT \(^{13}\)C NMR spectra enables us to conclude that A is diisobutyl ketone:

\[(CH(CH_3)_2)CHCH(C)CH(CH_3)_2\]

Assignments:
(a) \(\delta 22.6\)
(b) \(\delta 24.4\)
(c) \(\delta 52.3\)
(d) \(\delta 210.0\)

16.44 That the \(^{13}\)C spectrum of B contains only three signals indicates that B has a highly symmetrical structure. The information from DEPT spectra indicates the presence of equivalent methyl groups (CH\(_3\) at \(\delta 18.8\)), equivalent –C\(_2\) groups (at \(\delta 70.4\)), and equivalent C=O groups (at \(\delta 215.0\)). These features allow only one possible structure for B:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{O} \\
\text{O} & \quad \text{CH}_3
\end{align*}
\]

Assignments:
(a) \(\delta 18.8\)
(b) \(\delta 70.4\)
(c) \(\delta 215.0\)

16.45 The two nitrogen atoms of semicarbazide that are adjacent to the C=O group bear partial positive charges because of resonance contributions made by the second and third structures below.

\[
H\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}} \quad \leftrightarrow \quad H\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}} \quad \leftrightarrow \quad H\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}}\overset{\text{N}}{\text{H}}
\]

Only this nitrogen is nucleophilic.

16.46 Hydrolysis of the acetal linkage of multistriatin produces the ketodiol below.

\[
\text{O} \quad \text{O} \quad \text{H} \quad \text{HO}
\]

16.47

\[
\text{CH}_3 \quad \text{Cl}_2 \quad \text{CH}_3 \\
\text{heat, Ag}, \text{or peroxide}
\]

The gem-diol formed in the alkaline hydrolysis step readily loses water to form the aldehyde:

16.48

\[
\text{CH}_3 \quad \text{C} = \text{C} - \text{CH}_3 \quad \text{or its enantiomer}
\]

16.49 The general formula for an oxime is

\[
\begin{align*}
\text{C} & = \text{N} \\
\text{OH}
\end{align*}
\]

Both carbon and nitrogen are sp\(^2\) hybridized; the electron pair on nitrogen occupies one sp\(^2\) orbital. Aldoximes and ketoximes can exist in either of these two stereoisomeric forms:

\[
\begin{align*}
(R')\text{H} & = \text{N} \quad \text{OH} \\
(R')\text{H} & = \text{N} \quad \text{OH}
\end{align*}
\]

This type of stereoisomerism is also observed in the case of other compounds that possess the \(\text{C}=\text{N}\) group, for example, phenylhydrazones and semicarbazones.
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16.50

\[
\begin{align*}
\text{AcO} & \quad \text{H} \\
\phi \quad \text{O} \\
\phi \quad \text{O}
\end{align*}
\]

\[
\text{NaH} \to \quad \text{AcO} \quad \text{H} \\
\phi \quad \text{O} \\
\phi \quad \text{O}
\]

16.51

\[
R \quad \text{HCO} \quad \overset{\text{Imine exchange with}}{\rightarrow} \quad \overset{\text{Enz—N=PLP}}{\rightarrow} \quad \overset{\text{Enz—N=PLP}}{\rightarrow} \quad -\text{CO}_2
\]

16.52 (a) \( \text{O—H stretch at about } 3300 \text{ cm}^{-1} \); \( \text{C=O stretch at about } 1710 \text{ cm}^{-1} \)

(b) Intramolecular hemiacetal from A

16.53

\[
\begin{align*}
\text{CH}_3 \quad \text{O—H} \\
\phi \quad \text{O} \\
\phi \quad \text{CH}, \text{OH}
\end{align*}
\]

QUIZ

16.1 Which Wittig reagent could be used to synthesize \( \text{C}_6\text{H}_5\text{CH=CHCH}_2\text{CH}_3 \)? (Assume any other needed reagents are available.)

(a) \( \text{C}_6\text{H}_5\text{CHP(C}_6\text{H}_3\text{)}_3 \)

(b) \( \text{C}_6\text{H}_5\text{CH=CHCHP(C}_6\text{H}_3\text{)}_3 \)

(c) \( \text{CH}_3\text{CH}=\text{CHCHP(C}_6\text{H}_3\text{)}_3 \)

(d) More than one of these

(e) None of these

16.2 Which compound is an acetal?

(a) \( \text{C}_6\text{H}_5\text{CHOCH}_3 \)

(b) \( \overset{\text{O}}{\text{OCH}}_3 \)

(c) \( \overset{\text{O}}{\text{OCH}}_3 \)

(d) More than one of these

(e) None of these

16.3 Which reaction sequence could be used to convert \( \text{C}_6\text{H}_5\text{C}≡\text{CH} \) to \( \text{C}_6\text{H}_5\text{CCH}_3 \)?

(a) \( \text{O}_2 \), then \( \text{Zn, HOAc, then AlCl}_3 \), then \( \text{CH}_3\text{CO}_2\text{H} \)

(b) \( \text{H}_2\text{SO}_4, \text{HgSO}_4, \text{H}_2\text{O, heat} \)

(c) \( \text{HCl, then CH}_3\text{CO}_2\text{H} \)

(d) \( \text{O}_2 \), then \( \text{Zn, HOAc, then H}_2\text{SO}_4, \text{HgSO}_4, \text{H}_2\text{O, heat} \)

(e) \( \text{CH}_3\text{CO}_2\text{H, then H}_2\text{O, OH}^-\text{H}_2\text{O} \)
16.4 Complete the following syntheses. If more than one step is required for a transformation, list them as (1), (2), (3), and so on.

(a) \( \text{CH}_2\text{CH}_3 \xrightarrow{\text{NBS}} \text{A} \xrightarrow{\text{THF}} \text{B} \)

(b) \( \text{CH}_2\text{CH}_3\text{OH} \xrightarrow{\text{A}} \text{B} \xrightarrow{\text{C}} \text{C} \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{A}} \text{B} \xrightarrow{\text{C}} \text{C}_3\text{H}_5\text{Li} \)

(d) \( \text{OH} \xrightarrow{\text{A}} \text{B} \xrightarrow{\text{C}} \text{OH} \)

17.1 2,4-Cyclohexadien-1-one (keto form) \( \xrightarrow{\text{Phenol}} \) Phenol (enol form)

The enol form is aromatic, and it is therefore stabilized by the resonance energy of the benzene ring.

17.2 No. \( \text{PhC}_6\text{H}_5\) does not have a hydrogen attached to its \( \alpha \)-carbon atom (which is a stereocenter) and thus enol formation involving the stereocenter is not possible. With \( \text{PhC}_6\text{H}_5\text{C}(\text{enol form}) \) the stereocenter is a \( \beta \) carbon and thus enol formation does not affect it.

17.3 In OD/D\(_2\)O:

\[
\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 + \text{OD}^- \xrightarrow{\text{D}_2\text{O}} \text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 \xrightarrow{\text{D}_2\text{O}^-} \text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 + \text{enantiomer}
\]

In D\(_2\)O/D\(_2\)O:

\[
\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 + \text{D}_2\text{O}^- \xrightarrow{\text{D}^-} \text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 \xrightarrow{\text{H}^-} \text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 + \text{enantiomer}
\]
17.4  

\[
\begin{align*}
\text{cis-Decalone} & \quad \xrightarrow{\text{Protonation on the bottom face}} \quad \text{ trans-Decalone} \\
\end{align*}
\]

A large group is axial in cis-decalone.

17.5  The reaction is said to be “base promoted” because base is consumed as the reaction takes place. A catalyst is, by definition, not consumed.

17.6  (a) The slow step in base-catalyzed racemization is the same as that in base-promoted halogenation—the formation of an enolate ion. (Formation of an enolate ion from sec-butyl phenyl ketone leads to racemization because the enolate ion is achiral. When it accepts a proton, it yields a racemic form.) The slow step in acid-catalyzed racemization is also the same as that in acid-catalyzed halogenation—the formation of an enol. (The enol, like the enolate ion, is achiral and tautomizes to yield a racemic form of the ketone.)

(b) According to the mechanism given, the slow step for acid-catalyzed iodination (formation of the enol) is the same as that for acid-catalyzed bromination. Thus, we would expect both reactions to occur at the same rate.

(c) Again, the slow step for both reactions (formation of the enolate ion) is the same, and consequently, both reactions take place at the same rate.

17.7  (a)  
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{OH}^- & \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^- + \text{H}_2\text{O} \\
\text{CH}_3\text{CH}_2\text{CH}^- \xrightarrow{\text{H}^+} & \text{CH}_3\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}^- \xrightarrow{\text{H}^+} & \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{OH}^- \\
\end{align*}
\]

17.8  (a) \(\text{CH}_3\text{CHO} \xrightarrow{\text{19% NaOH, } 5^\circ\text{C}} \text{CH}_3\text{CHCH}_2\text{CHO} \xrightarrow{\text{heat}} \text{CH}_3\text{C}=\text{CHCHO} \xrightarrow{\text{H}_2\text{N}} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH}\)

(b) Product of (a):  
\[
\begin{align*}
\text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{OH} \xrightarrow{\text{LiAlH}_4, \text{Et}_2\text{O}} \text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{CH}_2\text{OH} \\
\end{align*}
\]

(c) Product of (b):  
\[
\begin{align*}
\text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{OH} \xrightarrow{\text{H}_2\text{Pt}} \text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{OH} \\
\end{align*}
\]

(d) Product of (a):  
\[
\begin{align*}
\text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{OH} \xrightarrow{\text{NaOH}} \text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{OH} \\
\end{align*}
\]
**ALDEHYDES AND KETONES II: ALDOL REACTIONS**

17.10

\[
\begin{align*}
\ce{CH₃C=CH₂ + HCl &<-> CH₃C=CH₂ + Cl⁻ & \text{(shown in text)}}
\end{align*}
\]

\[
\begin{align*}
\text{CH₃CH₂OH} + CH₂=CH=CH₂ &<-> \text{CH₃CH₂OH} + \text{CH₂=CH=CH₂}
\end{align*}
\]

\[
\begin{align*}
\text{H₂O} + \text{CH₃CH=CHCH₃} &<-> \text{CH₃C=CHCH₃}
\end{align*}
\]

2,6-Dimethyl-2,5-heptadien-4-one

17.11 Drawing the molecules as they will appear in the final product helps to visualize the necessary steps:

Mesitylene

The two molecules that lead to mesitylene are shown as follows:

This molecule (4-methyl-3-penten-2-one) is formed by an acid-catalyzed condensation between two molecules of acetone as shown in the text.

17.12

The mechanism is:

\[
\begin{align*}
\text{O} &= \text{Cl} + H⁺ &<-> \text{HO-CH₂=CH₂} \\
\end{align*}
\]

Propanal

Lily aldehyde (C₁₄H₂₀O)

\[
\begin{align*}
\text{C₆H₆OH} \text{PCC} &<-> \text{C₆H₆-OH} \\
\text{C₆H₆OH} \text{H₂/Pt, C} &<-> \text{C₆H₆CH₃} \\
\text{C₆H₆CH₃} \text{OH} &<-> \text{C₆H₆CH₂CH₂CH₃} \\
\end{align*}
\]
ALDEHYDES AND KETONES II: ALDOL REACTIONS

17.13 \[ \text{CH}_2\text{CHO} + \text{CH}_3\text{CHO} \xrightarrow{10\% \text{ NaOH}, 5^\circ\text{C}} \text{H}_2\text{C} = \text{CHCHO} \]

17.14 Three successive aldol additions occur.

First Aldol Addition
\[
\begin{align*}
\text{CH}_3\text{CH} + \text{OH}^- & \xrightarrow{+} \text{C} = \text{CHCH} + \text{H}_2\text{O} \\
\text{HCH} + \text{C} = \text{CHCH} & \xrightarrow{+} \text{OCH}_2\text{CHCH} \\
\text{OCH}_2\text{CHCH} + \text{H}_2\text{O} & \xrightarrow{+} \text{HOCH}_2\text{CHCH} + \text{OH}^-
\end{align*}
\]

Second Aldol Addition
\[
\begin{align*}
\text{HOCH}_2\text{CHCH} + \text{OH}^- & \xrightarrow{+} \text{HOCH}_2\text{CH} = \text{C} = \text{CHCHO} \\
\text{HOCH}_2\text{CHCH} + \text{H}_2\text{O} & \xrightarrow{+} \text{HOCH}_2\text{CHCH} + \text{OH}^-
\end{align*}
\]

Third Aldol Addition
\[
\begin{align*}
\text{CH}_2\text{OH} & \xrightarrow{+} \text{HOCH}_2\text{C} = \text{C} = \text{CHO} + \text{H}_2\text{O} \\
\text{HOCH}_2\text{C} = \text{C} = \text{CHO} + \text{H}_2\text{O} & \xrightarrow{+} \text{HOCH}_2\text{C} = \text{C} = \text{CHO} + \text{OH}^-
\end{align*}
\]

17.15 (a) \[ \text{CH}_2\text{CO}_2\text{H} + \text{BF}_3 \xrightarrow{\text{H}^+} \text{CH}_2\text{CO}_2\text{BF}_3^- + \text{H}^+ \]

(b) In \( \beta \)-ionone both double bonds and the carbonyl group are conjugated; thus it is more stable.

(c) \( \beta \)-ionone, because it is a fully conjugated unsaturated system.

17.16 (a) \[ \text{CH}_3\text{C} = \text{O} + \text{CH}_3\text{NO}_2 \xrightarrow{\text{H}^+} \text{CH}_3\text{C} = \text{NO}_2 \]

(b) \[ \text{HCH} + \text{CH}_3\text{NO}_2 \xrightarrow{\text{H}^+} \text{HOCH}_2\text{CH}_3\text{NO}_2 \]

17.17 (a) \[ \text{HCH} + \text{C} = \text{N} : \text{CH} \xrightarrow{\text{H}^+} \text{CH} = \text{C} = \text{N} : \text{CH} \]

(b) \[ \text{CH}_3\text{C} = \text{N} : \xrightarrow{\text{H}^+} \text{CH}_3\text{C} = \text{N} : + \text{EtOH} \]

(c) \[ \text{HCH} + \text{C} = \text{N} : \xrightarrow{\text{H}^+} \text{CH} = \text{C} = \text{N} : \xrightarrow{\text{EtOH}} \]
ALDEHYDES AND KETONES II: ALDOL REACTIONS

17.18
\[
\begin{align*}
\text{CH}_3\text{(CH}_2\text{)}_2\text{CHO} & \xrightarrow{\text{OH}} \text{CH}_3\text{(CH}_2\text{)}_2\text{C}^{\text{O-H}} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{(CH}_2\text{)}_4\text{CO} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H} & \xrightarrow{\text{OH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H}
\end{align*}
\]

Notice that starting compounds are drawn so as to indicate which atoms are involved in the cyclization reaction.

17.20
It is necessary for conditions to favor the intramolecular reaction rather than the intermolecular one. One way to create these conditions is to use very dilute solutions when we carry out the reaction. When the concentration of the compound to be cyclized is very low (i.e., when we use what we call a "high dilution technique"), the probability is greater that one end of a molecule will react with the other end of that same molecule rather than with a different molecule.

17.21
\[
\begin{align*}
\text{(a)} & \quad \text{CH}_3\text{C(CH}_3\text{)}=\text{CH} \xrightarrow{\text{LDA}} \text{CH}_3\text{C(CH}_3\text{)}=\text{CH} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C(CH}_3\text{)}=\text{CH} \\
\text{Step 1} & \quad \text{Step 2} \quad \text{Step 3}
\end{align*}
\]

(a) \hspace{1cm} \text{Kinetic enolate}
(a) 2-Methyl-1,3-cyclohexanedione is more acidic because its enolate ion is stabilized by an additional resonance structure.

(b) 2-Methyl-1,3-cyclohexanone is more acidic because its enolate ion is stabilized by an additional resonance structure.
ALDEHYDES AND KETONES II: ALDOL REACTIONS

17.27  \( \text{H}_2\text{N} - \text{NH}_2 + \text{CH}_3\text{CH} = \text{CHCH} \rightarrow \text{H}_2\text{N} - \text{NH} \),

\[ \text{H}_2\text{N} - \text{NH}_2 + \text{CH}_3\text{CH} = \text{CHCH} \rightarrow \text{H}_2\text{N} - \text{NH} \]  

17.28  (a) \( \text{CH}_3\text{CHCHCHO} \)   (b) \( \text{CH}_3\text{CHCHCHO} \)   (c) \( \text{CH}_3\text{CHCHCN} \)   (d) \( \text{CH}_3\text{CHCHOH} \)   (e) \( \text{CH}_3\text{CHCH} \)  

17.29  (a) \( \text{CH}_3\text{C} = \text{CHCH}_3 \)   (b) \( \text{C}_2\text{H}_4\text{CH} = \text{CHCH}_3 \)   (c) \( \text{CH}_3\text{CHCH} \)   (d) \( \text{CH}_3\text{CHCH} \)   (e) \( \text{CH}_3\text{CHCH} \)  

17.30  (a) \( \text{CH}_3\text{C} = \text{CHCHCHO} \)   (b) \( \text{CH}_3\text{C} = \text{CHCHCHO} \)   (c) \( \text{CH}_3\text{C} = \text{CHCHCHO} \)   (d) \( \text{CH}_3\text{C} = \text{CHCHCHO} \)   (e) \( \text{CH}_3\text{C} = \text{CHCHCHO} \)  

(m) \( \text{CH}_3\text{CHCH} \)   (n) \( \text{CH}_3\text{CHCH} \)   (o) \( \text{CH}_3\text{CHCH} \)   (p) \( \text{CH}_3\text{CHCH} \)   (q) \( \text{CH}_3\text{CHCH} \)  

322
17.31  (a) \( \text{CHO} + \text{CH}_3\text{C}(-\text{C})(\text{CH}_3) \xrightarrow{\text{dil OH}} \text{C}(-\text{C})(\text{CH}_3)\text{CHO} \)

(b) \( \text{CHO} + \text{CH}_2\text{O} \xrightarrow{\text{dil OH}} \text{CHO} \)

(c) \( \text{CHO} + \text{CH}_2\text{NO}_2 \xrightarrow{\text{dil OH}} \text{CHO} \)

(d) \( \text{CHO} \xrightarrow{\text{dil OH}} \text{CHO} \)

(e) \( \text{CHO} + \text{CH}_2\text{CN} \xrightarrow{\text{base}} \text{CHO} \)

(f) \( 2\text{CHO} \xrightarrow{\text{dil OH}, 5^\circ\text{C}} \text{CHO} \)

(g) \( \text{CHO} \xrightarrow{\text{dil OH}} \text{CHO} \)

17.32  \( \text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{dil OH}} \text{C}_6\text{H}_5\text{CH} = \text{CHCHO} \)

17.33  \( \text{HC} = \text{CH} \xrightarrow{(1)\text{NaNH}_2, \text{CH}_3\text{COCH}_2, (3)\text{H}_2\text{O}} \text{HC} = \text{C}(-\text{C})(\text{OH}) \)

17.34  (a) The conjugate base is a hybrid of the following structures:

\[ \text{CH}_2\text{CH} = \text{CH} \quad \text{CH}_2\text{CH} = \text{CH} \quad \text{CH}_2\text{CH} = \text{CH} \quad \text{CH}_2\text{CH} = \text{CH} \]

This structure is especially stable because the negative charge is on the oxygen atom.

(b) \( \text{CH}_3\text{CH} = \text{CHCHO} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH} = \text{CHCHO} \)

\( \text{C}_6\text{H}_5\text{CHO} \)
17.35 (a) \[ \text{Zn, HCOAc} \rightarrow \text{CH}_3\text{CHO} \]
(b) \[ \text{Zn, HCOAc} \rightarrow \text{CH}_3\text{CHO} \]
(c) \[ \text{Zn, HCOAc} \rightarrow \text{CH}_3\text{CHO} \]
(d) \[ \text{Zn, HCOAc} \rightarrow \text{CH}_3\text{CHO} \]

17.36 (a) In simple addition, the carbonyl peak (1665–1780-cm\(^{-1}\) region) does not appear in the product; in conjugate addition it does.
(b) As the reaction takes place, the long-wavelength absorption arising from the conjugated system should disappear. One could follow the rate of the reaction by following the rate at which this absorption peak disappears.

17.37 (a) Compound \( U \) is ethyl phenyl ketone: \[ \text{CH}_3\text{CCH}_2\text{CHO} \]
(b) Compound \( V \) is benzyl methyl ketone: \[ \text{CH}_3\text{CCH}_2\text{CHO} \]

17.38 A is \( \text{CH}_3\text{CCH}_2\text{CH(OCH}_3)_2 \)
(b) \[ \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} \]
(c) \[ \text{Ag(NH}_3)_2\text{O}^- \rightarrow \text{Ag}^+ + \text{CH}_3\text{CCH}_2\text{CO}^- \]

17.39 Abstraction of an \( \alpha \) hydrogen at the ring junction yields an enolate ion that can then accept a proton to form either \( \text{trans-1-decalone} \) or \( \text{cis-1-decalone} \). Since \( \text{trans-1-decalone} \) is more stable, it predominates at equilibrium.

17.40 (a) \[ \text{CH}_3\text{OCH}_2\text{Br} + \text{(C}_6\text{H}_5)_2\text{P} \rightarrow \text{CH}_3\text{OCH} = \text{P(C}_6\text{H}_5)_2 \]
(b) Hydrolysis of the ether yields a hemiacetal that then goes on to form an aldehyde.
(c) \[ \text{CHOCH}_3 + \text{H}_2\text{C}=\text{P(C}_6\text{H}_3\text{)})_3 \rightarrow \text{CH}-\text{CHOCH}_3 + \text{H}_2\text{C} \]

**17.41** (a) The hydrogen atom that is added to the aldehyde carbon atom in the reduction must come from the other aldehyde rather than from the solvent. It must be transferred as a hydride ion and directly from molecule to molecule, since if it were ever a free species it would react immediately with the solvent. A possible mechanism is the following:

\[ \text{C-H} + \text{OH} \rightarrow \text{C-OH} \rightarrow \text{C-OH} + \text{OH} \]

Then

\[ \text{C-OH} + \text{H} \rightarrow \text{C-OH} + \text{H} \rightarrow \text{C-OH} \rightarrow \text{C-OH} \]

(b) Although an aldol reaction occurs initially, the aldol reaction is reversible. The Cannizzaro reaction, though slower, is irreversible. Eventually, all the product is in the form of the alcohol and the carboxylate ion.

**17.42** This difference in behavior indicates that, for acetaldehyde, the capture of a proton from the solvent (the reverse of the reaction by which the enolate ion is formed) occurs much more slowly than the attack by the enolate ion on another molecule.

When acetone is used, the equilibrium for the formation of the enolate ion is unfavorable, but more importantly, enolate attack on another acetone molecule is disfavored due to steric hindrance. Here proton capture (actually deuteron capture) competes very well with the aldol reaction.
17.1 Supply formulas for the missing reagents and intermediates in the following synthesis.

\[
\begin{align*}
\text{(a)} & \quad \text{CH}_3\text{CH}_2\text{CH} & \quad \text{NaBH}_4 \\
\text{(b)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}_2\text{OH} \\
\text{(c)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}(\text{OCH}_3)_2 \\
\text{(d)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}_2\text{OH} \\
\text{(e)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}(\text{OCH}_3)_2 \\
\text{(f)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}_2\text{OH} \\
\text{(g)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}(\text{OCH}_3)_2 \\
\text{(h)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}_2\text{OH} \\
\text{(i)} & \quad \text{CH}_3\text{CH}_2\text{CH} &= \text{CCH}(\text{OCH}_3)_2 \\
\end{align*}
\]
ALDEHYDES AND KETONES II: ALDOL REACTIONS

(a) $\text{C}_2\text{H}_4\text{CCBrCH}_3$  
(b) $\text{C}_2\text{H}_4\text{CCHCH}_2\text{Br}$  
(c) $\text{C}_2\text{H}_4\text{CCCH}_2\text{OH}$  
(d) $\text{C}_2\text{H}_4\text{CBrCHCH}_3$  
(e) None of these

(c) $\text{C}_6\text{H}_5\text{CCHCH}_2\text{Br}$

18.1 (a) 2-Methylbutanoic acid
(b) 3-Pentenoic acid
(c) Sodium 4-bromobutanoate
(d) 5-Phenylpentanoic acid
(e) 3-Methyl-3-pentenoic acid

18.2 Acetic acid, in the absence of solvating molecules, exists as a dimer owing to the formation of two intermolecular hydrogen bonds:

At temperatures much above the boiling point, the dimer dissociates into the individual molecules.

18.3 (a) $\text{CH}_3\text{FCO}_2\text{H}$ ($\text{F}^-$ is more electronegative than $\text{H}^-$)
(b) $\text{CH}_3\text{FCO}_2\text{H}$ ($\text{F}^-$ is more electronegative than $\text{Cl}^-$)
(c) $\text{CH}_3\text{CICO}_2\text{H}$ ($\text{Cl}^-$ is more electronegative than $\text{Br}^-$)
(d) $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$ ($\text{F}^-$ is closer to $\text{CO}_2\text{H}$)
(e) $\text{CH}_3\text{CH}_2\text{CHFCO}_2\text{H}$ ($\text{F}^-$ is closer to $\text{CO}_2\text{H}$)
(f) $\text{CH}_3\text{N}^+-\text{CO}_2\text{H}$ [$\text{CH}_3\text{N}^+$ is more electronegative than $\text{H}^+$]
(g) $\text{CF}_3\text{CO}_2\text{H}$ ($\text{CF}_3^-$ is more electronegative than $\text{CH}_3^-$)

18.4 (a) The carboxyl group is an electron-withdrawing group; thus, in a dicarboxylic acid such as those in Table 18.3, one carboxyl group increases the acidity of the other.
(b) As the distance between the carboxyl groups increases the acid-strengthening, inductive effect decreases.
18.5 (a) CH₃CH₂COOCH₃  
(b) O₃N—CH=OCH₂CH₃  
(c) CH₃O—CH₂COOCH₃  
(d) O₃N—CH(N(CH₃)₂)  
(e) CH₃CH₂CH₂CH₂CN  
(f) CH₃C—C—OCH₃  
(g) CH₃C—C—OCH₂CH₃  
(h) H—C=NO(CH₃)₂  
(i) CH₂=CH—Br  
(j) CH₃COOCH₂CH₃

18.6 (a) CH₂—CH₃  \[\xrightarrow{(1) \text{K}_2\text{MnO₄}, \text{OH}^-, \text{heat}}\] \(\text{HOCH}_{2} \text{COOH} + \text{CO}_2\)  
(b) Br—CH₂—Br  \[\xrightarrow{\text{K}_2\text{MnO₄}, \text{EtOH, heat}}\] \(\text{HOCHCH₃COOMgBr} \xrightarrow{\text{H}_2\text{O}}\) \(\text{HOCH}_{2} \text{COOH}\)  
(c) CH₂—CH₂—CH₃  \[\xrightarrow{\text{K}_2\text{MnO₄}, \text{H}_2\text{O}^-, \text{heat}}\] \(\text{HOCH}_{2} \text{COOH} + \text{CHCl}_3\)  
(d) CH₃C=CH₂  \[\xrightarrow{(1) \text{K}_2\text{MnO₄}, \text{OH}^-, \text{heat}}\] \(\text{HOCH}_{2} \text{COOH}\)  
(e) CH₂=CH—OH  \[\xrightarrow{(1) \text{K}_2\text{MnO₄}, \text{OH}^-, \text{heat}}\] \(\text{HOCH}_{2} \text{COOH}\)  
(f) CH₃C=CH₂  \[\xrightarrow{(1) \text{K}_2\text{MnO₄}, \text{OH}^-, \text{heat}}\] \(\text{HOCH}_{2} \text{COOH}\)

18.7 These syntheses are easy to see if we work backward.
(a) \(\text{C}_2\text{H}_5\text{CH}_2\text{COOH} \xrightarrow{(1) \text{CO}_2, (2) \text{H}^+}\) \(\text{C}_2\text{H}_4\text{CH}_2\text{MgBr} \xrightarrow{\text{EtOH}}\) \(\text{C}_2\text{H}_5\text{CH}_2\text{Br}\)  
(b) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{(1) \text{CO}_2, (2) \text{H}^+}\) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{MgBr} \xrightarrow{\text{EtOH}}\) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}\)  
(c) \(\text{CH}_2=\text{CHCH}_2\text{COOH} \xrightarrow{(1) \text{CO}_2, (2) \text{H}^+}\) \(\text{CH}_2=\text{CHCH}_2\text{MgBr} \xrightarrow{\text{EtOH}}\) \(\text{CH}_2=\text{CHCH}_2\text{Br}\)  
(d) \(\text{H}_2\text{C}=\text{CH}—\text{COOH} \xrightarrow{(1) \text{CO}_2, (2) \text{H}^+}\) \(\text{H}_2\text{C}=\text{CH}—\text{MgBr} \xrightarrow{\text{EtOH}}\) \(\text{H}_2\text{C}=\text{CHCH}_2\text{Br}\)  
(e) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{(1) \text{CO}_2, (2) \text{H}^+}\) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{MgBr} \xrightarrow{\text{EtOH}}\) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}\)

18.8 (a) \(\text{C}_2\text{H}_5\text{CH}_2\text{COOH} \xrightarrow{(1) \text{CN}, (2) \text{H}^+, \text{H}_2\text{O}, \text{heat}}\) \(\text{C}_2\text{H}_5\text{CH}_2\text{Br}\)  
(b) \(\text{CH}_2=\text{CHCH}_2\text{COOH} \xrightarrow{(1) \text{CN}, (2) \text{H}^+, \text{H}_2\text{O}, \text{heat}}\) \(\text{CH}_2=\text{CHCH}_2\text{Br}\)  
(c) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{(1) \text{CN}, (2) \text{H}^+, \text{H}_2\text{O}, \text{heat}}\) \(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}\)  

(b) A nitrile synthesis. Preparation of a Grignard reagent from HOCH₃CH₂CH₂CH₂Br would not be possible because of the presence of the acidic hydroxyl group.

18.9 Since maleic acid is a cis dicarboxylic acid, dehydration occurs readily:

\[
\begin{align*}
\text{Maleic acid} & \xrightarrow{200°C} \text{Maleic anhydride} + \text{H}_2\text{O}
\end{align*}
\]
Being a trans di-carboxylic acid, fumaric acid must undergo isomerization to maleic acid first. This isomerization requires a higher temperature.

18.10 The labeled oxygen atom should appear in the carboxyl group of the acid. (Follow the reverse steps of the mechanism in Section 18.7A of the text using $\text{H}_2^{18}\text{O}$.)

18.11 Method (3) should give a higher yield of $F$ than method (4). Since the hydroxide ion is a strong base and since the alkyl halide is secondary, method (4) is likely to be accompanied by considerable elimination. Method (3), on the other hand, employs a weaker base, acetate ion, in the $S_2$ step and is less likely to be complicated by elimination. Hydrolysis of the ester $E$ that results should also proceed in high yield.

18.12 (a) Steric hindrance presented by the di-ortho methyl groups of methyl mesitote prevents formation of the tetrahedral intermediate that must accompany attack at the acyl carbon.

(b) Carry out hydrolysis with labeled $^{18}\text{OH}^-$ in labeled $\text{H}_2^{18}\text{O}$. The label should appear in the methanol.

18.13 

(a) 

(b) 

18.14 (a) 

(b)
CARBOXYLIC ACIDS AND THEIR DERIVATIVES

18.15 (a) \((\text{CH}_3)_2\text{CCO}_2\text{H} \xrightarrow{\text{SOCl}_2} (\text{CH}_3)_2\text{CCOCI} \xrightarrow{\text{NH}_3} (\text{CH}_3)_2\text{CCONH}_2\)

P_{\text{O}_2} \xrightarrow{\text{heat}} (\text{CH}_3)_2\text{CC}=\text{N}

(b) An elimination reaction would take place because CN\(^-\) is a strong base.

\[
\text{CN} + \text{H} = \text{C} = \text{Br} \rightarrow \text{HCN} + \text{CH}_2 = \text{CH}_3 + \text{Br}^-
\]

18.16 (a) \[\text{CH}_2\text{OH} + \text{O} = \text{C} = \text{N} \rightarrow \text{CH}_2\text{O} = \text{C} = \text{N} \]

(b) \[\text{Cl} = \text{C} = \text{Cl} + 4\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{N} = \text{C} = \text{NCH}_3 + 2\text{CH}_3\text{NH}_3 + 2\text{Cl}^-\]

(c) \[\text{CH}_2\text{O} = \text{Cl}^- + \text{H}_2\text{NCH}_2\text{CO}_2^- \xrightarrow{\text{HF}} \text{CH}_2\text{O} = \text{C} = \text{NCH}_2\text{CO}_2^- + \text{Cl}^-\]

(d) \[\text{CH}_2\text{OCNHCH}_2\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{PO}_4} \text{H}_2\text{NCH}_2\text{CO}_2^- + \text{CO}_2 + \text{CH}_3\text{H}_2\]

18.17 (a) By decarboxylation of a \(\beta\)-keto acid:

\[
\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} + \text{CO}_2
\]

(b) By decarboxylation of a substituted malonic acid:

\[
\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} + \text{CO}_2
\]

(c) By decarboxylation of a \(\beta\)-keto acid:

\[
\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} + \text{CO}_2
\]

(d) By decarboxylation of a substituted malonic acid:

\[
\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H} + \text{CO}_2
\]

18.18 (a) The oxygen-oxygen bond of the dialky peroxide has a low homolytic bond dissociation energy \((\Delta H^\circ = 146 \text{ kJ mol}^{-1})\). This allows the following reaction to occur at a moderate temperature.

\[
\text{R} = \text{C} = \text{O} = \text{O} = \text{R} \rightarrow 2 \text{R} = \text{C} = \text{O} \quad \Delta H^\circ = 146 \text{ kJ mol}^{-1}
\]

(b) By decarboxylation of the carboxylate radical produced in part (a).

\[\text{R} = \text{C} = \text{O}^\bullet \rightarrow \text{R}^\bullet + \text{CO}_2\]
(c) Chain Initiation

\[
\text{Step 1: } R\text{-C-O-O-C-R} \xrightarrow{\text{heat}} 2 R\text{-C-O-}.
\]

\[
\text{Step 2: } R\text{-C-O} \rightarrow R^* + \text{CO}_2.
\]

Chain Propagation

\[
\text{Step 3: } R^* + \text{CH} = \text{CH}_2 \rightarrow \text{RCH}_2\text{CH}_2^*.
\]

\[
\text{Step 4: } \text{RCH}_2\text{CH}_2^* + \text{CH} = \text{CH}_2 \rightarrow \text{RCH}_2\text{CHCHCH}_2^*.
\]

Step 3, 4, 3, 4, and so on.

18.20

(a) Benzoic acid
(b) Benzoyl chloride
(c) Benzamide
(d) Benzoic anhydride
(e) Benzyl benzoate
(f) Phenyl benzoate
(g) Isopropyl acetate or 1-methylethyl ethanoate
(h) N,N-Dimethylacetamide or N,N-dimethyl ethanamide
(i) Acetonitrile or ethanenitrile

18.21

(a) CH\text{O}\text{H}\text{-CH}_3 \xrightarrow{(1) \text{KMnO}_4, \text{OH}^-, \text{heat}} \text{CH}_3\text{-COO}^-
\]

(b) Cl\text{H}\text{-CH}_3 \xrightarrow{\text{NBS}} \text{Cl}\text{-CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaCN}} \text{Cl}\text{-CH}_2\text{CH} = \text{CH}_2
\]

(c) Cl\text{H}\text{-CO}_2\text{H} \xrightarrow{(1) \text{SOCl}_2} \text{Cl}\text{-CH} = \text{CHCH} \xrightarrow{[\text{from (a)}]} \text{Cl}\text{-CH} = \text{CHCH} \xrightarrow{\text{HCN}}
\]

(d) Cl\text{H}\text{-CH} = \text{CHCN} \xrightarrow{\text{H}_2\text{O}^+, \text{H}_2\text{O} \text{heat}} \text{Cl}\text{-CH}_2\text{CHCO}_2\text{H}
\]

(e) HO\text{CCH}_2\text{OH} \xrightarrow{\text{H}_2\text{O}^+, \text{H}_2\text{O} \text{heat}} \text{Cl}\text{-CH}_2\text{CHCO}_2\text{H}
\]

(f) HO\text{CCH}_2\text{OH} \xrightarrow{\text{H}_2\text{O}^+, \text{H}_2\text{O} \text{heat}} \text{Cl}\text{-CH}_2\text{CHCO}_2\text{H}
\]

(g) HO\text{CCH}_2\text{OH} \xrightarrow{\text{H}_2\text{O}^+, \text{H}_2\text{O} \text{heat}} \text{Cl}\text{-CH}_2\text{CHCO}_2\text{H}
\]
CARBOXYLIC ACIDS AND THEIR DERIVATIVES

18.24 (a) $\text{CH}_3\text{CO}_2\text{H} + \text{HCl}$
(b) $\text{CH}_3\text{C}(\text{CH}_3)_2$
(c) $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}(\text{CH}_3)_2\text{CH}_3$
(d) $\text{CH}_3\text{CONH}_2$
(e) $\text{CH}_2\text{C}=\text{CH}_2$
(f) $\text{CH}_2\text{CHO}$

(g) $\text{CH}_2\text{CO}_2\text{Na}$
(h) $\text{CH}_3\text{CO}_2\text{Na}$
(i) $\text{CH}_2\text{CONHCH}_3$
(j) $\text{CH}_3\text{CONHCH}_3$
(k) $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)_2$
(l) $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$

18.25 (a) $\text{CH}_3\text{CONH}_2 + \text{CH}_3\text{CO}_2^- + \text{NH}_4^+$
(b) $2\text{CH}_3\text{CO}_2\text{H}$
(c) $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CO}_2\text{H}$
(d) $\text{C}_6\text{H}_5\text{COCH}_2$ + $\text{CH}_3\text{CO}_2\text{H}$
(e) $\text{CH}_3\text{CONHCH}_2\text{CH}_3 + \text{CH}_3\text{CO}_2^- + \text{CH}_3\text{NH}_4^+$
(f) $\text{CH}_3\text{CONCH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CO}_2^- (\text{CH}_3\text{CH}_2)_2\text{NH}_4^+$

18.26 (a) $\text{CONH}_2$
(b) $\text{CH}_2\text{CO}_2^- \text{NH}_4^+$
(c) $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$
(d) $\text{CONHCH}_2\text{CH}_3$
(e) $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$
(f) $\text{CH}_2\text{CO}_2^- (\text{CH}_3\text{CH}_2)_2\text{NH}_4^+$
18.27

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H} + \text{NaOEt} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}
\]

18.28

(a) \[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{HCO}_2\text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCO}_2\text{H}
\]

(b) \[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCO}_2\text{H}
\]

(c) \[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{HCO}_2\text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCO}_2\text{H}
\]

18.29

(a) \[
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
\]

(b) \[
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
\]

(c) \[
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
\]

(d) \[
\text{CH}_3\text{CH}_2\text{CONHCH}_3 + \text{CH}_3\text{CH}_2\text{OH}
\]

(e) \[
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{OH}
\]

(f) \[
\text{CH}_3\text{CH} = \text{C}_2\text{H}_5 + \text{CH}_3\text{CH}_2\text{OH}
\]

18.30

(a) \[
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{NaOEt} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{Et}
\]

(b) \[
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
\]

(c) \[
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
\]

18.31 See the mechanisms in Section 18.8F, where R = CH$_2$CH$_3$ for propanamide.

18.32

(a) \[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{HCO}_2\text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCO}_2\text{H}
\]

(b) \[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCO}_2\text{H}
\]

(c) \[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{HCO}_2\text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCO}_2\text{H}
\]

(f) \[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CH} = \text{CHCO}_2\text{H}
\]

18.33

(a) \[
\text{HO}_2\text{CH} = \text{CH}_2 + \text{TsCl}, \text{pyridine} \rightarrow \text{TsO}_2\text{CH} = \text{CH}_2
\]

(b) \[
\text{TsO}_2\text{CH} = \text{CH}_2 \rightarrow \text{CN}^- \rightarrow \text{TsO}_2\text{CH} = \text{CH}_2
\]

(R)-(-)-2-butanol

(+ C) \[
\text{H}_2\text{SO}_4, \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_2\text{H}
\]

(-) D

(-) D

See text, p. 677.
An interpretation of the $^1$H NMR spectral data for phenacetin is as follows:

(a) triplet $\delta 1.4$
(b) singlet $\delta 2.1$
(c) quartet $\delta 3.95$
(d) multiplet $\delta 6.8-7.4$
(e) broad singlet $\delta 9.0$

18.36 (a) $\text{CH}_3\text{CH}_2\text{O} - \text{C} - \text{CH}_3 - \text{O} - \text{CH}_3\text{CH}_2$

Interpretation:
(a) triplet $\delta 1.2$ (6H)  $\text{C} - \text{O} -$, 1740 cm$^{-1}$ (ester)
(b) singlet $\delta 2.3$ (4H)
(c) quartet $\delta 4.1$ (4H)

(b) $\text{O} - \text{C} - \text{CH}_3$

Interpretation:
(a) doublet $\delta 1.0$ (6H)  $\text{C} - \text{O} -$, 1720 cm$^{-1}$ (ester)
(b) multiplet $\delta 2.1$ (1H)
(c) doublet $\delta 4.1$ (2H)
(d) multiplet $\delta 7.8$ (5H)

18.37 $\text{Ph} + \text{SOCl}_2 \rightarrow \text{PhCOCl} \rightarrow \text{PhCON(CH}_2\text{CH}_3)_2$
18.38 Alkyl groups are electron releasing; they help disperse the positive charge of an alkylammonium salt and thereby help to stabilize it.

\[
R\text{NH}_2 + \text{H}_2\text{O}^+ \rightarrow R+\text{NH}_3^+ + \text{H}_2\text{O}
\]
Stabilized by electron-releasing alkyl group

Consequently, alkylamines are somewhat stronger bases than ammonia.

Amides, on the other hand, have acyl groups, \(R=\_\text{O}\), attached to nitrogen, and acyl groups are electron withdrawing. They are especially electron withdrawing because of resonance contributions of the kind shown here.

\[
R\text{C} \equiv \text{N}-\text{H}_2 \leftrightarrow R\text{C} \equiv \text{N}=\text{H}_2
\]
This kind of resonance also stabilizes the amide. The tendency of the acyl group to be electron withdrawing, however, destabilizes the conjugate acid of an amide, and reactions such as the following do not take place to an appreciable extent.

\[
R\text{C} \equiv \text{N}-\text{H}_2 + \text{H}_2\text{O}' \leftrightarrow R\text{C} \equiv \text{N}=\text{H}_2^+ + \text{H}_2\text{O}
\]
Stabilized by resonance

18.39 (a) The conjugate base of an amide is stabilized by resonance.

\[
R\text{C} \equiv \text{N}=\text{H}^- + \text{BH} \leftrightarrow R\text{C} \equiv \text{N}-\text{H}_2 + \text{H}_2\text{O}
\]
Stabilized by electron-withdrawing acyl group

18.40 That compound \(X\) does not dissolve in aqueous sodium bicarbonate indicates that \(X\) is not a carboxylic acid. That \(X\) has an IR absorption peak at 1740 cm\(^{-1}\) indicates the presence of a carbonyl group, probably that of an ester (Table 18.5). That the molecular formula of \(X/(\text{C}_2\text{H}_4\text{O}_2)\) contains four oxygen atoms suggests that \(X\) is a diester.

The \(^{13}\text{C}\) spectrum shows only four signals indicating a high degree of symmetry for \(X\). The single signal at 166.7 is that of an ester carbonyl carbon, indicating that both ester groups of \(X\) are equivalent.

Putting these observations together with the information gathered from DEPT \(^{13}\text{C}\) spectra and the molecular formula leads us to the conclusion that \(X\) is diethyl malonate. The assignments are

<table>
<thead>
<tr>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{O} \equiv \text{C} \equiv \text{O} \text{CH}_2\text{CH}_3)</td>
</tr>
<tr>
<td>(a) 84.12</td>
</tr>
<tr>
<td>(b) 41.6</td>
</tr>
<tr>
<td>(c) 61.3</td>
</tr>
<tr>
<td>(d) 166.7</td>
</tr>
</tbody>
</table>

18.41 (a) Chain Initiation

Step 1 \(\text{RO} \equiv \text{OR} \rightarrow 2 \text{RO}^*\)

Step 2 \(\text{CH}_3\text{CS} \equiv \text{H} + \text{RO}^* \rightarrow \text{CH}_3\text{CS}^* + \text{ROH}\)

Chain Propagation

Step 3 \(\text{CH}_3\text{CS}^* + \text{CH} \equiv \text{CHR} \rightarrow \text{CH}_3\text{CS} \equiv \text{CHR}\)

Step 4 \(\text{CH}_3\text{CSS} \equiv \text{CHR} + \text{CH}_3\text{CS} \equiv \text{H} \rightarrow \text{CH}_3\text{CSS} \equiv \text{CHR} + \text{CH}_3\text{CS}^*\)
18.42 *cis*-4-Hydroxycyclohexanecarboxylic acid can assume a boat conformation that permits lactone formation.

Neither of the chair conformations nor the boat form of *trans*-4-hydroxycyclohexanecarboxylic acid places the -OH group and the -CO₂H group close enough together to permit lactonization.

18.43

(a) Replacement of either alcoholic -OH by a reaction that proceeds with inversion produces the same stereoisomer.

(b) Two. The stereoisomer given in (b) and the one given next, below.
18.45 (a) CH$_3$O$_2$C—C==C—CO$_2$CH$_3$. This is a Diels-Alder reaction. 
(b) H$_2$, Pd. The disubstituted double bond is less hindered than the tetrasubstituted double bond and hence is more reactive.
(c) CH$_3$==CH—CH==CH$_2$. Another Diels-Alder reaction.
(d) LiAlH$_4$
(e) CH$_3$SO$_2$Cl and pyridine
(f) CH$_3$CH$_2$S$^-$
(g) OsO$_4$
(h) Raney Ni
(i) Base. This is an aldol condensation.
(j) C$_5$H$_5$Li (or C$_5$H$_5$MgBr) followed by H$_2$O$^+$
(k) H$_2$O$^+$. This is an acid-catalyzed rearrangement of an allylic alcohol.
(l) CH$_3$CCl$_3$, pyridine
(m) O$_3$, followed by oxidation
(n) Heat

18.46 (a) Furan + Dimethylmaleic anhydride

(b) Cantharidin apparently undergoes dehydrogenation to the Diels-Alder adduct shown here, and then the adduct spontaneously decomposes through a reverse Diels-Alder reaction to furan and dimethylmaleic anhydride. These results suggest that the attempted Diels-Alder synthesis fails because the position of equilibrium favors reactants rather than products.

18.47 The very low hydrogen content of the molecular formula of Y ($C_7H_8O_3$) indicates that Y is highly unsaturated. That Y dissolves slowly in warm aqueous NaHCO$_3$ suggests that Y is a carboxylic acid anhydride that hydrolyzes and dissolves because it forms a carboxylate salt:

The infrared absorption peaks at 1779 and 1754 cm$^{-1}$ are consistent with those of an aromatic carboxylic anhydride (Table 18.5).

That only four signals appear in the $^{13}$C spectrum of Y indicates a high degree of symmetry for Y. Three of the signals occur in the aromatic region (δ 120–140) and one signal is downfield (δ 163.1)

These signals and the information from the DEPT $^{13}$C NMR spectra lead us to conclude that Y is phthalic anhydride. The assignments are

Z is phthalic acid and AA is ethyl hydrogen phthalate.

18.48 (a) Ethyl acetate (b) Acetic anhydride (c) N-Ethylacetamide.

18.49 In the first instance, nucleophilic attack by the amine occurs preferentially at the less hindered carbon of the formyl group. (Recall that aldehydes are more reactive than ketones toward nucleophiles for the same reason.) In the second case, CF$_3$CO$_2$ $^-$ is a better leaving group than CF$_3$CO$_2$ $^+$ since the former is the conjugate base of the stronger acid.

18.50
18.51 \[ \text{C}_2\text{H}_4 + (\text{CH}_3)_2\text{CHCl} \xrightarrow{\text{AlCl}_3} \text{C}(\text{CH}_3)_2\text{CHCH} = \text{C}(\text{CH}_3)_2 \]  
Clemmensen or Wolff-Kishner

18.52

\[
\begin{align*}
A &= \text{CH}_3\text{C} = \text{C}(\text{CH}_3)_2 \\
B &= \text{CH}_3\text{CH}_2\text{CH} = \text{C}(\text{CH}_3)_2 \\
C &= \text{CH}_3\text{CH}_2\text{CH} = \text{C}(\text{CH}_3)_2 \\
D &= \text{CH}_3\text{CH}_2\text{CH} = \text{C}(\text{CH}_3)_2 \\
\end{align*}
\]

In the last step, Hi/red P accomplishes both the reduction of \(-\text{OH}\) to \(-\text{H}\) and the hydrolysis of the nitrile function.

18.53

(a) The signal at \(\delta 193.8\) is consistent with the carbonyl carbon of an aldehyde and shows that the PCC reaction produced cinnamaldehyde.

(b) The signal at \(\delta 164.5\) is consistent with the carbonyl carbon of a carboxylic acid and suggests that the oxidation with \(\text{K}_2\text{Cr}_2\text{O}_7\) in sulfuric acid produced cinnamic acid.

18.54

\[
\begin{align*}
&\text{S} = \text{C} \quad \text{HO}^- \\
&\text{C} = \text{C} \quad \text{O} \\
&\text{O} = \text{C} \quad \text{S} \\
&\text{H} = \text{O} \\
\end{align*}
\]

(IN absorption at 2550 cm\(^{-1}\) is \(\text{S} = \text{H}\) stretch)

18.55

\[
\begin{align*}
&\text{C} = \text{O} \\
&\text{D} = \text{O} \\
&\text{E} = \text{Cl} \\
&\text{F} = \text{N} \\
\end{align*}
\]

**QUIZ**

18.1 Which of the following would be the strongest acid?

(a) Benzoic acid  (b) 4-Nitrobenzoic acid  (c) 4-Methylbenzoic acid  
(d) 4-Methoxybenzoic acid  (e) 4-Ethylbenzoic acid

18.2 Which of the following would yield (S)-2-butanol?

(a) (R)-2-Bromobutane + \(\text{CH}_3\text{CO}^-\text{Na}^+\) \(\xrightarrow{\text{heat}}\) product \(\text{OH}^-\text{H}_2\text{O}\)  
(b) (R)-2-Bromobutane \(\xrightarrow{\text{OH}^-\text{H}_2\text{O}^\text{heat}}\)  
(c) (S)-2-Butyl acetate \(\xrightarrow{\text{OH}^-\text{H}_2\text{O}^\text{heat}}\)  
(d) All of the above  
(e) None of the above
18.3 Which reagent would serve as the basis for a simple chemical test to distinguish between hexanoic acid and hexanamide?
(a) Cold dilute NaOH  
(b) Cold dilute NaHCO₃  
(c) Cold concd. H₂SO₄  
(d) More than one of these  
(e) None of these

18.4 Give an acceptable name for:

CH₃CH₂CH₂OH  
CO₂CH₃  
NHCH₃

18.5 Complete the following syntheses.

(a) \( \text{CH}_3\text{CHCOH} \xrightarrow{\text{H}_2\text{O}} \text{COOH} \)

(b) \( \text{CCl}_3 + \text{CH}_2\text{OH} \xrightarrow{\text{NaOH, H}_2\text{O, heat}} \text{Cl} \)

(c) \( \text{C}_6\text{H}_5\text{NHCl} + \text{NH}_3(\text{aq}) \xrightarrow{\text{NaOH, H}_2\text{O, heat}} \text{Cl} + \text{NH}_4\text{Cl} \)

(d) \( \text{C}_6\text{H}_5\text{COCl} + \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{DIBAL-H, hexane, -78°C}} \text{Cl} + \text{C}_6\text{H}_5\text{CO}_2\text{H} \)

(e) \( \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{CH}_3\text{COOH}} \text{Cl} + \text{C}_6\text{H}_5\text{NH}_2\text{C}_6\text{H}_5\text{CO}_2^- \)
SPECIAL TOPIC B
Step-Growth Polymers

SOLUTIONS TO PROBLEMS

B.1 (a) \[ \text{R}^3 \xrightarrow{\text{HCOOH}} \text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H} \]

(b) \[ \text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H} + 2 \text{NH}_3 \rightarrow \text{NH}_2\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{NH}_4 \xrightarrow{\text{heat}} -2\text{H}_2\text{O} \]

(c) \[ \text{OH} \xrightarrow{\text{N} = \text{C}(\text{CH}_2)_2\text{C} = \text{N}} \text{H}_2\text{NCH}_2(\text{CH}_2)_2\text{CH}_2\text{NH}_2 \]

(d) \[ \text{OH} \xrightarrow{\text{N} = \text{C}(\text{CH}_2)_2\text{C} = \text{N}} \text{H}_2\text{NCH}_2(\text{CH}_2)_2\text{CH}_2\text{NH}_2 \]

B.2 (a) \[ \text{HOCH}_2\text{CH}_2\text{OH} + \text{BH}^- \xleftrightarrow{\text{HB}} \text{HOCH}_2\text{CH}_2\text{O}^- + \text{HB} \]

(b) \[ \text{ROC-} \xrightarrow{\text{O}} \text{ROC-} + \text{OCH}_2\text{CH}_2\text{OH} \]

(c) \[ \text{ROC-} \xrightarrow{\text{O}} \text{ROC-} + \text{OCH}_2\text{CH}_2\text{OH} \]

B.3 (a) \[ \text{CH}_3\text{OC} \xrightarrow{\text{O}} \text{CH}_3\text{OH} + \text{HOCH}_2\text{CH}_2\text{OH} \]

(b) By high-pressure catalytic hydrogenation

B.4 etc-\text{OCH}_2\text{CH}_2\text{OC} \xrightarrow{\text{O}} \text{etc-CH}_2\text{CH}_2\text{OC} \xrightarrow{\text{O}} \text{etc.}

B.5 \[ \text{HO-} \xrightarrow{\text{Cl} = \text{O}} \text{CH}_3 \xrightarrow{\text{Cl} = \text{O}} \text{etc.} \]

Lexan
B.6 (a) The resin is probably formed in the following way. Base converts the bisphenol A to a phenoxide ion that attacks a carbon atom of the epoxide ring of epichlorohydrin:

\[
\begin{align*}
\text{ClCH}_2\text{CH}_2\text{O} & \quad \text{OH} + \text{[polymer]} - \text{CH}_2(\text{OH}) - \text{CH}_2 \\
\text{ClCH}_2\text{CH}_2\text{O} & \quad \text{Cl} \quad \text{O} \\
\text{ClCH}_2\text{CH}_2\text{O} & \quad \text{OH} \quad \text{OH}
\end{align*}
\]

(b) The excess of epichlorohydrin limits the molecular weight and ensures that the resin has epoxy ends.

(c) Adding the hardener brings about cross-linking by reacting at the terminal epoxide groups of the resin:

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \quad \text{H}_2\text{O} \quad \text{CH}_2(\text{OH}) \quad \text{CH}_2 \\
\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \quad \text{H}_2\text{O} \quad \text{CH}_2(\text{OH}) \quad \text{CH}_2
\end{align*}
\]

B.7 (a) Bakelite

B.8 Because the para position is occupied by a methyl group, cross-linking does not occur and the resulting polymer remains thermoplastic (See Section B.4.)

B.9 (as before)
SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS: MORE CHEMISTRY OF ENOLATE ANIONS

SUMMARY OF ACETOACETIC ESTER AND MALONIC ESTER SYNTHESSES

A. Acetoacetic Ester Synthesis

\[
\text{R'COCH}_{2}\text{COEt} \xrightarrow{\text{NaOEt}} \text{R'COCH}_{2}\text{COEt} \xrightarrow{\text{RX}} \text{R'COCH}_{2}\text{COEt} \xrightarrow{\text{HX-H2O}} \text{R'COCH}_{2}\text{COEt} \xrightarrow{\text{heat}} \text{R'COCH}_{2}\text{COEt}
\]

B. Malonic Ester Synthesis

\[
\text{HOOCCH}_{2}\text{COEt} \xrightarrow{\text{NaOEt}} \text{HOOCCH}_{2}\text{COEt} \xrightarrow{\text{RX}} \text{HOOCCH}_{2}\text{COEt} \xrightarrow{\text{HX-H2O}} \text{HOOCCH}_{2}\text{COEt} \xrightarrow{\text{heat}} \text{HOOCCH}_{2}\text{COEt}
\]

SOLUTIONS TO PROBLEMS

19.1 (a) Step 1
\[
\text{CH}_3\text{CH}=-\text{COCH}_3 \xrightarrow{\text{OCCH}_3} \text{CH}_3\text{CH}=-\text{COCH}_3 + \text{C}_2\text{H}_5\text{OH}
\]

19.2 (b) To undergo a Dieckmann condensation, diethyl glutarate would have to form a highly strained four-membered ring.

19.3
\[
\text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5\text{O}^- \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5\text{OH}
\]

\[
\text{C}_4\text{H}_6\text{OCHOAc} + \text{CH}_3\text{COCH}_3 \xrightarrow{\text{H}_2\text{O}} \text{C}_4\text{H}_6\text{OCHOAc} + \text{CH}_3\text{COCH}_3
\]

\[
\text{C}_4\text{H}_6\text{OCHOAc} + \text{C}_2\text{H}_5\text{O}^- \xrightarrow{\text{H}_2\text{O}} \text{C}_4\text{H}_6\text{OCHOAc} + \text{C}_2\text{H}_5\text{OH}
\]

\[
\text{C}_4\text{H}_6\text{OCHOAc} + \text{C}_2\text{H}_5\text{O}^- \xrightarrow{\text{H}_2\text{O}} \text{C}_4\text{H}_6\text{OCHOAc} + \text{C}_2\text{H}_5\text{OH}
\]
366 SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS

19.4 (a) \( \text{CH}_3\text{CH}_2\text{O}C\text{H}_3 + \text{C}_2\text{H}_5\text{OCOC}_2\text{H}_5 \xrightarrow{(1) \text{NaOCH}_2\text{CH}_3} \text{CH}_3\text{CHOC}_2\text{H}_5 \xrightarrow{(2) \text{H}_2\text{O}^+} \text{CH}_3\text{CHOC}_2\text{H}_5 \)

(b) \( \text{CH}_3\text{COOC}_2\text{H}_5 + \text{HCOC}_2\text{H}_5 \xrightarrow{(1) \text{NaOCH}_2\text{CH}_3} \text{HCOCOC}_2\text{H}_5 \xrightarrow{(2) \text{H}_2\text{O}^+} \text{HCOCOC}_2\text{H}_5 \)

19.5 (a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{O} \xrightarrow{(1) \text{NaOCH}_2\text{CH}_3} \text{CH}_3\text{CH}_2\text{O} \xrightarrow{(2) \text{H}_2\text{O}^+} \text{CH}_3\text{CH}_2\text{O} \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OCOC}_2\text{H}_5 \xrightarrow{(1) \text{NaOCH}_2\text{CH}_3} \text{CH}_3\text{CH}_2\text{OCOC}_2\text{H}_5 \xrightarrow{(2) \text{H}_2\text{O}^+} \text{CH}_3\text{CH}_2\text{OCOC}_2\text{H}_5 \)

(c) \( \text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{OCOC}_2\text{H}_5 \xrightarrow{(1) \text{NaOCH}_2\text{CH}_3} \text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{OCOC}_2\text{H}_5 \xrightarrow{(2) \text{H}_2\text{O}^+} \text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{OCOC}_2\text{H}_5 \)

The partially negative oxygen atom of sodioacetoacetic ester acts as the nucleophile.

19.6 \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCOC}_2\text{H}_5 + \text{C}_4\text{H}_6 \xrightarrow{\text{dil. NaOH, heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCOC}_2\text{H}_5 \)

19.7 Again, working backward.

(a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO} \xrightarrow{(1) \text{dil. NaOH, heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2 \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO} \xrightarrow{(1) \text{dil. NaOH, heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2 \)
Synthesis and Reactions of \( \beta \)-Dicarbonyl Compounds

19.9 (a) Reactivity is the same as with any \( S_n^2 \) reaction. With primary halides substitution is highly favored, with secondary halides elimination competes with substitution, and with tertiary halides elimination is the exclusive course of reaction.

(b) Acetoacetic ester and 2-methylpropene

(c) Bromobenzene is unreactive to nucleophilic substitution.

19.10 \( \text{CH}_3\text{CCH}_2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H} \)

19.11 The carboxyl group that is lost more readily is the one that is \( \beta \) to the keto group (cf. Section 18.11 of the text).
Then the anion of acetoacetic ester adds to the benzene as it forms in the mixture.

This is the end product of the addition.

(b) 1-phenyl-2-propanone, as follows:

(c) By treating bromobenzene with diethyl malonate and two molar equivalents of NaNH₂ to form diethyl phenylmaleinate.

The mechanism for this reaction is analogous to that given in part (a).

Then hydrolysis and decarbonylation will convert diethyl phenylmaleinate to phenylacetic acid.

19.15 Here we alkylate the dianion,

19.16 Working backward,

19.17 2H₂-C-CH₂-CH₂-Br + H₂C-CH₂-Br

base

-COEt

H₂O
SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS

19.18 (a) Formaldehyde, H-O-H

(b) C4H4 Li - C3H3

(c) C6H5CH3 + HSCH2CH2SH → HA → H2C=CH2

19.19 By treating the thioetel with Raney nickel.

19.20 (a) 2 C6H5Li → C6H5CH3 + HSCH2CH2SH → hydrolysis

(b) C6H5C=CH3 + 2 HSCH2CH2SH → HA → C6H5CH3 + HSCH2CH2SH

19.21 (a) Valproic acid

(b) A malonic acid

19.22 (a) C=O + HN(CH3)2 → CH3N(CH3)2 + H2O

(b) C=O + CH3CH2CH2CH2CH3 → CH3CH2CH2CH2CH3
SYNTHESIS AND REACTIONS OF $\beta$-DICARBONYL COMPOUNDS

19.23 These syntheses are easier to see if we work backward.

19.24 (a) See Section 19.3.
SYNTHESIS AND REACTIONS OF \( \beta \)-DICARBONYL COMPOUNDS

19.28 (a) \( \text{CH}_3\text{CHCH}_2\text{CO}_2\text{H} \) → heat \( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \) (1) NaOCH, heat \( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \) (2) H\(_2\)O

(b) \( \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \) → LiAlH\(_4\) \( \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H} \) (1) NaOCH, heat

(c) \( \text{CH}_3\text{CHCH}_2\text{CO}_2\text{H} \) → heat \( \text{CH}_3\text{CHCH}_2\text{CO}_2\text{H} \) (1) NaOCH, heat \( \text{CH}_3\text{CHCH}_2\text{CO}_2\text{H} \) (2) H\(_2\)O

19.29 The following reaction took place:

\( \text{CH}_3\text{CHCH}_2\text{CO}_2\text{H} + \text{BrCH}_2\text{CH}_2\text{Br} \) heat \( \text{BrCH}_2\text{CH}_2\text{CO}_2\text{H} \)
SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS

19.30 (a) \( \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{CO}_2\text{H}_2 + \text{NaOC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4\text{O}_2\text{C}_2\text{H}_5 \)

\[
\begin{align*}
\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}_5 & \xrightarrow{\text{KOC}_2\text{H}_5} \text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}_5 \\
\text{H}_2\text{C} \xrightarrow{\text{OH}, \text{H}_2\text{O}, \text{heat}} \text{H}_2\text{C} \text{CO}_2\text{H}_5
\end{align*}
\]

19.31 (a) \( \text{CH}_2(\text{CO}_2\text{H}_2)_2 + \text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4\text{O}_2\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \)

\[
\begin{align*}
\text{CH}_2(\text{CH} = \text{CH})_2\text{CO}_2\text{H}_5 & \xrightarrow{\text{OH}, \text{H}_2\text{O}, \text{heat}} \text{CH}_2(\text{CH} = \text{CH})_2\text{CO}_2\text{H}_5 \\
\text{CH}_2(\text{CH} = \text{CH})_2\text{CO}_2\text{H}_5 & \xrightarrow{\text{NaOC}_2\text{H}_5} \text{CH}_2(\text{CH} = \text{CH})_2\text{CO}_2\text{H}_5
\end{align*}
\]
SYNTHESIS AND REACTIONS OF \( \beta \)-DICARBONYL COMPOUNDS

(e) \[
\text{CH}_\text{3} \text{C}=\text{CH}_2 \text{COCH}_\text{3} + \text{H}_2\text{C}\text{==C} \text{CH} = \text{CH}_2 \rightleftharpoons \text{CH}_\text{3} \text{C}=\text{CH} \text{COCH}_\text{3} + \text{C}_2\text{H}_\text{5} \text{OH}
\]

The Michael reaction is reversible, and the reaction just given is an example of a reverse Michael reaction.

19.32 Two reactions take place. The first is a normal Knoevenagel condensation.

\[
\text{R} - \text{C} = \text{O} + \text{CH}_2(\text{COCH}_3)_2 \xrightarrow{\text{base}} \text{R} - \text{C} = \text{C} = \text{CH} \text{COCH}_3_2
\]

Then the \( \alpha, \beta \)-unsaturated diketone reacts with a second mole of the active methylene compound in a Michael addition.

19.33 \[
\text{CH}_3\text{CH}_2\text{OCOC}_\text{3} \xrightarrow{\text{HCO}_\text{2} \text{O}} \text{CH}_3\text{CH}_2\text{OCOC}_\text{3}
\]

\[
\text{H}_2\text{N}-\text{C}=\text{NH}_2 \xrightarrow{\text{NaO}_\text{2} \text{H}} \text{C}_\text{3} \text{H}_4 \text{O}_2 \text{N}
\]

\[
\text{thymine}
\]

19.34

\[
\text{O}
\]

\[
\text{CH}_3\text{CHBr}_{\text{2}} \xrightarrow{(1) \text{CH}_3\text{Mgl}} \xrightarrow{(2) \text{NH}_4^+ \text{ heat}} \xrightarrow{(1) \text{O}_2 \text{ (2) Zn, HOAc}}
\]

\[
\text{CH}_3\text{H}_2\text{Br}_2 \xrightarrow{\text{CH}_3(\text{COCH}_3)_2} \xrightarrow{2 \text{NaO}_\text{2} \text{H}} \text{C}_{13} \text{H}_2\text{O}_2
\]

19.35 \[
\text{CH}_2\text{C}=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_2\text{C}=\text{CHCH}_\text{Br}
\]

\[
\text{CH}_\text{3}\text{C}=\text{CHCH}_\text{3} \xrightarrow{\text{H}_2\text{O}} \text{OH} \xrightarrow{(1) \text{dil. NaOH, (2) H}_2\text{O, (3) heat}} \text{CH}_3\text{C}=\text{CHCH}_3\text{H}_2\text{CCH}_3
\]

\[
\text{G}
\]

\[
\text{H}
\]

19.36

\[
\text{CH}_3(\text{H}_2\text{O})_2 \xrightarrow{(1) \text{LiAlH}_4 \text{ (2) H}_2\text{O}} \text{CH}_3\text{OH}
\]

\[
\text{LiAlH}_4
\]

\[
\text{CH}_3\text{OH}
\]

\[
\text{HBr}
\]

\[
\text{C}_{13} \text{H}_2\text{O}_2
\]

\[
\text{C}_{13} \text{H}_2\text{O}_2
\]

\[
\text{C}_{13} \text{H}_2\text{O}_2
\]

\[
\text{C}_{13} \text{H}_2\text{O}_2
\]
SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS

19.37 (a) \( \text{ClCH}_2\text{CO},\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{O}^- \rightleftharpoons \text{Cl}-\text{CHCO},\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \)

(b) Decarboxylation of the epoxy acid gives an enol anion which, on protonation, gives an aldehyde.

(c) \( \beta\)-I onone

19.38 (a) \( \text{CH}_2\text{C} = \text{O} + \text{CH}_3\text{CH}_2\text{CO},\text{K} \rightleftharpoons \text{CH}_2\text{C} = \text{C}-\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{CO},\text{H} \)

19.39 (a) \( \text{CH} = \text{C}-\text{CO}_2\text{CH}_3 \)

(b) \( \text{KMn}_4\cdot\text{OH}^-, \text{then } \text{H}_2\text{O}^+ \)

(c) \( \text{CH}_3\text{OH}, \text{H}^+ \)

(d) \( \text{CH}_3\text{ONa}, \text{then } \text{H}^+ \)

(e) and (f) 

(g) \( \text{OH}^-, \text{H}_2\text{O}, \text{then } \text{H}_2\text{O}^+ \)

(i) \( \text{H}_2, \text{Pt} \)

(j) \( \text{BrCH}_2\text{CO},\text{CH}_3, \text{Zn}, \text{then } \text{H}_2\text{O}^+ \)

(k) 

(l) \( \text{Na}_2\text{NaNH}, \text{then } 2\text{CH}_3\text{I} \)

19.40 \( \text{CH}_3\text{CH}_2\text{CO},\text{CH}_3 + \text{HCHO} + \text{HN(CH}_3)_2 \xrightarrow{\text{Mannich reaction}} \)

19.41 In a polar solvent, such as water, the keto form is stabilized by solvation. When the interaction with the solvent becomes minimal, the enol form achieves stability by internal hydrogen bonding.
19.42 Intramolecular cyclization (which would give a product of formula \( C_6H_4O_3 \)) is not favored because of ring strain. The formula of the product actually obtained suggests a 1:1 intermolecular reaction:

\[
2 C_{12}H_{22}O_5 + NaOCH_3 \rightarrow
\]

\[
\text{Product}
\]

19.43 A gamma hydrogen is abstracted by base (as is an alpha hydrogen in the usual Claisen) to give a resonance-stabilized species:

\[
\begin{align*}
\text{CH}_3\text{CH} \equiv \text{CH} \equiv \text{COCH}_3 & \quad \text{CH}_3\text{CH} \equiv \text{CH} \equiv \text{OCCH}_3 \\
\end{align*}
\]

Ethyl crotonate differs from ethyl acetate by \(-\text{CH} \equiv \text{CH}-\), a vinyl group. The transmission of the stabilizing effect of the \(-\text{COOC}_2H_5\) group is an example of the principle of vinylogy.

19.44 The synthesis actually involves two sequential Claisen condensations, with ethyl acetate serving as the source of the carbanionic species.

\[
\begin{align*}
\text{Product} & \quad \text{not isolated}
\end{align*}
\]

\*19.45

\[
\begin{align*}
\text{Product} & \quad \text{Product}
\end{align*}
\]

\*19.46

\[
\begin{align*}
\text{HO} & \quad \text{Br} \quad \text{COOH} \\
\text{OH} & \quad \text{Br} \\
\text{OH} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

**Mannich reaction**

\[
\begin{align*}
\text{HO} & \quad \text{Br} \quad \text{COOH} \\
\text{OH} & \quad \text{Br} \\
\text{OH} & \quad \text{Br}
\end{align*}
\]

**Hydrogenolysis**
**QUIZ**

19.1 Which hydrogen atoms in the following ester are most acidic?

\[
\text{CH}_3\text{CH}_2\text{C}^\equiv\text{CH}_2\text{C}^\equiv\text{OCH}_2\text{CH}_3
\]

(a) \(a\) (b) \(b\) (c) \(c\) (d) \(d\) (e) \(e\)

19.2 What would be the product of the following reaction?

\[
\text{CH}_3\text{CH}_2\text{COEt} \xrightarrow{(1) \text{NaOCH}_2\text{CH}_3} \text{?} \xrightarrow{(2) \text{H}^+}
\]

(a) \(\text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_2\text{COEt}\) (b) \(\text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_3\)

(c) \(\text{CH}_3\text{CH}_2\text{CCH}_2\text{COEt}\) (d) \(\text{CH}_3\text{CCH}_2\text{CH}_2\text{COEt}\)

(e) \(\text{CH}_3\text{CH}_2\text{CHCH}_2\text{COEt}\)

19.3 What starting materials could be used in a crossed Claisen condensation to prepare the following compound?

\[
\text{EtO}^\equiv\text{C}^\equiv\text{CH}_2\text{COEt}
\]

(a) \(\text{CH}_3\text{CO}_2\text{Et}\) and \(\text{EtO}^\equiv\text{C}^\equiv\text{CH}_3\)

(b) \(\text{CH}_3\text{CH}_2\text{CO}_2\text{Et}\) and \(\text{EtO}^\equiv\text{C}^\equiv\text{CO}_2\text{Et}\)

(c) \(\text{CH}_3\text{CH}_2\text{CO}_2\text{Et}\) and \(\text{HCO}_2\text{Et}\)

(d) \(\text{EtO}_2\text{CCH}_2\text{CO}_2\text{Et}\) and \(\text{HCO}_2\text{Et}\)

(e) More than one of the above

19.4 Supply the missing reagents, intermediates, and products.

(a) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{COEt} + \text{EtO}_2\text{COEt}\) \(\xrightarrow{(1) \text{NaOCH}_2\text{CH}_3} \) \(\xrightarrow{(2) \text{H}^+ \text{(-EtOH)}}\) A

B

(c) \(\text{LDA} \xrightarrow{\text{THF}} \) A

B

(-Li)
SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS

SPECIAL TOPIC
Thiols, Sulfur Ylides, and Disulfides

SOLUTIONS TO PROBLEMS

C.1 (a) \( \text{cyclohexanone} + \text{CH}_2\text{S(CH}_3\text{)}_2 \rightarrow \text{cyclohexene} + \text{CH}_3\text{SCH}_3 \)

(b) \( \text{CH}_3\text{CH}_2\text{C}=\text{O} + \text{CH}_2\text{S(CH}_3\text{)}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{CH}_3 + \text{CH}_3\text{SCH}_3 \)

C.2 (a) \( \text{phenylketene} + \text{NH}_2\text{Br}^- \)

(b) \( \text{phenylketene} + \text{CH}_3\text{SH} \)

(c) \( \text{phenylketene} + \text{CH}_2\text{S-S-CH}_2\text{CH}_3 \)

(d) \( \text{phenylketene} + \text{Na}^+ \)

(e) \( \text{phenylketene} + \text{CH}_2\text{S-S-CH}_2\text{CH}_3 \)

C.3 \( \text{CH}_2\text{=CHCH}_2\text{Br} + \text{S}^\text{=C}\text{H}_2\text{NH}_2 \)

(1) \( \text{CH}_3\text{CH}_2\text{OH} \)

(2) \( \text{H}_2\text{O} \)

\( \text{CH}_2\text{=CHCH}_2\text{SH} \)

\( \text{CH}_2\text{=CHCH}_2\text{SH} \)

C.4 \( \text{CH}_2\text{=CHCH}_2\text{OH} \)

\( \text{Br}_2 \rightarrow \text{CH}_2\text{BrCHBrCH}_2\text{OH} \)

\( \text{NaSH} \rightarrow \text{CH}_2\text{=CH}-\text{CH}_2\text{OH} \)

\( \text{OH} \rightarrow \text{OH} \)
C.5 (a) \( \text{CICH}_2\text{CH}_3\text{C(CH}_2\text{)}_4\text{CO}_2\text{C}_2\text{H}_5 \) (This step is the Friedel-Crafts alkylation of an alkene)

(b) \( \text{SOCl}_2 \)

(c) \( 2 \text{C}_6\text{H}_5\text{CH}_2\text{SH and KOH} \)

(d) \( \text{H}_2\text{O}^+ \)

(e) \( \text{H}_2\text{C} \begin{array}{c} \text{S} \text{H} \text{C} \text{CH}_2 \text{CH}_2 \text{CO}_2 \text{H} \end{array} \)

C.6 \( \text{H}_2\text{S}^+ + \text{H}_2\text{C} \begin{array}{c} \text{C} \text{H}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{OH} \end{array} \rightarrow \text{H}_2\text{S} \begin{array}{c} \text{C} \text{H}_2 \text{CH}_2 \text{CH}_2 \text{OH} \end{array} \text{H}_2\text{O}^+ \text{H}_2\text{C} \begin{array}{c} \text{C} \text{H}_2 \text{CH}_2 \text{CH}_2 \text{OH} \end{array} \)

\( \text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH} \) \( \text{HCl} \rightarrow \text{CICH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{Cl} \) Mustard gas

SOLUTIONS TO PROBLEM

D.1 Farnesol

\( \text{Farnesol} \rightarrow \text{H}^+ \rightarrow \text{Bisabolene} \)
AMINES

PREPARATION AND REACTIONS OF AMINES

A. Preparation

1. Preparation via nucleophilic substitution reactions.

- Preparation through reduction of nitro compounds.

2. Preparation via reductive amination.

3. Preparation through reduction of nitro compounds.

4. Preparation of amines through reduction of amides, oximes, and nitriles.

B. Reaction of Amines

1. As a base or a nucleophile

   - As a base
   
   - As a nucleophile in alkylation
   
   - As a nucleophile in acylation

2. With nitrous acid

   - Alkenes, alcohols, and so on
SOLUTIONS TO PROBLEMS

20.1 Dissolve both compounds in diethyl ether and extract with aqueous HCl. This procedure gives an ether layer that contains cyclohexane and an aqueous layer that contains hexylaminium chloride. Cyclohexane may then be recovered from the ether layer by distillation. Hexylamine may be recovered from the aqueous layer by adding aqueous NaOH (to convert hexylaminium chloride to the hexylamine) and then by ether extraction and distillation.

\[
C_6H_{12} + C_6H_{13}NH_2 \quad \text{(in diethyl ether)}
\]

ether layer

\[
\xrightarrow{H_2O/CH_3OH}
\]

aqueous layer

\[
C_6H_{12}/NH_3^+ \quad \text{Cl} \quad \text{OH} \quad \rightarrow \quad C_6H_{12}/NH_2 \quad \text{(extract into ether and distill)}
\]

20.2 We begin by dissolving the mixture in a water-immiscible organic solvent such as CH₂Cl₂ or diethyl ether. Then, extract with aqueous acids and bases allow us to separate the components. [We separate 4-methylphenol (p-cresol) from benzoic acid by taking advantage of benzoic acid's solubility in the more weakly basic aqueous NaHCO₃, whereas p-cresol requires the more strongly basic aqueous NaOH.]

\[
C_6H₅CO₂H, p-CH₃C₆H₄OH, C₆H₅NH₂, C₆H₆
\]

(in CH₂Cl₂)

\[
\xrightarrow{CH₂Cl₂, layer}
\]

aqueous layer

\[
C₆H₅CO₂⁻ \quad Na^+
\]

\[
\xrightarrow{H₂O'}
\]

p-CH₃C₆H₄OH, C₆H₅NH₂, C₆H₆

Separate and recrystallize

\[
\xrightarrow{p-CH₃C₆H₄OH}
\]

aqueous layer

\[
\xrightarrow{NaOH, H₂O, CH₂Cl₂ layer}
\]

\[
C₆H₅CO₂⁻ \quad Na^+
\]

\[
\xrightarrow{H₂O'}
\]

p-CH₃C₆H₄OH

Extract into CH₂Cl₂ and distill

\[
\xrightarrow{CH₂Cl₂ and distill}
\]

C₆H₅NH₂, C₆H₆

Extract into CH₂Cl₂ and distill

\[
\xrightarrow{CH₂Cl₂}
\]

C₆H₆

Isolate by distillation

396 AMINES
20.3 (a) Neglecting Kekulé forms of the ring, we can write the following resonance structures for the phthalimide anion.

(b) Phthalimide is more acidic than benzamide because its anion is stabilized by resonance to a greater extent than the anion of benzamide. (Benzamide has only one carbonyl group attached to the nitrogen atom, and thus fewer resonance contributors are possible.)

(c) Then,

20.4

20.5 (a) \( \text{CH}_3(\text{CH}_2)_3\text{CHO} + \text{NH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{NH}_3 \)

(b) \( \text{C}_6\text{H}_5\text{CH}_3\text{CCH}_3 + \text{NH}_3 \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3 \)

(c) \( \text{CH}_3(\text{CH}_2)_3\text{CHO} + \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{LiBH}_3,\text{CN},\text{CH}_3\text{OH}} \text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{NH}_2\text{C}_6\text{H}_5 \)

(d) \( \text{C}_6\text{H}_5\text{CHO} + \text{(CH}_3)_2\text{NH} \xrightarrow{\text{LiBH}_3,\text{CN},\text{CH}_3\text{OH}} \text{C}_6\text{H}_5\text{CH}_2\text{N(CH}_3)_2 \)

20.6 The reaction of a secondary halide with ammonia would inevitably be accompanied by considerable elimination, thus decreasing the yield.

\[
\begin{align*}
\text{R'} \quad \text{RCH-X} + \text{NH}_3 & \xrightarrow{\text{substitution}} \text{R'CHNH}_2 \\
\text{RCH-X} + \text{NH}_3 & \xrightarrow{\text{elimination}} \text{RCH=CH}_2
\end{align*}
\]

20.7 (a) \( \text{C}_6\text{H}_5\text{CO}_2\text{H} \xrightarrow{\text{SOCl}_2} \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{CH}_3\text{CHNH}_2} \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaCN}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{\text{LiAIH}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)

(c) \( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{CH}_2\text{COCl} \xrightarrow{\text{CH}_3\text{CH}_2\text{NH}_2} \text{CH}_3\text{CH}_2\text{CON(CH}_3)_2 \xrightarrow{\text{LiAIH}_4} \text{N(CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)

(d) \( \text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{NH}_2\text{OH}} \text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{NaOH, ethanol}} \text{CH}_3\text{CH}_2\text{CH}_3 \)
20.8 (a) CH₃O⁻ → HNO₃(H₂SO₄) → CH₂O⁻ → CH₃NO₃ → Fe HCl → CH₂O⁻ → CH₃NH²⁺ + H₂O

(b) CH₂O⁻ → CH₃COCl → CH₂O⁻ → CH₃CH₂O⁻ → Ni → CH₃CH₃NH₂

(c) O₢⁻ → Cl⁻ → (excess) → CH₂ClCH₂ + (CH₃)₃N → CH₂(CH₃)₃NHCl

(d) O₢⁻ → Cl⁻ → (1) K₂MnO₄, OH⁻ → O₢⁻ → CO₂H → SOCl₂

(e) (excess) → CH₃Cl → CH₂(N(CH₃)₃)Cl

20.9 An amine acting as a base.

CH₂CH₂NH₂ + H₂O → CH₂CH₂NH₃⁺ + H₂O

An amine acting as a nucleophile in an alkylation reaction.

(CH₃CH₂)₂N⁻ + CH₃I → (CH₃CH₂)₂NCH₂I

An amine acting as a nucleophile in an acylation reaction.

(CH₃)₂NH + CH₃COCl (excess) → (CH₃)₂NCCH₃ + (CH₃)₂NCH₂Cl⁻

An aminio group acting as an activating group and as an ortho-para director in electrophilic aromatic substitution.

NH₂ + Br₂, H₂O (room temp.) → Br⁻NH₂Br

20.10 (a, b) "O⁻N=O + H₂O ⇌ HO⁻N=O + H₂O

HO⁻N=O + H₂O ⇌ HO⁻N=O + H²⁺

HO⁻N=O ⇌ H₂O + N=O

(c) The NO⁻ ion is a weak electrophile. For it to react with an aromatic ring, the ring must have a powerful activating group such as -OH or -NR₂.

20.11 (a) Fuming HNO₃, H₂SO₄, heat → NO₂ + H₂SO₄ → NO₂ + NH₄⁺, C₂H₅OH → NO₂ + NH₃

(b) NH₄Cl → NO₂ → CuCl → NO₂ → N₂H⁺Cl⁻ → NO₂ → NH₂Cl

(c) (by nitration of benzene) → Br₂ → Br⁻NO₂ → Br⁻NO₂ → Br⁻NO₂ → (1) Fe/HCl, heat → (2) NH₁H₂O
(d) [as in (c)]

\[
\begin{align*}
\text{NHSCOCCH}_3 & \xrightarrow{(1) \text{Fe}, \text{HCl, heat}} \text{CH}_2\text{CO}_2\text{H} \\
& \xrightarrow{(2) \text{OH}^-} \text{NHCOCH}_3
\end{align*}
\]

(e) [from part (d)]

\[
\text{NHSCOCCH}_3 \xrightarrow{(1) \text{HNO}_3, \text{H}_2\text{SO}_4} \text{NHSCOCCH}_3 \xrightarrow{(2) \text{H}^+} \text{NH}_2\text{COCH}_3 \text{NO}_2 \\
\xrightarrow{\text{heat} 57\% \text{H}_2\text{SO}_4} \text{NH}_2\text{COCH}_3 \text{NO}_2
\]

\[
\begin{align*}
\text{NH}_2\text{COCH}_3 \xrightarrow{(1) \text{Fe}, \text{HCl, heat}} \text{CH}_2\text{CO}_2\text{H} \\
& \xrightarrow{(2) \text{OH}^-} \text{NHCOCH}_3
\end{align*}
\]

20.12 p-Toluidine

\[
\begin{align*}
\text{CH}_3\text{Br} & \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{CH}_2\text{Br}_2 \xrightarrow{\text{NH}_2, \text{H}_2\text{O}} \text{NH}_2\text{Br}_2 \xrightarrow{\text{H}_2\text{PO}_4, \text{H}_2\text{O}} \text{Br}_2\text{Br}_2 \xrightarrow{\text{N}_2} \text{Br}_2\text{Br}_2
\end{align*}
\]

20.13 (a) Toluene \(\xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} p\)-Nitrotoluene \(\xrightarrow{(1) \text{Fe}, \text{HCl}} \text{CH}_2\text{CO}_2\text{H} \)

\[
\begin{align*}
\text{CH}_3\text{NO}_2 & \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_2\text{NO}_2 \\
& \xrightarrow{\text{H}_2\text{O}} \text{NH}_2\text{COCH}_3 \text{NO}_2 \\
& \xrightarrow{\text{H}_2\text{PO}_4, \text{H}_2\text{O}} \text{Br}_2\text{Br}_2
\end{align*}
\]

20.15 \(\xrightarrow{\text{H}_2\text{SO}_4, \text{NaNO}_3 \text{(0-5°C)}} \text{HO}_2\text{S} \)

\[
\begin{align*}
\text{HO}_2\text{S} \xrightarrow{\text{H}_2\text{PO}_4, \text{H}_2\text{O}} \text{Br}_2\text{Br}_2 \\
& \xrightarrow{\text{NaOH pH=10}} \text{Orange II}
\end{align*}
\]
20.16 \[ \text{HNO}_2 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{Fe} \rightarrow \text{H}_2\text{SO}_4/\text{NaNO}_2 \rightarrow \text{N}_2^+ \]

20.17 \[ \text{CH}_3\text{CH}_2\text{O} \rightarrow \text{N}_2^+ \rightarrow \text{OH}^- \rightarrow \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{Br} \]

20.18 (1) That A reacts with benzenesulfonyl chloride in aqueous KOH to give a clear solution, which on acidification yields a precipitate, shows that A is a primary amine.

(2) That diazotization of A followed by treatment with 2-naphthol gives an intensely colored precipitate shows that A is a primary aromatic amine; that is, A is a substituted aniline.

(3) Consideration of the molecular formula of A leads us to conclude that A is a methylamine (i.e., a toluidine).

\[ \text{C}_6\text{H}_5\text{N} \quad \begin{array}{c} \text{But is A 2-methylaniline, 3-methylaniline, or 4-methylaniline?} \\
\text{C}_6\text{H}_4\text{N} \quad \text{CH}_3 \end{array} \]

(4) This question is answered by the IR data. A single absorption peak in the 680-840 cm\(^{-1}\) region at 815 cm\(^{-1}\) is indicative of a para substituted benzene. Thus, A is 4-methylaniline (p-toluidine).

20.19 First convert the sulfonamide to its anion, then alkylate the anion with an alkyl halide, then remove the -SO\(_2\text{C}_6\text{H}_5\) group by hydrolysis. For example.

\[ \text{R-N-SO}_2\text{C}_6\text{H}_5 \rightarrow \text{OH}^- \rightarrow \text{R-N-SO}_2\text{C}_6\text{H}_5 \rightarrow \text{R-N-H} + \text{C}_6\text{H}_5\text{SO}_3^- \]

20.20 (a) Aniline

20.21 (a) C\(_6\)H\(_4\)CH\(_2\)NHCH\(_3\)

(b) (CH\(_3\))\(_2\)N

(c) \( \text{N} \quad \text{CH}_3 \)

(d) \( \text{NH}_2 \quad \text{CH}_3 \)

(e) \( \text{NH}_2 \quad \text{CH}_3 \)

(f) \( \text{NH}_2 \quad \text{CH}_3 \)

Sulfathiazole

Succinylsulfathiazole
20.22 (a) Propylamine
(b)  N-Methylaniline
(c) Isopropyltrimethylammonium iodide
(d) 2-Methylaniline (o-toluidine)
(e) 2-Methoxyaniline (or o-methoxyaniline)
(f) Pyrazole
(g) 2-Aminopyrimidine

20.23 (a) [\text{C-H}_3\text{N} + \text{LiAlH}_4 \xrightarrow{(2\text{H}_2\text{O})} \text{C-H}_2\text{NH}_2]
(b) [\text{C-N}_3 + \text{LiAlH}_4 \xrightarrow{(2\text{H}_2\text{O})} \text{C-H}_2\text{NH}_2]

(h) Benzylationimium chloride
(i)  N,N-Dipropylamine
(j) Benzenesulfonamide
(k) Methylaminium acetate
(l) 3-Amino-1-propanol
(m) Purine
(n) N-Methylpyrrole

20.24 (a) [BNO_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{C-N}_2 \xrightarrow{(1\text{Fe, HCl heat})} \text{C-N}_2 \xrightarrow{(2\text{OH}^-)} \text{C-N}_2]
(b) [\text{Br} \xrightarrow{\text{Mg, Et}_2\text{O}} \text{C} \xrightarrow{(1\text{CO}_2) \xrightarrow{(2\text{H}_2\text{O}^+)} \text{SO}_2} \text{C} \xrightarrow{\text{NH}_3} \text{C} \xrightarrow{\text{excess}} \text{C} \xrightarrow{\text{Br}_2, \text{NaOH}} \text{C} \xrightarrow{\text{Hofmann rearrangement}}]
20.25 (a) \[ \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{OH} \xrightarrow{\text{HBr}} \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{Br} \]

(b) \[ \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaCN}} \text{CH}_3\text{(CH}_2\text{)}_2\text{CN} \xrightarrow{(1)\text{LiAlH}_4, \text{Et}_2\text{O}} (2)\text{H}_2\text{O} \rightarrow \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{NH}_2 \]

(c) \[ \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{OH} \xrightarrow{(1)\text{KMnO}_4, \text{OH}^+} (2)\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \]

(d) \[ \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{OH} \xrightarrow{\text{PCC, CH}_2\text{CH}_2} \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{CHO} \xrightarrow{\text{CH}_2\text{NH}_2, \text{Ni}} \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{CH}_2\text{NHCH}_3 \]

20.26 (a) \[ \text{NH}_3 \xrightarrow{\text{(CH}_3\text{CO}_2\text{H} \text{O}}} \text{NHCOCH}_3 \]

(b) \[ \text{NH}_2 \xrightarrow{\text{heat}} \text{NH}_2 \text{COCH}_3 \text{OH} \]

(c) \[ \text{NHCOCH}_3 \xrightarrow{\text{HNO}_2, \text{H}_2\text{SO}_4} (1)\text{H}^+, \text{H}_2\text{O} \xrightarrow{(2)\text{OH}^+} \text{NH}_2 \text{COCH}_3 \text{NO}_2 \]

(d) \[ \text{NHCOCH}_3 \xrightarrow{\text{HOSO}_2\text{Cl}} \text{NHCOCH}_3 \xrightarrow{(1)\text{NH}_3, (2)\text{H}_2\text{O}} \text{NHCOCH}_3 \rightarrow \text{NH}_2 \text{SO}_2\text{Cl} \rightarrow \text{NH}_2 \text{SO}_2\text{NH}_2 \]

(e) \[ \text{NH}_2 \rightarrow 2\text{CH}_2\text{J} \xrightarrow{\text{base}} \text{NH}_2 \text{CH}_2\text{J} \]

(f) \[ \text{NH}_2 \xrightarrow{\text{HONO}} \text{N}^+ \text{X}^- \xrightarrow{\text{HBF}_4} \text{N}^+ \text{BF}_4^- \text{heat} \rightarrow \text{F} \]

(g) \[ \text{N}^+ \text{X}^- \xrightarrow{\text{CuCl}} \text{Cl} \]

(h) \[ \text{N}^+ \text{X}^- \xrightarrow{\text{CuBr}} \text{Br} \]

(i) \[ \text{N}^+ \text{X}^- \xrightarrow{\text{RI}} \text{I} \]

(j) \[ \text{N}^+ \text{X}^- \xrightarrow{\text{CuCN}} \text{CN}^- \]
20.27 (a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \stackrel{\text{HONO, NaNO}_2/\text{HCl}}{\longrightarrow} [\text{CH}_3\text{CH}_2\text{CH}_2\text{N}_2]^+ \stackrel{\text{N}_2}{\longrightarrow} \) [from part(f)]

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \stackrel{\text{HONO, NaNO}_2/\text{HCl}}{\longrightarrow} (\text{CH}_3\text{CH}_2\text{CH}_2\text{N}_2)^+ \stackrel{\text{N}_2}{\longrightarrow} \) [from part(f)]

20.28 (a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \stackrel{\text{KOH, H}_2\text{O}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CH}_2\text{N}_2\text{SO}_2\text{C}_6\text{H}_5 \)
- Clear solution
- \( \stackrel{\text{H}_2\text{O}}{\longrightarrow} \text{CH}_3\text{CH}_2\text{CH}_2\text{N}_2\text{SO}_2\text{C}_6\text{H}_5 \)
- Precipitate

(b) \( (\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \stackrel{\text{KOH, H}_2\text{O}}{\longrightarrow} (\text{CH}_3\text{CH}_2\text{CH}_2\text{N}_2\text{SO}_2\text{C}_6\text{H}_5 \)
- \( \stackrel{\text{H}_2\text{O}}{\longrightarrow} \) No reaction (precipitate remains)

(c) \( \text{H}_3\text{C} = \text{CH}_2\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \stackrel{\text{KOH, H}_2\text{O}}{\longrightarrow} \text{N}_2^+\text{SO}_2\text{C}_6\text{H}_5 \)
- \( \stackrel{\text{H}_2\text{O}}{\longrightarrow} \) No reaction (precipitate remains)

(d) \( \text{H}_3\text{C} = \text{CH}_2\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \stackrel{\text{KOH, H}_2\text{O}}{\longrightarrow} \text{N}_2^+\text{SO}_2\text{C}_6\text{H}_5 \)
- \( \stackrel{\text{H}_2\text{O}}{\longrightarrow} \) No reaction (3° amine is insoluble)

3° Amines dissolve
AMINES

(b) \[
\text{CH}_3\text{NO}_2 \xrightarrow{(1) \text{Fe}, \text{HCl}} \text{CH}_3\text{NH}_2 \xrightarrow{\text{HONO}} 0-5^\circ\text{C}
\]
[from part (a)]

(c) \[
\text{CH}_3\text{NO}_2 \xrightarrow{(1) \text{Fe}, \text{HCl, heat}} \text{CH}_3\text{NH}_2 \xrightarrow{(1) \text{H}_2\text{SO}_4/\text{NaNO}_2, (2) \text{Cu}_2\text{O}, \text{Cu}^{2+}, \text{H}_2\text{O}} \text{OH}
\]
[from part (a)]

(d) \[
\text{NH}_2\text{NH}_2 \xrightarrow{\text{HCl/NaNO}_2} \text{N}_2^+ \text{X}^- \xrightarrow{\text{CuCl}} \text{Cl}
\]
[by reduction of m-dinitrobenzene, cf. Problem 20.11(o)]

(e) \[
\text{N}_2^+ \text{X}^- \xrightarrow{\text{CuCN}} \text{CN}
\]
[from part (d)]

(f) \[
\text{NO}_2 \xrightarrow{(1) \text{H}_2\text{SO}_4/\text{NaNO}_2, (2) \text{KI}} \text{NH}_2 \xrightarrow{(1) \text{Fe, HCl, heat}} \text{OH}
\]
[from Problem 20.11(a)]

(g) \[
\text{NH}_2\text{NH}_2 \xrightarrow{(1) \text{HBr/NaNO}_2, (2) \text{CuBr}} \text{NO}_2 \xrightarrow{(1) \text{Fe, HCl, heat}} \text{NH}_2 \xrightarrow{(2) \text{OH}} \text{CN}
\]
[from Problem 20.11(o)]

(h) \[
\text{NH}_2\text{Br} \xrightarrow{(1) \text{Fe, HCl, heat}} \text{NH}_2\text{Br} \xrightarrow{(3) \text{OH}} \text{Br}
\]
[from part (b)]

(i) \[
\text{NO}_2 \xrightarrow{(1) \text{Fe, HCl, heat}} \text{NH}_2 \xrightarrow{(3) \text{OH}} \text{Br}
\]
[from part (h)]

(j) \[
\text{NO}_2 \xrightarrow{(1) \text{HBr/NaNO}_2, (2) \text{CuBr}} \text{Br} \xrightarrow{(1) \text{Fe, HCl, heat}} \text{Br} \xrightarrow{(2) \text{OH}} \text{Br}
\]
[from part (h)]

(k) \[
\text{NH}_2\text{Br} \xrightarrow{(1) \text{H}_2\text{SO}_4/\text{NaNO}_2, (2) \text{CuCN}} \text{Br} \xrightarrow{(2) \text{CuCN}} \text{CN}
\]
[from part (j)]

(l) \[
\text{NO}_2 \xrightarrow{(1) \text{H}_2\text{SO}_4/\text{NaNO}_2, (2) \text{CuCN}} \text{Br} \xrightarrow{(2) \text{CuCN}} \text{CN}
\]
[from part (b)]
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(4) H₂C-CH₂-NH₂ + H₂SO₄/NaNO₂ \rightarrow H₂C-CH₂-N₂⁺ X⁻
[from part (c)]

[8] H₂C-CH₂-N₂⁺ X⁻ + OH⁻, pH 8-10

H₂C-CH₂-N=N-CH₂-OH

(5) H₂C-CH₂-NH₂ + H₂SO₄/NaNO₂ \rightarrow H₂C-CH₂-N₂⁺ X⁻
[from part (q)]

[8] H₂C-CH₂-N₂⁺ X⁻ + OH⁻, pH 8-10

H₂C-CH₂-N=N-CH₂-OH

20.32 (a) Benzylamine dissolves in dilute HCl at room temperature.

C₆H₅CH₂NH₂ + H₂O⁺ + Cl⁻ \(\rightarrow\) C₆H₅CH₂NH₃⁺ Cl⁻

Benzamide does not dissolve:

C₆H₅CONH₂ + H₂O⁺ + Cl⁻ \(\rightarrow\) No reaction
[25°C]

(b) Allylamine reacts with (and decolorizes) bromine in carbon tetrachloride instantly.

CH₃=CHCH₂NH₂ + Br₂ \(\rightarrow\) CH₃CHBrCH₂NH₂

Propylamine does not:

CH₃CH₂CH₂NH₂ + Br₂ \(\rightarrow\) No reaction if the mixture is not heated or irradiated
[25°C]

(c) The Hinsberg test:

H₂C-CH₂-NH₂ + C₆H₅SO₄Cl \(\rightarrow\) H₂C-CH₂-N⁺SO₂C₆H₅\(\rightarrow\)

H₂O

Soluble

H₂C-CH₂-NH₂ + C₆H₅SO₄Cl \(\rightarrow\) H₂C-CH₂-NHSO₂C₆H₅

Precipitate
The Hinsberg test:

\[
\text{(d) } \text{NH}_{3} + C_{4}H_{6}SO_{4}Cl \xrightarrow{\text{KOH, H}_{2}O} \text{N}-C_{4}H_{6}SO_{4}C_{6}H_{5} \xrightarrow{\text{H}_{2}O^{'}} \text{Precipitate remains}
\]

\[
\text{The Hinsberg test:}
\]

\[
\text{(e) } \text{NH}_{3} + C_{4}H_{6}SO_{4}Cl \xrightarrow{\text{KOH, H}_{2}O} \text{K}^{+}\text{N}=C_{4}H_{6}SO_{4}C_{6}H_{5} \xrightarrow{\text{H}_{2}O^{'}} \text{Precipitate remains}
\]

(b) Tetrapropylammonium chloride reacts with aqueous NaOH to give a water insoluble tertiary amine.

\[
\text{(CH}_{3}\text{CH}_{2}\text{CH}_{2})_{3}\text{N}^{+} \text{Cl}^{-} \xrightarrow{\text{NaOH, H}_{2}O} \text{(CH}_{3}\text{CH}_{2}\text{CH}_{2})_{3}\text{N}^{+} \text{Cl}^{-} \xrightarrow{\text{H}_{2}O} \text{Water soluble}
\]

\[
\text{Water soluble}
\]

\[
\text{(g) } \text{The Hinsberg test:}
\]

\[
\text{(C}_{2}\text{H}_{5})_{2}\text{NH} + C_{4}H_{6}SO_{4}Cl \xrightarrow{\text{KOH, H}_{2}O} \text{No reaction} \xrightarrow{\text{H}_{2}O^{'}} \text{(C}_{2}\text{H}_{5})_{2}\text{NH}
\]

\[
\text{Soluble}
\]

\[
\text{(C}_{2}\text{H}_{5})_{2}\text{NH} + C_{4}H_{6}SO_{4}Cl \xrightarrow{\text{KOH, H}_{2}O} \text{(C}_{2}\text{H}_{5})_{2}\text{N}=C_{4}H_{6}SO_{4}C_{6}H_{5} \xrightarrow{\text{H}_{2}O^{'}} \text{Precipitate remains}
\]

\[
\text{(h) } \text{Tetrapropylammonium chloride does not react with aqueous NaOH at room temperature, and the tetrapropylammonium ion remains in solution.}
\]

\[
\text{(CH}_{3}\text{CH}_{2}\text{CH}_{2})_{3}\text{N}^{+} \text{Cl}^{-} \xrightarrow{\text{NaOH, H}_{2}O} \text{(CH}_{3}\text{CH}_{2}\text{CH}_{2})_{3}\text{N}^{+} \text{Cl}^{-} \xrightarrow{\text{H}_{2}O} \text{Water soluble}
\]

\[
\text{Water soluble}
\]

\[
\text{(i) } \text{Tetrapropylammonium chloride dissolves in water to give a neutral solution. Tetrapropylammonium hydroxide dissolves in water to give a strongly basic solution.}
\]

\[
\text{20.33 Follow the procedure outlined in the answer to Problem 20.2. Toluene will show the same solubility behavior as benzene.}
\]

\[
\text{20.34}
\]

\[
\text{20.35 (a) HOCH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}\text{OH} \xrightarrow{\text{2 Br}} \text{BrCH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}\text{Br} \xrightarrow{2(CH}_{3})_{2}\text{N} \xrightarrow{\text{(CH}_{3}\text{)}_{2}N\text{CH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}N\text{(CH}_{3})_{2}} \text{2 Br}^{-}
\]

\[
\text{(b) HO}_{2}\text{CHCH}_{2}\text{CH}_{2}\text{CO}_{2}H + 2 \text{BrCH}_{2}\text{CH}_{2}\text{OH} \xrightarrow{\text{H}^{+}, \sim 2 \text{H}_{2}O} \text{BrCH}_{2}\text{CH}_{2}\text{OCH}_{2}\text{CH}_{2}\text{CH}_{2}\text{Br} \xrightarrow{2(CH}_{3})_{2}\text{N} \xrightarrow{\text{(CH}_{3}\text{)}_{2}N\text{CH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}N\text{(CH}_{3})_{2}} \text{2 Br}^{-}
\]

\[
\text{(CH}_{3}\text{)}_{2}N\text{CH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}N\text{(CH}_{3})_{2}
\]

\[
\text{20.34 H}_{2}\text{NCH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CO}_{2}H \xrightarrow{\text{H}^{+}} \text{H}_{2}\text{NCH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CO}_{2}^{-} \xrightarrow{\text{Br}_{2}, \text{OH}^{-}} \text{H}_{2}\text{NCH}_{2}\text{CH}_{2}\text{CO}_{2}^{-} \xrightarrow{\text{H}^{+}} \text{H}_{2}\text{NCH}_{2}\text{CH}_{2}\text{CO}_{2}^{-}
\]

\[
\text{20.35 (a) HOCH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}\text{OH} \xrightarrow{\text{2 Br}} \text{BrCH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}\text{Br} \xrightarrow{2(CH}_{3})_{2}\text{N} \xrightarrow{\text{(CH}_{3}\text{)}_{2}N\text{CH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}N\text{(CH}_{3})_{2}} \text{2 Br}^{-}
\]

\[
\text{(b) HO}_{2}\text{CHCH}_{2}\text{CH}_{2}\text{CO}_{2}H + 2 \text{BrCH}_{2}\text{CH}_{2}\text{OH} \xrightarrow{\text{H}^{+}, \sim 2 \text{H}_{2}O} \text{BrCH}_{2}\text{CH}_{2}\text{OCH}_{2}\text{CH}_{2}\text{CH}_{2}\text{Br} \xrightarrow{2(CH}_{3})_{2}\text{N} \xrightarrow{\text{(CH}_{3}\text{)}_{2}N\text{CH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}N\text{(CH}_{3})_{2}} \text{2 Br}^{-}
\]

\[
\text{(CH}_{3}\text{)}_{2}N\text{CH}_{2}\text{(CH}_{3}\text{)}_{2}\text{CH}_{2}N\text{(CH}_{3})_{2}
\]
20.36

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N}-\text{NH}_2 \quad + \quad \text{CHBr}_2 \quad \xrightarrow{-\text{H}_2\text{O}} \quad \text{H}_2\text{N} \quad \text{N}-\text{NH}_2 \\
\text{OH} & \quad \text{Br} \quad \xrightarrow{\text{HCO}_2} \quad \text{OH} \\
\end{align*}
\]

\[
\text{H}_2\text{N} \quad \text{N} \quad \text{OH} \quad \text{Br} \quad \xrightarrow{\text{HBr}} \quad \text{H}_2\text{N} \quad \text{N} \quad \text{Br} \quad \xrightarrow{\text{HCO}_2} \quad \text{H}_2\text{N} \quad \text{N} \quad \text{CO}_2 \quad \text{H} \quad \xrightarrow{\text{HBr}} \quad \text{folic acid}
\]

20.37 The results of the Hinsberg test indicate that compound W is a tertiary amine. The \( ^1H \) NMR provides evidence for the following:

1. Two different \( \text{C}_6\text{H}_5 \)-groups (one absorbing at \( \delta 7.2 \) and one at \( \delta 6.7 \)).
2. A \( \text{CH}_3\text{CH}_2 \)-group (the quartet at \( \delta 3.5 \) and the triplet at \( \delta 1.2 \)).
3. An unsplit \( \text{CH}_3 \)-group (the singlet at \( \delta 4.5 \)).

There is only one reasonable way to pull all of this together.

\[
\text{CH}_2\text{N} \quad \text{H}_2\text{N} \quad \text{CH}_3
\]

Thus W is \( \text{N} \)-benzyl-\( \text{N} \)-ethylaniline.

20.38 Compound X is benzyl bromide, \( \text{C}_6\text{H}_5\text{CH}_2\text{Br} \). This is the only structure consistent with the \( ^1H \) NMR and IR data. (The monosubstituted benzene ring is strongly indicated by the \( \delta 7.3 \) \( ^1H \) NMR absorption and is confirmed by the peaks at 690 and 770 cm\(^{-1} \) in the IR spectrum.)

Compound Y, therefore, must be phenylacetonitrile, \( \text{C}_6\text{H}_5\text{CH}_2\text{CN} \) and Z must be 2-phenylethylamine, \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2 \).

\[
\begin{align*}
\text{X} & \quad \text{CH}_2\text{Br} \quad \text{NaCN} \quad \text{Y} \quad \text{CH}_2\text{CN} \quad \text{LiAlH}_4 \quad \text{Z} \quad \text{CH}_2\text{CH}_2\text{NH}_2 \\
\text{C}_6\text{H}_5\text{Br} & \quad & \quad \text{C}_6\text{H}_5\text{N} \quad & \quad \text{C}_6\text{H}_5\text{N} \\
\end{align*}
\]

Interpretations of the IR and \( ^1H \) NMR spectra of Z are as follows.

- \( \text{a} \) singlet \( \delta 1.0 \)
- \( \text{b} \) triplet \( \delta 2.7 \)
- \( \text{c} \) triplet \( \delta 2.9 \)
- \( \text{d} \) multiplet \( \delta 7.25 \)

20.39

\[
\begin{align*}
\text{H}_2\text{Pd} & \quad \text{H}_2 \quad \xrightarrow{\text{(several steps) \text{H}_2\text{O}}} \\
\text{H}_2\text{Pd} & \quad \text{H}_2 \quad \xrightarrow{\text{(several steps) \text{H}_2\text{O}}} \\
\end{align*}
\]
20.40

\[ \text{CH}_3 + \text{CH}_3 \rightarrow \text{H}_3\text{C}-\text{N} \quad \text{Ag}_2\text{O} \quad \text{H}_2\text{O} \rightarrow \text{CH}_2\text{CH}_3\text{CH}_2\text{CH}_3 \]

20.41 That A contains nitrogen and is soluble in dilute HCl suggests that A is an amine. The two IR absorption bands in the 3300–3500-cm\(^{-1}\) region suggest that A is a primary amine. The \(\delta^1\)C spectrum shows only two signals in the upfield aliphatic region. There are four signals downfield in the aromatic region. The information from the DEPT spectra suggests an ethyl group or two equivalent ethyl groups. Assuming the latter, and assuming that A is a primary amine, we can conclude from the molecular formula that A is 2,6-diethyl-4-methylpyridine. The assignments are:

(a) \(\delta 12.9\)
(b) \(\delta 24.2\)
(c) \(\delta 118.1\)
(d) \(\delta 125.9\)
(e) \(\delta 127.4\)
(f) \(\delta 141.5\)

(An equally plausible answer would be that A is 3,5-diethylpyridine.)

20.42 That B dissolves in dilute HCl suggests that B is an amine. That the IR spectrum of B lacks bands in the 3300–3500-cm\(^{-1}\) region suggests that B is a tertiary amine. The upfield signals in the \(\delta^1\)C spectrum and the DEPT information suggest two equivalent ethyl groups (as was also true of A in the preceding problem). The DEPT information for the downfield peaks in the aromatic region is consistent with a monosubstituted benzene ring. Plugging all of these observations together with the molecular formula leads us to conclude that B is \(N,N\)-diethyl-2,4-dimethylbenzylamine. The assignments are:

(a) \(\delta 12.5\)
(b) \(\delta 44.2\)
(c) \(\delta 112.0\)
(d) \(\delta 115.5\)
(e) \(\delta 128.1\)
(f) \(\delta 147.8\)

20.43 That C gives a positive Tollens' test indicates the presence of an aldehyde group; the solubility of C in aqueous HCl suggests that C is also an amine. The absence of bands in the 3300–3500-cm\(^{-1}\) region of the IR spectrum of C suggests that C is a tertiary amine. The signal at \(\delta 139.7\) is the only one in the aliphatic region and is consistent with a methyl group or with two equivalent methyl groups. The remaining signals are in the aromatic region. If we assume that C has a benzene ring containing a \(-CH\) group and a \(-N(CH_3)_2\) group, then the aromatic signals and their DEPT spectra are consistent with C being \(p-(N,N\text{-dimethylamino})benzaldehyde. The assignments are:

20.44 \(\text{CH}_3\text{Cl} + \text{O} \rightarrow \text{CH}_3\text{COCl} \quad \text{base (-HCl)} \)

20.45 \(\text{NH}_3 \rightarrow \text{HOCH}_2\text{CH}_2\text{NH}_2 \)

20.46 \(\text{CH}_3\text{CH}_2\text{COCl} \quad \text{AlCl}_3 \rightarrow \text{CH}_3\text{COCH}_3 \quad \text{CH}_2\text{COH} \quad \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_3 \quad \text{Diethylpropion} \)
20.47 Carry out the Hofmann reaction using a mixture of $^{15}$N labeled benzamide, $\text{C}_6\text{H}_5\text{CO}^+\text{NH}_2$, and $p$-chlorobenzamide. If the process is intramolecular, only labeled aniline, $\text{C}_6\text{H}_5\text{NH}^+$, and $p$-chloroaniline, will be produced.

If the process is one in which the migrating moiety truly separates from the remainder of the molecule, then, in addition to the two products mentioned above, there should be produced both the unlabeled aniline and labeled $p$-chloroaniline, $p\text{-ClC}_6\text{H}_5\text{NH}_2$.

Note: When this experiment is actually carried out, analysis of the reaction mixture by mass spectrometry shows that the process is intramolecular.

20.48

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} & \xrightarrow{\text{Cl}_2} \text{CH}_3\text{CH}_2\text{CCl}_2 \\
 & \xrightarrow{\text{Cl}} \text{CH}_2\text{CH}_2\text{NH} \\
& \xrightarrow{\text{O}} \text{CH}_2\text{CH}_2\text{NH} \\
\end{align*}
\]

20.49 (a) $\text{C}_6\text{H}_5\text{N}^+\text{CH}_3$

(b) 1 $\xrightarrow{-\text{e}^-}$ (during electron impact mass spectrometry) $\text{C}_6\text{H}_5\text{N}^+\text{CH}_2$  

$m/z$ 107

$m/z$ 106
20.52 An abbreviated version of one of several possible routes:

```
O

\[ \text{repeated sequence} \]

```

"triacetoneamine"

---

**QUIZ**

20.1 Which of the following would be soluble in dilute aqueous HCl?

(a) \( \text{C}_6\text{H}_5\text{NH}_2 \)

(b) \( \text{C}_6\text{H}_5\text{CHNH}_2 \)

(c) \( \text{C}_6\text{H}_5\text{S} \)

(d) Two of the above

(e) All of the above

20.2 Which would yield propylamine?

(a) \( \text{CH}_3\text{CH}_2\text{Br} \xrightarrow{(1) \text{NaCN}} \xrightarrow{(2) \text{LiAIH}_4} \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3 \xrightarrow{\text{B}_2\text{O}} \)

(d) Two of the above

(e) All of the above

---

20.3 Select the reagent from the list below that could be the basis of a simple chemical test that would distinguish between each of the following:

(a) \( \text{C}_6\text{H}_5\text{CNH}_2 \) and \( \text{C}_6\text{H}_5\text{CHNH}_2 \)

(b) \( \text{C}_6\text{H}_5\text{NHCH}_3 \) and \( \text{C}_6\text{H}_5\text{SCH}_2\text{NH}_2 \)

(c) \( \text{NH}_2 \) and \( \text{NH}_2 \)

1. Cold dilute \( \text{NaHCO}_3 \)
2. Cold dilute \( \text{HCl} \)
3. \( \text{NaNO}_2, \text{HCl}, 5^\circ\text{C}, \text{then 2-naphthol} \)
4. \( \text{C}_6\text{H}_5\text{SO}_2\text{Cl}, \text{OH}^-, \text{then HCl} \)
5. Cold dilute \( \text{NaOH} \)

20.4 Complete the following syntheses:

(a) \( \text{H}_2\text{C} \xrightarrow{\text{A}} \xrightarrow{(1) \text{Fe, HCl}} \xrightarrow{(2) \text{OH}^-} \text{CH}_3\text{NH}_2 \)

---

---
20.5 Select the stronger base from each pair:

(a) \( \text{H}_2\text{C}-\text{NH}_2 \) or \( \text{O}^\text{CH}_3\text{NH}_2 \)

(b) \( \text{H}_2\text{C}=\text{C-NH}_2 \) or \( \text{O}^\text{CH}_3\text{NH}_2 \)

(c) \( \text{H}_2\text{C}-\text{NH}_2 \) or \( \text{O}^\text{N}^\text{Cl}-\text{NH}_2 \)

---

**E SPECIAL TOPIC**

Reactions and Synthesis of Heterocyclic Amines

**SOLUTIONS TO PROBLEMS**

E.1 (a) \( \text{N}^\text{O} \) or \( \text{N}^\text{H} \)

(b) \( \text{CH}_3\text{I} \) or \( \text{CH}_3\text{S} \)

(c) \( \text{CH}_2=\text{CHCH}_2\text{N}^\text{CH}_3 \) or \( \text{CH}_2=\text{CHCH}_2\text{N}^\text{CH}_3 \)

(d) \( \text{CH}_2=\text{CHCH}_2\text{N}^\text{CH}_3 \) or \( \text{CH}_2=\text{CHCH}_2\text{N}^\text{CH}_3 \)

E.2 (a) The cyclopentadienyl anion.

(b) The pyrrole anion is a resonance hybrid of the following structures:

The imidazole anion is a hybrid of these:

E.3 A mechanism involving a "pyridyne" intermediate would involve a net loss (of 50%) of the deuterium label.
Since in the actual experiment there was no loss of deuterium, this mechanism was disallowed.

The mechanism given in Section E.4 would not be expected to result in a loss of deuterium; thus, it is consistent with the labeling experiment.

E.4 When pyridine undergoes nucleophilic substitution, the leaving group is a hydride ion—an ion that is a strong base and, consequently, a poor leaving group. With 2-halopyridines, on the other hand, the leaving groups are halide ions—ions that are weak bases and thus good leaving groups.

E.5 If we write the reactants in the following way, we can better see how the reaction occurs.
SPECIAL TOPIC E

Alkaloids

SOLUTIONS TO PROBLEMS

F.1  
(a) The first step is similar to a crossed Claisen condensation (see Section 19.2A):

(b) This step involves hydrolysis of an amide (lactam) and can be carried out with either acid or base. Here we use acid.

(c) This step is the decarboxylation of a substituted malonic acid; it requires only the application of heat and takes place during the acid hydrolysis of step (b).

(d) This is the reduction of a ketone to a secondary alcohol. A variety of reducing agents can be used, sodium borohydride, for example.

(e) Here we convert the secondary alcohol to an alkyl bromide with hydrogen bromide; this reagent also gives a hydrobromide salt of the aliphatic amine.
(f) Treating the salt with base produces the secondary amine; it then acts as a nucleophile and attacks the carbon atom bearing the bromine. This reaction leads to the formation of a five-membered ring and \((\pm)\) nicotine.

\[
\begin{array}{c}
\text{base} \quad \text{base}
\end{array}
\]

\[
\text{Br} \quad \text{H}
\]

\[
\text{HCH}_3\text{CH}_2\text{CH}_2\text{N-CH}_3
\]

\[
\text{HCH}_3\text{CH}_2\text{CH}_2\text{N-CH}_3
\]

F.2 (a) The stereocenter adjacent to the ester carbonyl group is racemized by base (probably through the formation of an anion that can undergo inversion of configuration; cf. Section 17.3).

(b) Tropine is a meso compound; it has a plane of symmetry that passes through the \(\text{CHOH} \) group, the \(\text{NCH}_3 \) group, and between the two \(-\text{CH}_2-\) groups of the five-membered ring.

F.3 (a)

\[
\begin{align*}
\text{Tropine} & : \quad \text{C}_9\text{H}_9\text{N} \quad \text{CHCO,H} \\
\text{CH}_3 & : \quad \text{CH}_3 \quad \text{C}_6\text{H}_5
\end{align*}
\]

(c) Tropine acid

(b) Tropine

F.4

(c) Tropine

\[
\text{HO} \quad \text{CH}_3
\]

\[
\text{HO} \quad \text{CH}_3
\]

F.5 One possible sequence of steps is the following:

\[
\begin{align*}
\text{H}_2\text{C} & \text{CHO} + \text{CH}_3\text{NH}_2 & \text{H}_2\text{C} & \text{CHO} + \text{CH}_3\text{NH}_2 \\
\text{CH} & \text{CO,H} & \text{CH} & \text{CO,H} \\
\text{CO,H} & \text{CO,H} & \text{CO,H} & \text{CO,H} \\
\text{CHO} & \text{CHO} & \text{CHO} & \text{CHO}
\end{align*}
\]

Mannich reaction (See Section 19.10)
E8. Acetic anhydride acetylates both -OH groups.

E9. (a) A Mannich reaction (see Section 19.10).

(b) \( \text{CH}_3\text{O} + \text{HN(CH}_3\text{)}_2 \xrightarrow{4\text{H}_2\text{O} + \text{H}^+} \text{CH}_2\text{N(CH}_3\text{)}_2 \)
Solutions to Problems

21.1 An electron-releasing group (i.e., –CH₃) changes the charge distribution in the molecule so as to make the hydroxyl oxygen less positive, causing the proton to be held more strongly; it also destabilizes the phenoxide anion by intensifying its negative charge. These effects make the substituted phenol less acidic than phenol itself.

\[
\text{OH} + \text{H₂O} \rightleftharpoons \text{HO}^- + \text{H₃O}^+
\]

Electron-releasing –CH₃ destabilizes the anion more than the acid—pKₐ is larger than for phenol.

21.2 An electron-drawing group such as chlorine changes the charge distribution in the molecule so as to make the hydroxyl oxygen more positive, causing the proton to be held less strongly; it also can stabilize the phenoxide ion by dispersing its negative charge. These effects make the substituted phenol more acidic than phenol itself.

\[
\text{OH} + \text{H₂O} \rightleftharpoons \text{O}^- + \text{H₃O}^+
\]

Electron-drawing chlorine stabilizes the anion by dispersing the negative charge. pKₐ is smaller than for phenol.

21.3 Dissolve the mixture in a solvent such as CH₂Cl₂ (one that is immiscible with water). Using a separatory funnel, extract this solution with an aqueous solution of sodium bicarbonate. This extraction will remove the benzoic acid from the CH₂Cl₂ solution and transfer it (as a sodium benzoate) to the aqueous bicarbonate solution. Acidification of this aqueous extract will cause benzoic acid to precipitate; it can then be separated by filtration and purified by recrystallization.

The CH₂Cl₂ solution can now be extracted with an aqueous solution of sodium hydroxide. This will remove the 4-methylphenol (as its sodium salt). Acidification of the aqueous extract will cause the formation of 4-methylphenol as a water-insoluble layer. The 4-methylphenol can then be extracted into ether, the ether removed, and the 4-methylphenol purified by distillation.

The CH₂Cl₂ solution will now contain only toluene (and CH₂Cl₂). These can be separated easily by fractional distillation.

21.4 (a) The para-sulfonated phenol, because it is the major product at the higher temperature—when the reaction is at equilibrium control.

(b) For ortho sulfonation, because it is the major reaction pathway at the lower temperature—when the reaction is under rate control.
If the mechanism involved dissociation into an allyl cation and a phenoxide ion, then recombination would lead to two products: one in which the labeled carbon atom is bonded to the ring and one in which an unlabeled carbon atom is bonded to the ring.

\[
\text{O-CH}_2\text{CH=CH}_2 \xrightarrow{\text{dissociation}} \text{O}^- + \text{CH}_2=\text{CH=CH}_2 \xrightarrow{\text{recombination}} \text{OH} \text{CH}_2\text{CH}=\text{CH}_2 + \text{OH} \text{CH}_2\text{CH}=\text{CH}_2
\]

The fact that all of the product has the labeled carbon atom bonded to the ring eliminates this mechanism from consideration.

21.6

\[
\text{O-CH}_2\text{CH=CH}_2 + \text{NaBr} \rightarrow \text{Na}^+ \text{CH}_2=\text{CHCH}_2\text{Br} \rightarrow \text{OCH}_2\text{CH=CH}_2 + \text{NaBr}
\]

21.7

(a) \[
\text{O} \quad \text{O}
\]

(b) \[
\text{O} \quad \text{O}
\]

(c) \[
\text{CH}_3\text{C}=\text{CH}
\]

21.8

\[
\text{O} \quad \text{O} \xrightarrow{+} \text{O} \quad \text{O} \xrightarrow{2 \text{NaBH}_3} \text{O} \quad \text{O}
\]

21.9

(a) \[
\text{OCH}_2\text{CH}_3, \quad \text{OCH}_2\text{CH}_3
\]

(b) \[
\text{NH}_2, \quad \text{NH}_2
\]

(c) \[
\text{NHCH}_2\text{CH}_3, \quad \text{NHCH}_2\text{CH}_3
\]

(d) \[
\text{SCCH}_3, \quad \text{SCCH}_3
\]

21.10 That \(\alpha\)-chlorotoluene leads to the formation of two products (\(\alpha\)-cresol and \(m\)-cresol) when subjected to the conditions used in the Dow process suggests that an elimination-addition mechanism takes place.

21.11 2-Bromo-1,3-dimethylbenzene, because it has no \(\alpha\)-hydrogen, cannot undergo an elimination. Its lack of reactivity toward sodium amide in liquid ammonia suggests that those compounds (e.g., bromobenzene) that do react do so by a mechanism that begins with an elimination.

21.12

(a) \[
\text{O} \quad \text{O} \quad \text{Na} + \text{CH}_2\text{CH}_2\text{OH}
\]

(b) \[
\text{O} \quad \text{O} \quad \text{Na} + \text{H}_2\text{O}
\]

(c) \[
\text{O} \quad \text{O} \quad \text{Na} + \text{Cl}^{-}
\]

(d) \[
\text{O} \quad \text{O} \quad \text{CO}_2\text{Na}
\]

21.13

(a) \[
\text{OH} \quad \text{Br}
\]

(b) \[
\text{OH} \quad \text{SO}_3\text{H}
\] (major)
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(c) \[
\begin{align*}
\text{S} & \text{O}_2 \text{H} \\
\text{O} & \text{H} \\
\text{S} & \text{O}_2 \text{H} \\
\end{align*}
\]
(major)

(d) \[
\begin{align*}
\text{H}_2\text{C} & \text{C} \text{–O} \text{–SO}_2 \text{C} \text{H}_3
\end{align*}
\]

(e) \[
\begin{align*}
\text{Br} & \text{H} \\
\text{Br} & \text{Br}
\end{align*}
\]

(f) \[
\begin{align*}
\text{C} & \text{O} \text{CH}_3
\end{align*}
\]

(g) \[
\begin{align*}
\text{Br} & \text{H} \\
\text{Br} & \text{Br}
\end{align*}
\]

(h) \[
\begin{align*}
\text{C} & \text{C} \text{–O} \text{–C} \text{H}_3
\end{align*}
\]

(i) Same as (h)

(j) \[
\begin{align*}
\text{O} & \text{Na}
\end{align*}
\]

(k) \[
\begin{align*}
\text{O} & \text{H} \\
\end{align*}
\]

(l) Same as (k)

(m) \[
\begin{align*}
\text{O} & \text{CH}_3 \text{C}_2 \text{H}_5
\end{align*}
\]

21.14 (a) 4-Chlorophenol will dissolve in aqueous NaOH; 4-chloro-1-methylbenzene will not.
(b) 4-Methybenzoic acid will dissolve in aqueous NaHCO₃; 4-methylphenol will not.
(c) Phenyl vinyl ether will react with bromine in carbon tetrachloride by addition (thus decolorizing the solution); ethyl phenyl ether will not.
(d) 2,4,6-Trinitrophenol, because it is so exceptionally acidic (pKₐ = 0.38), will dissolve in aqueous NaHCO₃; 4-methylphenol (pKₐ = 10.17) will not.
(e) 4-Ethylphenol will dissolve in aqueous NaOH; ethyl phenyl ether will not.

21.15 Both \( \text{a-} \) and \( \text{m-} \)-toluidine are formed in the following way:

21.16 (a) 4-Fluorophenol because a fluorine substituent is more electron withdrawing than a methyl group.
(b) 4-Nitrophenol because a nitro group is more electron withdrawing than a methyl group.
(c) 4-Nitrophenol because the nitro group can exert an electron-withdrawing effect through a resonance effect.
Whereas in 3-nitrophenol this resonance effect is not possible.
(d) 4-Methylphenol because it is a phenol, not an alcohol.
(e) 4-Fluorophenol because fluoride is more electronegative than bromine.

21.17 (a) \[
\begin{align*}
\text{CH}_3 & \text{NH}_2 & \text{H} & \text{R} \\
\end{align*}
\]

(b) Because the phenolic radical is highly stabilized by resonance (see the following structures), it is relatively unreactive.
21.18

\[
\begin{align*}
\text{O-H} & \quad \Rightarrow \quad \text{O-H} \\
\text{O-H} & \quad \Rightarrow \quad \text{O-H} \\
\end{align*}
\]

Dibenzo-18-crown-6

21.19 X is a phenol because it dissolves in aqueous NaOH but not in aqueous NaHCO₃. It gives a dibromo derivative and must therefore be substituted in the ortho or para position. The broad IR peak at 3250 cm⁻¹ also suggests a phenol. The peak at 830 cm⁻¹ indicates para substitution. The ¹H NMR singlet at 8 1.3 (9H) suggests nine equivalent methyl hydrogen atoms, which must be a tert-butyl group. The structure of X is

\[
\begin{align*}
\text{OH} & \\
\text{CH₃} & \quad - \quad \text{CH₃} \\
\end{align*}
\]

21.20 (a) 

\[
\begin{align*}
\text{OH} & \quad + \quad \text{CH₂=C-CH₃} \quad \text{H}^+ \quad \Rightarrow \quad \text{OH} \quad \text{C(CH₃)₃} \\
\text{OCH₃} & \quad + \quad \text{CH₂=C-CH₃} \quad \text{H}^+ \quad \Rightarrow \quad \text{OCH₃} \quad \text{C(CH₃)₃} \\
\text{BHA} & \\
\end{align*}
\]

Notice that both reactions are Friedel-Crafts alkylations.

21.21

\[
\begin{align*}
\text{OH} & \quad \rightarrow \quad \text{SO₃H} \\
\text{2Cl} & \quad \rightarrow \quad \text{Cl} _{2} \quad \text{SO₃H} \quad \rightarrow \quad \text{Cl} \quad \text{H₂O} \quad \text{(steam)} \\
\text{H₂SO₄} & \quad \text{25°C} \\
\text{NaOH} & \quad \text{CICH₂COOH} \\
\end{align*}
\]

21.22 The broad IR peak at 3200–3600 cm⁻¹ suggests a hydroxyl group. The two ¹H NMR peaks at 8 1.67 and 8 1.74 are not a doublet because their separation is not equal to other splittings; therefore, these peaks are singlets. Reaction with Br₂/CCl₄ suggests an alkene. If we put these bits of information together, we conclude that Z is 3-methyl-2-buten-1-ol.

\[
\begin{align*}
\text{(a)} & \quad \text{OH} \quad \text{(b)} \quad \text{OH} \\
\text{(c)} & \quad \text{CH₃} \quad \text{CH₃} \\
\text{(d)} & \quad \text{CH₃} \\
\text{(e)} & \quad \text{CH₃} \\
\end{align*}
\]

(a) and (b) singlets at 8 1.67 and 8 1.74
(c) multiplet at 8 5.40
(d) doublet at 8 4.10
(e) singlet at 8 2.3
21.23 \[
\begin{align*}
\text{Phenol} + \text{Epichlorohydin} & \rightarrow \text{Epichlorohydin} \\
\text{OH} & \rightarrow \text{OH}
\end{align*}
\]

21.24 The proximity of the two -OH groups results in the two naphthalene nuclei being non-coplanar. As a result, the two enantiomeric forms are nonequivalent and can be separated by a resolution technique.

21.25 One can draw a resonance structure for the 2,6-di-tert-butylphenoxide ion which shows the carbon para to the oxygen as a nucleophilic center; that is, the species is an ambident nucleophile.

Given the steric hindrance about the oxygen, the nucleophilic character of the para carbon is dominant and an SNAr reaction occurs at that position to produce this biphenyl derivative:

21.26 The phenoxide ion has nucleophilic character both at the oxygen and at the carbon para to it; it is ambident.

21.27 H\(^+\) is expected to be a very poor leaving group because of the strong basicity of the hydride ion. In this case the reaction is favored not only by the activating nitro groups but also by the oxidant ferricyanide ion, which converts H\(^-\), as it forms, to H\(^2+\).

21.28

21.29

Given the steric hindrance about the oxygen, the nucleophilic character of the para carbon is dominant and an SNAr reaction occurs at that position to produce this biphenyl derivative:
QUIZ

21.1 Which of the following would be the strongest acid?
(a) $\text{O}_2\text{N}^-\text{Ph}^-\text{OH}$  (b) $\text{H}_2\text{C}^-\text{Ph}^-\text{OH}$  (c) $\text{Ph}^-\text{OH}$
(d) $\text{H}_2\text{C}^-\text{CH}_3^-\text{OH}$  (e) $\text{Ph}^-\text{OH}$

21.2 What products would you expect from the following reaction?

\[
\begin{align*}
\text{OCH}_3^+\text{C}^-\text{Cl}^- & \xrightarrow{\text{NaNH}_2, \text{NH}_3, \text{1CH}, \text{~)CH}} \text{Br}^-\text{OCH}_3\text{C}^-\text{H}_3^-\text{OH} \\
\text{OCH}_3^+\text{C}^-\text{Cl}^- & \xrightarrow{\text{NaNH}_2, \text{NH}_3, \text{1CH}, \text{~)CH}} \text{Br}^-\text{OCH}_3\text{C}^-\text{H}_3^-\text{OH} \\
\end{align*}
\]

(a) $\text{OCH}_3^+\text{C}^-\text{H}_3^-\text{NH}_2$ alone  (b) $\text{OCH}_3^+\text{C}^-\text{H}_3^-\text{NH}_2$ alone  (c) $\text{OCH}_3^+\text{C}^-\text{H}_3^-\text{NH}_2$ alone
(d) More than one of the above  (e) All of the above

21.3 Which of the reagents listed here would serve as the basis for a simple chemical test to distinguish between $\text{H}_2\text{C}^-\text{Ph}^-\text{OH}$ and (CH$_3$)$_2$CCH$_2$OH?
(a) Ag(NH$_3$)$_2$OH  (d) Cold concd. H$_2$SO$_4$
(b) NaOH/H$_2$O  (e) None of the above
(c) Dilute HCl

21.4 Indicate the correct product, if any, of the following reaction.

\[
\text{H}_2\text{C}^-\text{Ph}^-\text{OH} + \text{HBr} \rightarrow ?
\]

(a) $\text{H}_2\text{C}^-\text{Ph}^-\text{Br}$  (b) $\text{H}_2\text{C}^-\text{Ph}^-\text{OH}$  (c) $\text{H}_2\text{C}^-\text{Ph}^-\text{Br}$
(d) $\text{H}_2\text{C}^-\text{Ph}^-\text{Br}$  (e) There is no reaction.

21.5 Complete the following synthesis:

21.6 Give the products:

\[
\begin{align*}
\text{OCH}_3\text{C}^-\text{H}_3^-\text{Br}^- & \xrightarrow{\text{conc. HBr}, \text{heat}} \text{OCH}_3\text{C}^-\text{H}_3^-\text{OH} + \text{C}^-\text{Br}^-\text{OCH}_3\text{C}^-\text{H}_3^-\text{OH} \\
\end{align*}
\]

21.7 Select the stronger acid.

\[
\begin{align*}
\text{(I)} & \text{ or } \text{(2)} \\
\text{(a)} & \text{ (b)}
\end{align*}
\]

(a) \[\text{O}^-\text{Ph}^-\text{OH}\]  (b) \[\text{O}_2\text{N}^-\text{Ph}^-\text{OH}\]

ANSWERS TO SECOND REVIEW PROBLEM SET

The problems review concepts from Chapters 13-21.

1. Increasing acidity

(a) \( \text{CH}_3\text{CH}_3 < \text{CH}_3\text{CH}_2\text{OH} < \text{CH}_2\text{OCH}_2\text{COCH}_3 < \text{CH}_3\text{COH} \)

(b) \( \text{CH}_3=\text{CH} < \text{CH}_3\text{OH} < \text{CH}_2\text{OH} < \text{CH}_3\text{COH} \)

(c) \( \text{CH}_3\text{C} \equiv \text{CH} < \text{CH}_3\text{COH} < \text{CH}_3\text{OCCH}_2\text{COCH}_3 < \text{CH}_3\text{C} \equiv \text{CH} \)

(d) \( \text{CH}_3\text{CH}_2\text{COH} < \text{CH}_3\text{CHClCOH} < \text{CH}_3\text{Cl}_2\text{COH} \)

(e) \( \text{NH}_2 < \text{CH}_3\text{CN} < \text{CH}_3\text{C} \equiv \text{CH} \)

2. Increasing basicity

(a) \( \text{CH}_3\text{NH}_2 < \text{NH}_3 < \text{CH}_3\text{CH}_2\text{NH}_2 \)

(b) \( \text{NH}_2 < \text{H}_2\text{C} \equiv \text{CH} < \text{H}_2\text{C} \equiv \text{CH}_2 < \text{C}_6\text{H}_5\text{NH}_2 \)

(c) \( \text{O}_2\text{N} \equiv \text{NH}_2 < \text{NH}_2 < \text{H}_2\text{C} \equiv \text{C} \equiv \text{NH}_2 \)

(d) \( \text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{NHCH}_3 \)

3. (a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{Pb}_3 \text{O}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaCN, heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3 \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaCN, heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3 \)

(d) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{1\text{KmNO}_4, \text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{COH} \)

(e) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{\text{H}_2\text{O, heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{COH} + \text{NH}_4^+ \)

(f) \( \text{CH}_3\text{CH}_2\text{COH} \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{CH}_2\text{CCL} \)

(g) \( \text{CH}_3\text{CH}_2\text{CCL} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CH}_2\text{CNH}_2 \)

(h) \( \text{CH}_3\text{CH}_2\text{CCL} \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{OH \text{base}}} \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3 \)

(i) \( \text{CH}_3\text{CH}_2\text{CCL} \xrightarrow{1\text{Br}_2\text{OH} \xrightarrow{(2) \text{H}_2\text{O}}} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3 + \text{CO}_3^+ \)

(j) \( \text{CH}_3\text{CH}_2\text{CCL} \xrightarrow{\text{AlCl}_3} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{Zn(Hg), HCl}} \text{CH}_3\text{CH}_2\text{CH}_3 \)
ANSWERS TO SECOND REVIEW PROBLEM SET

(k) \( \text{CH}_3\text{(CH}_2\text{)}_2\text{Cl} \xrightarrow{\text{CH}_3\text{CH}_2\text{CONa}} \text{[from part (f)]} \text{CH}_3\text{(CH}_2\text{)}_2\text{Cl}_2 \)

(l) \( \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{Cl} \xrightarrow{\text{Na}^+\text{CO}_2\text{Et}} \text{[from part (a)]} \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{CO}_2\text{Et} \)

\( \xrightarrow{\text{1OH}, \text{H}_2\text{O}, \text{heat}} \text{CH}_3\text{(CH}_2\text{)}_2\text{CH}_2\text{CO}_2\text{H} \)

4. (a) \( \text{H}_3\text{C} = \text{O} \xrightarrow{\text{Br}^-} \text{H}_3\text{C} - \text{CBr} \xrightarrow{\text{Mg, Et}_2\text{O}} \text{H}_3\text{C} - \text{CBr} \)

(1) \( \text{H}_3\text{C} = \text{CCH}_2\text{OH} \xrightarrow{\text{PCC, CH}_3\text{CH}_2} \text{H}_3\text{C} - \text{CCH}_2\text{CH}_2\text{CH}_3 \)

\( \xrightarrow{\text{H}_2\text{O}, \text{heat}} \text{H}_3\text{C} - \text{CCH}_2\text{CH} = \text{CH} \)

(b) \( \text{CH}_2\text{=CHCH}_3 \xrightarrow{\text{HF}} \text{CH}_3\text{CH} = \text{CHCH}_3 \xrightarrow{\text{NBS, CHCl}_3 \text{[aq]}} \text{CH}_3\text{CH} = \text{BrCH}_3 \)

\( \xrightarrow{\text{base}} \text{CH}_3\text{CH} = \text{CHCH}_3 \xrightarrow{\text{1THF, BH}_3, \text{2H}_2\text{O}, \text{OH}} \text{CH}_3\text{CH} = \text{CHCH}_3\text{CH}_2\text{OH} \)

(c) \( \text{NH}_2 \xrightarrow{\text{[CH}_3\text{CH}_2\text{O}, \text{Cl}_2\text{FeCl}_3 \text{[separate from ortho isomer]}}} \text{Cl} - \text{NHCCCH}_3 \)

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6. (a) A is \( \text{CH}_3=\text{CH}C\equiv\text{CH} \quad \text{C is } \text{BrMgOCH}_2\text{CH}C\equiv\text{CMgBr} \)

(b) A is an allylic alcohol and thus forms a carbocation readily. B is a conjugated enyne and is therefore more stable than A.

\[
\begin{align*}
\text{CH}_2=\text{CH}-C\equiv\text{CH} & \xrightarrow{\text{H}^+} \text{CH}_2=\text{CH}-C\equiv\text{CH} \\
\text{CH}_2=\text{CH}-C\equiv\text{CH} & \xrightarrow{\text{H}_2O} \text{HOCH}_2-\text{CH}=C\equiv\text{CH}
\end{align*}
\]

7. \( \text{CH}_3 \text{CH}+ \text{BrMgOCH}_2\text{CH}C\equiv\text{CMgBr} \xrightarrow{(2) \text{H}_2O^+} \)

8. \( \text{CH}_3\text{CCH}_3 + \text{H}^+ \xleftrightarrow{\text{H}_2O} \text{HO}=\text{C} \xrightarrow{\text{H}_2O} \text{HO}^-\text{C} \xrightarrow{\text{H}_2O} \)

9. \( \text{O}_2\text{N}-\text{C}-\text{CH}_3 \xrightarrow{(1) \text{KMnO}_4, \text{OH}^- \text{heat}} \text{O}_2\text{N}-\text{C}-\text{CH}_3 \xrightarrow{(2) \text{H}_2O^+} \text{O}_2\text{N}-\text{C}-\text{CH}_3 \)

10. (1) \( \text{HC}=\text{CNa} \xrightarrow{\text{HCl}} \text{A} \xrightarrow{\text{CICCI}} \text{B} \xrightarrow{\text{NH}_3} \text{Ethinamate} \)
ANSWERS TO SECOND REVIEW PROBLEM SET

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16. CH₃CH₂CH₂CHCH₃ (aldol addition) → CH₃CH₂CH₂CHCHO (Cannizzaro reaction)

17. H₂C=CHCH₂OH → CH₃CH₂CH₂CH₂COCH₂CH₂COH → SOCl₂

18. + H₂C=CHNO₂ (Diels-Alder reaction) → A → NO₂

19. (1) OsO₄ → B → H₂Ni → NHCH₂CH₃ → Fenamfamine

20. Working backward, we notice that methyl trans-4-isopropylcyclohexanecarboxylate has both large groups equatorial and is, therefore, more stable than the corresponding cis isomer. This stability of the trans isomer means that, if we were to synthesize the cis isomer or a mixture of both the cis and trans isomers, we could obtain the desired trans isomer by a base-catalyzed isomerization (epimerization):

We could synthesize a mixture of the desired isomers from phenol in the following way:
6. (a) A is \( \text{CH}_2=\text{CHCC}==\text{CHOH} \) and C is \( \text{BrMgOCH}_2\text{CH}==\text{CC}==\text{CMgBr} \).

(b) A is an allylic alcohol and thus forms a carbocation readily. B is a conjugated enyne and is therefore more stable than A.

\[
\begin{align*}
\text{A} & \quad \xrightarrow{\text{H}_2\text{O}^+} \quad \text{B} \\
\text{CH}_2==\text{CHCC}==\text{CH} & \quad \xrightarrow{\text{H}_2\text{O}^+} \quad \text{HOCH}_2\text{CH}==\text{CC}==\text{CH}
\end{align*}
\]

7. \( \text{CH}_3\text{CHCH}==\text{O} + \text{BrMgOCH}_2\text{CH}==\text{CC}==\text{CMgBr} \xrightarrow{(2)\text{H}_2\text{O}^+} \)

8. \( \text{CH}_2\text{CH}_3 + \text{H}^+ \xrightarrow{\text{H}_2\text{O}^+} \text{HOCH}_2\text{CH}==\text{CH} \xrightarrow{\text{H}_2\text{O}^+} \text{HOCH}==\text{CH} \)

9. \( \text{O}_2\text{N}==\text{CH} \xrightarrow{(1)\text{KMnO}_4, \text{OH}^-, \text{heat}} \text{O}_2\text{N}==\text{CHCOH} \xrightarrow{(2)\text{H}_2\text{O}^+} \text{Bisphenol A} \)

10. \( \text{HC}==\text{CNa} \xrightarrow{(1)\text{HC}==\text{CNa}} \text{HC}==\text{C} \xrightarrow{\text{CICl}} \text{HC}==\text{C} \xrightarrow{\text{NH}_3} \text{Ethinamate} \)
11. (a) \[ \begin{align*}
\text{C}_6\text{H}_5\text{CH}_3 & \xrightarrow{(1) \text{CH}_3\text{MgBr}} \text{C}_6\text{H}_5\text{CHOH} \\
& \xrightarrow{(2) \text{H}_2\text{O}^+} \text{C}_6\text{H}_5\text{CH}_3 \\
& \xrightarrow{\text{PB}_{\text{Br}}} \text{C}_6\text{H}_5\text{CHBr}
\end{align*} \]

(b) The last step probably takes place by an \( S_N 1 \) mechanism. Diphenylmethyl bromide, \( \text{B} \), ionizes readily because it forms the resonance-stabilized benzylic carbocation,

\[ \text{C}_6\text{H}_5\text{CH}^+ \]

12. (a) For this synthesis we need to prepare the benzylic halide, \( \text{Br-CH}_3 \), and then allow it to react with \( (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH} \) as in Problem 11. This benzylic halide can be made as follows:

\[ \begin{align*}
\text{Br-CH}_3 & \xrightarrow{(1) \text{CH}_3\text{MgBr}} \text{Br-CH}_2\text{OH} \\
& \xrightarrow{(2) \text{H}_2\text{O}^+} \text{Br-CH}_3
\end{align*} \]

(b) For this synthesis we can prepare the requisite benzylic halide in two ways:

\[ \begin{align*}
\text{C}_6\text{H}_5\text{CH}_3 & \xrightarrow{(1) \text{CH}_3\text{MgBr}} \text{C}_6\text{H}_5\text{CHOH} \\
& \xrightarrow{(2) \text{H}_2\text{O}^+} \text{C}_6\text{H}_5\text{CHBr}
\end{align*} \]

We shall then allow the benzylic halide to react with \( (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH} \) as in Problem 11.

13. \[ \text{CH}_3\text{CHCO}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{COCl}, \text{H}_2\text{O}} \text{CH}_3\text{CHC}^=\text{CHCN, \text{EtO}}^+ \] (Michael addition)
ANSWERS TO SECOND REVIEW PROBLEM SET

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19. (Diels-Alder reaction)

Notice that the second step involves the oxidation of a secondary alcohol in the presence of a tertiary alcohol. This selectivity is possible because tertiary alcohols do not undergo oxidation readily (Section 11.8)

20. (Canizzaro reaction)

We could synthesize a mixture of the desired isomers from phenol in the following way:
21. That Y gives a green opaque solution when treated with CrO₃ in aqueous H₂SO₄ indicates that Y is a primary or secondary alcohol. That Y gives a negative iodoform test indicates that Y does not contain the grouping \(-\text{CHCH}_3\). The \(^1\text{H}\)NMR spectrum of Y contains only four signals indicating that some of the carbons in Y are equivalent. The information from DEPT spectra helps us conclude that Y is 2-ethyl-1-butanol.

\[
\begin{align*}
(a) & \quad \delta 11.1 \\
(b) & \quad \delta 23.0 \\
(c) & \quad \delta 43.6 \\
(d) & \quad \delta 64.6 
\end{align*}
\]

Notice that the most downfield signal is a \(\text{CH}_2\) group. This indicates that this carbon atom bears the \(-\text{OH}\) group and that Y is a primary alcohol. The most upfield signals indicate the presence of the ethyl groups.

22. That Z decolorizes bromine in CCl₄ indicates that Z is an alkene. We are told that Z is the more stable isomer of a pair of stereoisomers. This fact suggests that Z is a trans alkene. That the \(^1\text{C}\) NMR spectrum contains only three signals, even though Z contains eight carbon atoms, indicates that Z is highly symmetric. The information from DEPT spectra indicates that the upfield signals of the alkyl groups arise from equivalent isopropyl groups. We conclude, therefore, that Z is trans-2,5-dimethyl-3-hexene.

\[
\begin{align*}
(a) & \quad \delta 22.8 \\
(b) & \quad \delta 31.0 \\
(c) & \quad \delta 134.5 
\end{align*}
\]

23. Here we find that two consecutive electrocyclic reactions (the first photochemical, the second thermal), provide a stereospecific synthesis of cis,trans-2,4-hexadiene from trans, trans-2,4-hexadiene.
G.4 (a) This is a photochemical electrocyclic reaction of an eight \( \pi \)-electron system—a 4\( \pi \) \( \pi \)-electron system where \( n = 2 \). It should, therefore, proceed with disrotatory motion.

\[
\begin{align*}
\text{cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene} & \xrightarrow{\text{hv (disrotatory)}} & \text{cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene}
\end{align*}
\]

(b) This is a thermal electrocyclic reaction of the eight \( \pi \)-electron system. It should proceed with conrotatory motion.

G.5 (a) This is conrotatory motion, and since this is a 4\( \pi \) \( \pi \)-electron system (where \( n = 1 \)) it should occur under the influence of heat.

G.6 (a) This is a (4\( n + 2 \) \( \pi \)-electron system (where \( n = 1 \)); a thermal reaction should take place with disrotatory motion.

\[
\begin{align*}
\text{trans, cis, trans-2,4,6-octatriene} & \xrightarrow{\text{heat (disrotatory)}} & \text{trans, cis, trans-2,4,6-octatriene}
\end{align*}
\]

(b) This is also a (4\( n + 2 \) \( \pi \)-electron system; a photochemical reaction should take place with conrotatory motion.

G.7 Here we need a conrotatory ring opening of \textit{trans}-5,6-dimethyl-1,3-cyclohexadiene (to produce \textit{trans},\textit{cis},\textit{trans}-2,4,6-octatriene); then we need a disrotatory cyclization to produce \textit{cis}-5,6-dimethyl-1,3-cyclohexadiene.

Since both reactions involve (4\( n + 2 \) \( \pi \)-electron systems, we apply light to accomplish the first step and heat to accomplish the second. It would also be possible to use heat to produce \textit{trans},\textit{cis},\textit{cis}-2,4,6-octatriene and then use light to produce the desired product.
G.8 The first electrocyclic reaction is a thermal, conrotatory ring opening of a (4n - 2) π-electron system. The second electrocyclic reaction is a thermal, disrotatory ring closure of a (4n + 2) π-electron system.

\[ \text{cis} \rightarrow \text{heat (conrotatory)} \rightarrow \text{trans} \]

This double bond is not involved in the first reaction.

\[ \text{heat (disrotatory)} \rightarrow \text{cis} \]

All three double bonds are involved in the second reaction.

A

G.9 (a) There are two possible products that can result from a concerted cycloaddition. They are formed when cis-2-butene molecules come together in the following ways:

(b) There are two possible products that can be obtained from trans-2-butene as well.

G.10 This is an intramolecular [2 + 2] cycloaddition.

G.11 (a)

(b) Enantiomer
SPECIAL TOPIC
Organic Halides and Organometallic Compounds in the Environment

SOLUTIONS TO PROBLEMS

H.1
\[ \text{Cl}_3\text{C}-\text{CH} + \text{HSO}_4^- \rightarrow \text{Cl}_3\text{C}-\text{CHOH} \rightarrow \text{Cl}_3\text{C}-\text{CH}_2\text{OH} + \text{HSO}_4^- \]

H.2
An elimination reaction.

H.3
(a) An \( \text{S}_2 \) reaction:

\[ \text{Cl}_3\text{C}-\text{CH} + \text{OH}^- \rightarrow \text{Cl}_3\text{C}-\text{CHOH} \rightarrow \text{Cl}_3\text{C}-\text{CH}_2\text{OH} \]

(b) An \( \text{S}_2 \) reaction:

\[ \text{Cl}_3\text{C}-\text{CH} + \text{Cl}^- \rightarrow \text{Cl}_3\text{C}-\text{CH}_2\text{Cl} \]

H.4
An \( \text{S}_2 \) reaction:

\[ \text{Cl}_3\text{C}-\text{CH} + \text{C}_{6}\text{H}_5\text{Cl} \rightarrow \text{Cl}_3\text{C}-\text{CH}_{2}\text{C}_{6}\text{H}_5 \]

\[ \text{Cl}_3\text{C}-\text{CH} + \text{C}_{6}\text{H}_5\text{O}^- \rightarrow \text{Cl}_3\text{C}-\text{CH}_{2}\text{C}_{6}\text{H}_5 \]
**SPECIAL TOPIC**
Transition Metal Organometallic Compounds

**SOLUTIONS TO PROBLEMS**

1.1

**Cyclobutadiene Iron tricarbonyl**

- Total number of valence electrons (both s and d electrons) of elemental iron:
  \[ d^e = 8 - 0 = 8 \]
- Total number of valence electrons of iron in the complex:
  \[ d^e = 8 + 3(\text{CO}) + \text{cyclobutadiene} = 8 + 3(2) + 4 = 18 \]

**Cyclopentadienylnanganese tricarbonyl**

- Total number of valence electrons of Mn in complex:
  \[ d^e = 7 - 1 = 6 \]
- Total number of valence electrons of Mg in complex:
  \[ d^e = 6 + 3(\text{CO}) + \text{Cp} = 6 + 3(2) + 6 = 18 \]

1.2

A syn addition of \( \text{D}_2 \) to the \( \text{trans} \) alkene would produce the following racemic form.

\[
\text{H}^\prime \quad \text{CH}_2\text{CO}_2\text{Et} + \text{D}_2 \quad \text{Rh}(\text{Ph}_3\text{P})_2\text{Cl} \quad \text{D} \quad \text{Rh}^1
\]

\[
\begin{align*}
\text{R} & \quad \text{Rh}^1 \quad \text{D} \quad \text{Rh}^1 \\
\text{H}^\prime & \quad \text{CH}_2\text{CO}_2\text{Et} \\
\text{H} & \quad \text{CH}_2\text{CO}_2\text{Et}
\end{align*}
\]

1.3

\[
(\text{Ph}_3\text{P})_2\text{RhCl} + \text{CH}_3\text{Li} \quad \text{ligand exchange} \quad (\text{Ph}_3\text{P})_2\text{RhCH}_3 + \text{LiCl}
\]

\[
\begin{align*}
\text{Rh}^1 & \quad \text{R} \quad \text{Rh}^1 \\
\text{H}^\prime & \quad \text{CH}_2\text{CO}_2\text{Et} \\
\text{H} & \quad \text{CH}_2\text{CO}_2\text{Et}
\end{align*}
\]

**Oxidative addition**

\[
\text{Rh}^1 + \text{Ph}_3\text{P} \quad \text{Rh}^1 (16 \text{ electrons})
\]

**Reductive elimination**

\[
\text{Rh}^1 (18 \text{ electrons})
\]
**I.4**  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl} + \text{CH}_3\text{Li} \rightarrow (\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{CH}_3) + \text{LiCl}$

(a) Is a ligand exchange
(b) Is an oxidative addition
(c) Is a reductive elimination

$(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl} + \text{C}_6\text{H}_5\text{CCH}_3 \rightarrow (\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{COC}_6\text{H}_5)(\text{CH}_3)\text{Cl}$

(16 electrons)

(Rh$^i$)

$(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl} + \text{C}_6\text{H}_5\text{CCH}_3 \rightarrow (\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{COC}_6\text{H}_5)(\text{CH}_3)\text{Cl}$

(18 electrons)

(Rh$^{III}$)

(a) Is a ligand exchange
(b) Is an oxidative addition
(c) Is a reductive elimination

**I.5**  1.  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H} \rightarrow (\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H}$

(Ligand dissociation)

$(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H}$

(18 electrons, Rh$^i$)

$(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H}$

(16 electrons, Rh$^i$)

2.  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H} + \text{CH}_3\text{OCOCCOCH}_3 \rightarrow \text{OC} \quad \text{OC}$

(Ligand association)

$(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H}$

(16 electrons, Rh$^i$)

$(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H}$

(18 electrons, Rh$^i$)

3.  $(\text{Ph}_3\text{P})_2\text{Rh} \rightarrow \text{OC} \quad \text{OC}$

(Insertion)

$(\text{Ph}_3\text{P})_2\text{Rh}$

(18 electrons, Rh$^i$)

$(\text{Ph}_3\text{P})_2\text{Rh}$

(16 electrons, Rh$^i$)

**I.6**  $(\text{CH}_3)_2\text{CuLi} + \text{Ph} \rightarrow \text{PhCH}_3 + \text{CH}_3\text{Cu}$

(Reductive elimination)

$(\text{CH}_3)_2\text{CuLi}$

(18 electrons)

(Rh$^{III}$)

Oxidative addition

Reductive elimination

Ligand association

Insertion
SUMMARY OF SOME REACTIONS OF MONOSACCHARIDES

- **Br₂**: Aldonic acid
- **H₂O**: Aldaric acid
- **HNO₃**: Osazone
- **Na₂NNH₂**: Cyanohydrin
- **HCl**: Alditol
- **(1)Br₂/H₂O; (2)H₂O/Fe⁺**: Aldose with one fewer carbon atom
- **Cyclic form of D-glucose**: Methyl glucoside

SOLUTIONS TO PROBLEMS

22.1
(a) Two, CHO
(b) Two, CH₂OH
(c) There would be four stereoisomers (two sets of enantiomers) with each general structure: \(2^2 = 4\).

22.2

![Solutions to Problems Diagram](image-url)
22.3 (a) \[\text{D-}(\pm)-\text{Glucose} \quad \text{and} \quad \text{2-Hydroxybenzyl alcohol}\]

22.4 Dissolve D-glucose in ethanol and then bubble in gaseous HCl.

22.5 Since glycosides are acetals, they undergo hydrolysis in aqueous acid to form cyclic hemiacetals that then undergo mutarotation.

22.6 \(\alpha\)-D-Glucopyranose will give a positive test with Benedict's or Tollens' solution because it is a cyclic hemiacetal. Methyl \(\alpha\)-D-glucopyranoside, because it is a cyclic acetal, will not.

22.7 (a) Yes (b) \(\text{CO}_2\text{H}\) (c) Yes (d) \(\text{CO}_2\text{H}\)

(e) No (f) \(\text{CHO} \quad \text{HNO}_3 \quad \text{HO}_2\text{C} \quad \text{CO}_2\text{H}\)

\(\text{D-Mannaric acid}\)

(g) The aldric acid obtained from D-erythrose is \(\text{meso-tartaric acid}\); the aldric acid obtained from D-threose is \(\text{D-tartaric acid}\).

22.8

22.9 One way of predicting the products from a periodate oxidation is to place an \(-\text{OH}\) group on each carbon atom at the point where C-C bond cleavage has occurred:
Then if we recall (Section 16.7A) that gem-diols are usually unstable and lose water to produce carbonyl compounds, we get the following results:

\[
\begin{align*}
\text{H-C-OH} + \text{H}_{2}\text{O} & \rightarrow \text{H-C=O} + \text{H}_{2}\text{O} \\
\text{H-C-OH} - \text{H} & \rightarrow \text{H-C=O} + \text{H}_{2}\text{O}
\end{align*}
\]

Let us apply this procedure to several examples here while we remember that for every C-C bond that is broken 1 mol of HI0 is consumed.

(a) \[
\begin{align*}
\text{H-C-OH} + \text{HI0} & \rightarrow \text{H-C-OH} + \text{H}_{2}\text{O} \\
\text{H-C-OH} & \rightarrow 2 \text{CH}_{3}\text{C-H}
\end{align*}
\]

(b) \[
\begin{align*}
\text{H-C-OH} + 2 \text{HI0} & \rightarrow \text{H-C-OH} + 2 \text{H}_{2}\text{O} \\
\text{H-C-OH} & \rightarrow \text{H-C=O}
\end{align*}
\]

(c) \[
\begin{align*}
\text{H-C-OH} + \text{HI0} & \rightarrow \text{H-C-OH} + \text{H}_{2}\text{O} \\
\text{H-C-OH} - \text{H} & \rightarrow \text{H-C=O}
\end{align*}
\]

(d) \[
\begin{align*}
\text{H-C-OH} + 2 \text{HI0} & \rightarrow \text{H-C-OH} + 2 \text{H}_{2}\text{O} \\
\text{H-C-OH} & \rightarrow \text{H-C=O}
\end{align*}
\]

(e) \[
\begin{align*}
\text{H-C-OH} + 2 \text{HI0} & \rightarrow \text{H-C-OH} + 2 \text{H}_{2}\text{O} \\
\text{H-C-OH} & \rightarrow \text{H-C=O}
\end{align*}
\]

(f) \[
\begin{align*}
\text{H-C-OH} + \text{HI0} & \rightarrow \text{H-C-OH} + \text{H}_{2}\text{O} \\
\text{H-C-OH} - \text{H} & \rightarrow \text{H-C=O}
\end{align*}
\]

(g) \[
\begin{align*}
\text{H-C-OH} + \text{HI0} & \rightarrow \text{H-C-OH} + \text{H}_{2}\text{O} \\
\text{H-C-OH} & \rightarrow \text{H-C=O}
\end{align*}
\]
22.10 Oxidation of an aldohexose and a ketohexose would each require 5 mol of HIO₄ but would give different results.

\[
\text{CHO} + 5 \text{HIO}_4 \rightarrow \text{HCO}_2\text{H} + \text{H}_2\text{O} + \text{CO}_2
\]

Aldohexose

\[
\text{CH}_2\text{OH} + \text{CO}_2 + \text{H}_2\text{O} + \text{HCHO} + \text{HCO}_2\text{H}
\]

Ketohexose

22.11 (a) Yes, D-glucitol would be optically active; only those alditols whose molecules possess a plane of symmetry would be optically inactive.

\[
\text{CHO} + \text{NaBH}_4 \rightarrow \text{CH}_2\text{OH}
\]

Optically inactive

(b) This experiment shows that D-glucose and D-fructose have the same configurations at C3, C4, and C5.
22.14 (a) 

CHO
H — OH
H — OH
CH₂OH
D (-)-Erythrose

(b) 

O
C — H
H — OH
H — OH
H — OH
CH₂OH
D(-)-Ribose
Optically inactive

O
C — H
H — OH
H — OH
H — OH
CH₂OH
D(-)-Arabinose
Optically active

22.15 A Kihlni-Fischer synthesis starting with D(-)-threose would yield I and II.

CHO
H — OH
HO — H
H — OH
CH₂OH
I
D(+)-Xylose

CHO
H — OH
HO — H
H — OH
CH₂OH
II
D(-)-Lyxose

I must be D(-)-xylose because, when oxidized by nitric acid, it yields an optically inactive aldonic acid:

I
HNO₃

Optically inactive
II must be D-(−)-lyxose because, when oxidized by nitric acid, it yields an optically active aldaric acid:

\[
\text{\text{CHO}} \quad \text{H} \quad \text{H} \quad \text{CO}_2\text{H} \\
\text{II}
\]

Optically active

22.16

\[
\begin{array}{llll}
\text{CHO} & \text{HO} & \text{H} & \text{CHO} \\
\text{HO} & \text{H} & \text{HO} & \text{HO} \\
\text{HO} & \text{H} & \text{H} & \text{HO} \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH} & \text{CH}_2\text{OH} & \text{CH}_2\text{OH} \\
\text{L-(+)-Ribose} & \text{L-(+)-Arabinose} & \text{L-(−)-Xylose} & \text{L-(+)-Lyxose}
\end{array}
\]

22.17 Since D-(+)galactose yields an optically inactive aldaric acid, it must have either structure III or structure IV.

\[
\text{CHO} \quad \text{H} \quad \text{OH} \\
\text{III} \quad \text{HNO}_3 \\
\text{HO} \quad \text{H} \quad \text{OH} \\
\text{HO} \quad \text{H} \quad \text{H} \\
\text{CH}_2\text{OH} \\
\text{Optically inactive}
\]

\[
\text{CHO} \quad \text{H} \quad \text{OH} \\
\text{IV} \quad \text{HNO}_3 \\
\text{HO} \quad \text{H} \quad \text{OH} \\
\text{HO} \quad \text{H} \quad \text{H} \\
\text{CH}_2\text{OH} \\
\text{Optically inactive}
\]

A Ruff degradation beginning with III would yield D-(−)-ribose.

\[
\text{III} \quad \text{B}_2\text{O}_3 \quad \text{H}_2\text{O} \quad \text{Fe}_2\text{(SO}_4)_3 \\
\text{CHO} \quad \text{HO} \quad \text{H} \quad \text{CH}_2\text{OH} \\
\text{D-(−)-Ribose}
\]

A Ruff degradation beginning with IV would yield D-(−)-lyxose: thus, D-(+)galactose must have structure IV.

\[
\text{IV} \quad \text{B}_2\text{O}_3 \quad \text{H}_2\text{O} \quad \text{Fe}_2\text{(SO}_4)_3 \\
\text{CHO} \quad \text{H} \quad \text{OH} \quad \text{CH}_2\text{OH} \\
\text{D-(−)-Lyxose}
\]

22.18 D-(+)glucose, as shown here.

\[
\begin{array}{l}
\text{H} \quad \text{O} \quad \text{CHO} \\
\text{Na-Hg} \quad \text{PH 3-5} \\
\text{H} \quad \text{O} \quad \text{HO} \\
\text{CHO} \\
\text{D-(+)-Glucose}
\end{array}
\]

The other γ-lactone of D-glucaric acid

22.19

\[
\begin{array}{c}
\text{D-Galactose} \\
\text{D-Galacturonic acid}
\end{array}
\]

22.20 (a) CHO (b) CHOH (c) CHOH

\[
\begin{array}{c}
\text{(CHOH)}_n \quad \text{C} \quad \text{O} \\
\text{HO} \quad \text{H} \quad \text{OH} \\
\text{CH}_2\text{OH} \\
\text{HO} \quad \text{H} \quad \text{OH} \\
\text{CH}_2\text{OH} \\
\text{CHOH}
\end{array}
\]
Any two aldoses that differ only in configuration at C2. (See also Section 22.8 for a broader definition.) D-Erythrose and D-threose are examples.

Cyclic sugars that differ only in the configuration of C1. The following are examples:

Any sugar in which all potential carbonyl groups are present as acetals (i.e., as glycosides). Sucrose (Section 22.12A) is an example of a nonreducing disaccharide; the methyl D-glucopyranosides (Section 22.4) are examples of nonreducing monosaccharides.
22.22 (a) 

(b) 

CH₂OH OCH₃ 

HOC₁₅H₂₉O₄H₄N₃ 

CH₂OH OCH₃ 

2HIO₄ → HOCH₂OCH₃ 

A methyl ribofuranoside would consume only 1 mol of HIO₄; a methyl ribopyranoside would consume 2 mol of HIO₄ and would also produce 1 mol of formic acid.

22.23 One anomer of D-mannose is dextrorotatory ([α]D = +29.3°); the other is levorotatory ([α]D = -17.0°).

22.24 The microorganism selectively oxidizes the \(-\text{CHOH}\) group of D-glucitol that corresponds to C5 of D-glucose.

22.25 L-Gulose and L-idose would yield the same phenylosazone as L-sorbose.

22.26 The microorganism selectively oxidizes the \(-\text{CHOH}\) group of D-glucitol that corresponds to C5 of D-glucose.

22.27 A is D-altrose, B is D-talose, C is D-galactose.
Different phenylosazones

22.29

D-Glucose

D-Talose

Different phenylosazones

22.30 The conformation of D-idopyranose with four equatorial -OH groups and an axial -CH₂OH group is more stable than the one with four axial -OH groups and an equatorial -CH₂OH group.

22.31 (a) The anhydro sugar is formed when the axial -CH₂OH group reacts with Cl to form a cyclic acetal.
Because the anhydro sugar is an acetal (i.e., an internal glycoside), it is a nonreducing sugar.

Methylation followed by acid hydrolysis converts the anhydro sugar to 2,3,4-tri-O-methyl-D-altrose:

(h) Formation of an anhydro sugar requires that the monosaccharide adopt a chair conformation with the -CH₂OH group axial. With β-D-altropyranose this requires that two -OH groups be axial as well. With β-D-glucopyranose, however, it requires that all four -OH groups become axial and thus that the molecule adopt a very unstable conformation:

22.32 1. The molecular formula and the results of acid hydrolysis show that lactose is a disaccharide composed of D-glucose and D-galactose. The fact that lactose is hydrolyzed by a β-galactosidase indicates that galactose is present as a glycoside and that the glycosidic linkage is beta to the galactose ring.

2. That lactose is a reducing sugar, forms a phenyllosazone, and undergoes mutarotation indicates that one ring (presumably that of D-glucose) is present as a hemiacetal and thus is capable of existing to a limited extent as an aldehyde.

3. This experiment confirms that the D-glucose unit is present as a cyclic hemiacetal and that the D-galactose unit is present as a cyclic glycoside.

4. That 2,3,4,6-tetra-O-methyl-D-galactose is obtained in this experiment indicates (by virtue of the free -OH at C3) that the galactose ring of lactose is present as a pyranose. That the methylated glucosidic acid obtained from this experiment has a free -OH group at C4 indicates that the C4 oxygen atom of the glucose unit is connected in a glycosidic linkage to the galactose unit.

Now only the size of the glucose ring remains in question, and the answer to this is provided by experiment 5.

5. That methylation of lactose and subsequent hydrolysis gives 2,3,6-tri-O-methyl-D-glucose— that it gives a methylated glucose derivative with a free -OH at C4 and C5—demonstrates that the glucose ring is present as a pyranose. (We know already that the oxygen at C4 is connected in a glycosidic linkage to the galactose unit; thus, a free -OH at C5 indicates that the C5 oxygen atom is a part of the hemiacetal group of the glucose unit and that the ring is six-membered.)
22.34 Trehalose has the following structure:

\[
\begin{align*}
\alpha-D-Glucopyranosyl-\alpha-D-gluco\text{pyranoside} \\
\text{or}
\end{align*}
\]

We arrive at this structure in the following way:

1. Acid hydrolysis shows that trehalose is a disaccharide consisting only of D-glucose units.
2. Hydrolysis by \(\alpha\)-glucosidases and not by \(\beta\)-glucosidases shows that the glycosidic linkages are alpha.
3. That trehalose is a nonreducing sugar, that it does not form a phenyllosazone, and that it does not react with bromine water indicate that no hexitonal groups are present. This means that C1 of one glucose unit and C1 of the other must be joined in a glycosidic linkage. Fact 2 (just cited) indicates that this linkage is alpha to each ring.
4. That methylation of trehalose followed by hydrolysis yields only 2,3,4,6-tetra-O-methyl-D-glucose demonstrates that both rings are six membersed.

22.35 (a) Tollens' reagent or Benedict's reagent will give a positive test with D-glucose but will give no reaction with D-glctitol.
(b) D-Glucaric acid will give an acidic aqueous solution that can be detected with blue litmus paper. D-Glucitol will give a neutral aqueous solution.
(c) D-Glucose will be oxidized by bromine water and the red brown color of bromine will disappear. D-Fructose will not be oxidized by bromine water since it does not contain an aldehyde group.
(d) Nitric acid oxidation will produce an \textit{optically active} aldaric acid from D-glucose but an \textit{optically inactive} aldaric acid will result from D-galactose.
(e) Maltose is a reducing sugar and will give a positive test with Tollens' or Benedict's solution. Sucrose is a nonreducing sugar and will not react.
(f) Maltose will give a positive Tollens' or Benedict's test; maltic acid will not.
(g) 2,3,4,6-Tetra-O-methyl-\(\beta\)-D-glucopyranose will give a positive test with Tollens' or Benedict's solution; methyl \(\beta\)-D-glucopyranoside will not.
(h) Periodic acid will react with methyl \(\alpha\)-D-ribofuranoside because it has hydroxyl groups on adjacent carbons. Methyl 2-deoxy-\(\alpha\)-D-ribofuranoside will not react.

22.36 That the Schardinger dextrins are nonreducing shows that they have no free aldehyde or hemiacetal groups. This lack of reaction strongly suggests the presence of a cyclic structure. That methylation and subsequent hydrolysis yields only 2,3,6-tri-O-methyl-D-glucose indicates that the glycosidic linkages all involve C1 of one glucose unit and C4 of the next. That \(\alpha\)-glucosidases cause hydrolysis of the glycosidic linkages indicates that they are \(\alpha\)-glycosidic linkages. Thus, we are led to the following general structure:

![Cyclic structure of Schardinger dextrins](image)

\(n = 3, 4, \text{or} 5\)

Note: Schardinger dextrins are extremely interesting compounds. They are able to form complexes with a wide variety of compounds by incorporating these compounds in the cavity in the middle of the cyclic dextrin structure. Complex formation takes place, however, only when the cyclic dextrin and the guest molecule are the right size. Anthracene molecules, for example, will fit into the cavity of a cyclic dextrin with eight glucose units but will not fit into one with seven. For more information about these fascinating compounds, see Bergeron, R. J., "Cycloamyloses," J. Chem. Educ., 1977, 54, 204-207.

22.37 Isomaltose has the following structure:

![Isomaltose structure](image)

6-O-(\(\alpha\)-D-Glucopyranosyl)-D-glucopyranose

(1) The acid and enzymic hydrolysis experiments tell us that isomaltose has two glucose units linked by an \(\alpha\) linkage.
(2) That isomaltose is a reducing sugar indicates that one glucose unit is present as a cyclic hemiacetal.
(3) Methylation of isomaltonic acid followed by hydrolysis gives us information about the size of the nonreducing pyranoside ring and about its point of attachment to the reducing ring. The formation of the first product (2,3,4,6-tetra-O-methyl-D-glucose)—a compound with an -OH at C5—tells us that the nonreducing ring is present as a pyranoside. The formation of 2,3,4,5-tetra-O-methyl-D-glucuronic acid—a compound with an -OH at C6—shows that the nonreducing ring is linked to C6 of the reducing ring.

Methylation of maltose itself tells the size of the reducing ring. That 2,3,4-tri-O-methyl-D-glucose is formed shows that the reducing ring is also six membered; we know this because of the free -OH at C5.

22.38 Stachyose has the following structure:

The enzymic hydrolyses (as just indicated) give the basic structure of stachyose and raffinose. The only remaining question is the ring size of the first galactose unit of stachyose. That methylation of stachyose and subsequent hydrolysis yields 2,3,4,6-tetra-O-methyl-D-galactose establishes that this ring is a pyranoside.

22.39 Arbutin has the following structure:
The reactions that take place are the following:

22.40 Aldotetrose B must be D-threose because the alditol derived from it (D-threitol) is optically active (the alditol from D-erythrose, the other possible D aldotetrose, would be meso). Due to rotational symmetry, however, the alditol from B (D-threitol) would produce only two $^13C$ NMR signals. Compounds A-F are thus in the family of aldoses stemming from D-threose. Since reduction of aldopentose A produces an optically inactive alditol, A must be D-xylene. The two diastereomeric aldohexoses C and D produced from A by a Kiliani-Fischer synthesis must therefore be D-idose and D-gulose, respectively. E and F are the alditols derived from C and D, respectively. Alditol E would produce only three $^13C$ NMR signals due to rotational symmetry while F would produce six signals.

22.41 There are four closely spaced upfield alkyl signals in the $^13C$ NMR spectrum (826.5, 825.6, 824.9, 824.2), corresponding to the four methyls of the two acetone protecting groups. (The compound is, therefore, the 1,2,5,6-bis-acetone of mannofuranose, below.)
*22.45 (a) The proton at Cl. (b) Because of the single neighboring hydrogen (at C2). (c) and (d).

![Chemical structures](image)

**QUIZ**

22.1 Supply the appropriate structural formula or complete the partial formula for each of the following:

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ketotetrose</td>
<td>A D-sugar</td>
<td>An L-sugar</td>
<td>An aldose</td>
</tr>
</tbody>
</table>

![Chemical structures](image)

22.2 Which of the following monosaccharides yields an optically inactive alditol on NaBH₄ reduction?

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO</td>
<td>CHO</td>
<td>CHO</td>
<td>CHO</td>
</tr>
<tr>
<td>HO-H</td>
<td>HO-H</td>
<td>HO-H</td>
<td>HO-H</td>
</tr>
<tr>
<td>HO-H</td>
<td>HO-H</td>
<td>HO-H</td>
<td>HO-H</td>
</tr>
<tr>
<td>CH₂OH</td>
<td>CH₂OH</td>
<td>CH₂OH</td>
<td>CH₂OH</td>
</tr>
</tbody>
</table>

**Answer:**

22.3 Give the structural formula of the monosaccharide that you could use as starting material in the Kiliani-Fischer synthesis of the following compound:

![Chemical structure](image)

22.4 The D-aldopentose, (a), is oxidized to an aldaric acid, (b), which is optically active. Compound (a) undergoes a Ruff degradation to form an aldosterone, (c), which undergoes oxidation to an optically inactive aldaric acid, (d). Supply the reagents for these transformations and the structural formulas of (a), (b), (c), and (d).

![Chemical structures](image)

22.5 Give the structural formula of the β-pyranose form of (a) in the space just given.
22.6 Complete the following skeletal formulas and statements by filling in the blanks and circling the words that make the statements true.

The Haworth and conformational formulas of the β-cyclic hemiacetal of D-Mannose are (a) and (b) .

This cyclic hemiacetal is (c) reducing, nonreducing; on reaction with Br₂/H₂O it gives an optically (d) active, inactive (e) aldric, aldonic acid. On reaction with dilute HNO₃ it gives an optically (f) active, inactive (g) aldric, aldonic acid. Reaction of the cyclic hemiacetal with (h) converts it into an optically (i) active, inactive alditol.

22.7 Outline chemical tests that would allow you to distinguish between:

(a) Glucose

(b) Galactose

22.8 Hydrolysis of (+)-sucrose (ordinary table sugar) yields

(a) D-glucose
(b) D-mannose
(c) D-fructose
(d) D-galactose
(e) More than one of the above.

22.9 Select the reagent needed to perform the following transformation:

(a) CH₃OH, KOH
(b) (CH₃)₂O
(c) (CH₃)₂SO₄, OH⁻
(d) CH₃OH, HCl
(e) (CH₂OCH₃)₂HCl
23 LIPIDS

SOLUTIONS TO PROBLEMS

23.1 (a) There are two sets of enantiomers, giving a total of four stereoisomers:

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H} \\
(CH_2)_7 & \quad (CH_2)_7 \\
\text{H} & \quad \text{H} \\
\text{Br} & \quad \text{Br} \\
\text{H} & \quad \text{H} \\
(CH_2)_3 & \quad (CH_2)_3 \\
& + \\
\text{H} & \quad \text{H} \\
\text{Br} & \quad \text{Br} \\
\text{H} & \quad \text{H} \\
\text{Br} & \quad \text{Br} \\
(CH_2)_3 & \quad (CH_2)_3 \\
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H} \\

\text{erythro} & \quad \text{threo}
\end{align*}
\]

(b) Formation of a bromonium ion at the other face of palmitoleic acid gives a result such that the \textit{threo} enantiomers are the only products formed (obtained as a racemic modification).

The designations \textit{erythro} and \textit{threo} come from the names of the sugars called \textit{erythrose} and \textit{threose} (Section 22.9A).

23.2

Zingiberene
\textit{(a) sesquiterpene)}

\beta-Selinene
\textit{(a) sesquiterpene)}

Caryophyllene
\textit{(a) sesquiterpene)}

Squalene
\textit{(a triterpene)}

23.3

(a) (1) \textit{O}_2, \textit{Zn}, \textit{HOAc}

(b) (1) \textit{O}_2, \textit{Zn}, \textit{HOAc}

(c) \textit{a-Farnesene} (see Section 23.3) (1) \textit{O}_2, \textit{Zn}, \textit{HOAc}

\textit{(b)-threo-9,10-Dibromohexadecanoic acids}
(d) Geraniol (see Section 23.3)

\[
\begin{align*}
(1) \ce{O_3} & \rightarrow \ce{CH_3CCH_3 + HCH_2CH_2CH_3} \\
(2) \ce{Zn, HOAc} & \quad + \ce{HCH_2OH}
\end{align*}
\]

(e) Squalene (see Section 23.3)

\[
(1) \ce{O_3} \quad \rightarrow \quad 2\ce{CH_2CCH_3 + HCH_2CH_2CH_3}
\]

\[
+ \quad 4\ce{CH_3CCH_2CH_2CH_3}
\]

23.4 (a)  

\[
\text{(+ further oxidation products)}
\]

23.5 Br₃ in CCl₄ or KMnO₄ in H₂O at room temperature. Either reagent would give a positive result with geraniol and a negative result with menthol.

23.6

23.7 (a) 3α-Hydroxy-5α-androstan-17-one  
(b) 17α-Ethynyl-17β-hydroxy-5(10)-estren-3-one (androsterone, norethynodrel)

23.8 Absolute configuration of cholesterol (5-cholesten-3β-ol)

23.9 Estrone and estradiol are phenols and thus are soluble in aqueous sodium hydroxide. Extraction with aqueous sodium hydroxide separates the estrogens from the androgens.

23.10 (a)  

\[
\text{Cholesterol} \quad \ce{Br_3} \rightarrow \quad 5α,6β-Dibromocholestan-3β-ol
\]
5α,6α-Epoxycholestan-3β-ol
(prepared by epoxidation of cholesterol; cf. Section 23.4G)

Cholestan-3β,5α,6β-triol

5α-Cholestan-3β-ol
(prepared by hydrogenation of cholesterol; cf. Section 23.4G)

5α-Cholestan-3-one

5α,6α-Epoxycholestan-3β-ol
6β-Bromocholestan-3β,5α-diol

23.11 (a) CH₃OH + RCOH + R'COH + H₃PO₄ + HOCH₂CH₂N(CH₃)₂ X' →
CH₂OH
(b) CH₃OH + RCOH + R'COH + H₃PO₄ + HOCH₂CH₂NH₂
CH₂OH
(c) CH₃OH + CH₂(CH₃)₂CH₂CH + R'COH + H₃PO₄
CH₂OH
+ HOCH₂CH₂N(CH₃)₂ X'

23.12 (a) CH₃(CH₂)₄CO₂H + C₂H₅OH → H⁺ CH₃(CH₂)₄CO₂CH₂H + H₂O
CH₃(CH₂)₁₂CO₄H → CH₃(CH₂)₁₂CO₂C₂H₅
CH₂(CH₂)₄CO₂H → CH₃(CH₂)₁₂CO₂C₂H₅
(b) CH₃(CH₂)₁₂CO₂H + (CH₃)₂COH → CH₃(CH₂)₁₂CO₂C(CH₃)₂
(c) CH₃(CH₂)₁₂CO₂H → NH₂ → CH₃(CH₂)₁₂CONH₂
(d) CH₃(CH₂)₁₂CO₂H → (CH₃)₂NH → CH₃(CH₂)₁₂CON(CH₃)₂
(e) CH₃(CH₂)₁₂CONH₂ → LiAlH₄ → CH₃(CH₂)₁₂CH₂NH₂
(f) CH₃(CH₂)₁₂CONH₂ → Br₂ → CH₃(CH₂)₁₂CH₂NH₂
(g) CH₃(CH₂)₁₂CO₂H → LiAIH₄(OCH₂CH₃) → CH₃(CH₂)₁₂CHO
(h) CH₃(CH₂)₁₂CO₂CH₂H → H₂ → CH₃(CH₂)₁₂CH₂OH
CH₃(CH₂)₁₂CO₂H → CH₃(CH₂)₁₂CH₂OH
CH₃(CH₂)₁₂CO₂CH₂H → H₂ → CH₃(CH₂)₁₂CH₂OH
(i) CH₃(CH₂)₁₂CO₂CH₂H → (1)LiAlH₄ → CH₃(CH₂)₁₂CH₂OH
CH₃(CH₂)₁₂CO₂CH₂H → H₂ → CH₃(CH₂)₁₂CH₂OH
(j) CH₃(CH₂)₁₂CO₂H + (CH₃)₂CuLi → CH₃(CH₂)₁₂COCH₂
23.16 (a) \( \text{CH}_3\text{(CH}_2)_2\text{C}==\text{CH}\text{(CH}_2)_2\text{CO}_2\text{H} \) and \( \text{CH}_3\text{(CH}_2)_2\text{C}==\text{CH}\text{(CH}_2)_2\text{CO}_2\text{H} \)

(b) Infrared spectroscopy

(c) A peak in the 675–730-cm\(^{-1}\) region would indicate that the double bond is cis: a peak in the 960–975-cm\(^{-1}\) region would indicate that it is trans.

23.17 A reverse Diels-Alder reaction takes place.

23.18

α-Phellandrene  β-Phellandrene

Note: On permanganate oxidation, the =CH\(_2\) group of β-phellandrene is converted to CO\(_2\) and thus is not detected in the reaction.

23.19 \( \text{CH}_3\text{(CH}_2)_2\text{C}==\text{CH} + \text{NaNH}_2 \xrightarrow{\text{lin. NH}_2} \text{CH}_3\text{(CH}_2)_2\text{C}==\text{CNa} \)

23.15 Elaidic acid is trans-9-octadecenoic acid:

\( \text{CH}_3\text{(CH}_2)_7==\text{CH}==\text{(CH}_2)_2\text{CO}_2\text{H} \)

It is formed by the isomerization of oleic acid.
Here we find that epoxidation takes place at the less hindered α face (cf. Section 23.4G). Ring opening by HBr takes place in an anti fashion to give a product with diaxial substituents.

23.22
(a) CH₂=CH=CH=CH₂
(b) OH⁻ (Removal of the α hydrogen atom allows isomerization to the more stable compound with a trans ring junction.)
(c) LiAlH₄
(d) H₂O° and heat. (Hydrolysis of the enol ether is followed by dehydration of one alcohol group.)
(e) HCO₂C₆H₄, C₆H₄ONa
(f) OsO₄, then NaHSO₄
(g) CH₃CCH₂H₂, H⁺
(h) H₂, Pd catalyst
(i) H₂O°, H₂O
(j) HIO₄
(k) Base and heat. (This reaction is an aldol condensation.)
(l) and (m) Na₂CrO₄, CH₃CO₂H to oxidize the aldehyde to an acid, followed by esterification.
(n) H₂ and Pt. (Hydrogen addition takes place from the less hindered α face of the molecule.)
(o), (p), and (q) NaBH₄ to reduce the keto group; OH⁻, H₂O to hydrolyze the ester; and acetic anhydride to esterify the OH at the 3-position.
(r) and (s) SOCl₂ to make the acid chloride, followed by treatment with (CH₃)₂Cd.
(t) CH₃CH₂CH₂CH₂CH₂MgBr, followed by H₂O⁺.
(u), (v), and (w) Acetic acid and heat to dehydrate the tertiary alcohol; followed by acetic anhydride to acetylate the secondary alcohol; followed by H₂, Pt to hydrogenate the double bond.

23.23
(a) CH₃(CH₂)₂CH (b) C₂H₅Li (c) 
(d) 
(e) Michael addition using a basic catalyst.

23.24
First: an elimination takes place,
R₂NCH₂CH₂CH=CH₂ + NH₂⁺ → CH=CHCH₂CH₂ + R₂N + NH₃
Then a conjugate addition occurs, followed by an aldol addition:
The reaction is an intramolecular transesterification.

23.25  \[ \text{CH}_3\text{(CH}_2\text{)}_{12}\text{CHO} \rightarrow \text{CH}_3\text{(CH}_2\text{)}_{12}\text{CHCH}_2\text{COEt} \rightarrow \text{CH}_3\text{(CH}_2\text{)}_{12}\text{CHCH}_2\text{COH} \]

A naturally occurring fatty acid

A soap

23.26  \[ \text{A solid fat} \quad \text{An oil} \]

A synthetic detergent

5α-Estran-17-one

23.2  Give a reagent that would distinguish between each of the following:

(a)  Pregnane and 20-pregnane

23.1  Write an appropriate formula in each box.

(a)  

(b)  

(c)  

(d)  

(e)  

(f)  

A naturally occurring fatty acid

A soap

A solid fat

An oil

A synthetic detergent

5α-Estran-17-one
(b) Stearic acid and oleic acid

(c) 17α-Ethynyl-1,3,5(10)-estratriene-3,17β-diol (ethynylestradiol) and 1,3,5(10)-estratriene-3,17β-diol (estradiol)

23.3 What product would be obtained by catalytic hydrogenation of 4-androstone?

23.4 Supply the missing compounds:

\[ \text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_2\text{Br} \xrightarrow{\text{H}_2\text{CNs}} \]

\[ \text{NaNH}_3 \xrightarrow{} \]

\[ \xrightarrow{\text{KOH, } \text{H}_2\text{O, heat}} \]

\[ \xrightarrow{\text{CH}_3\text{(CH}_2\text{)}_3\text{C}≡\text{C(CH}_2\text{)}_3\text{CN}} \]

23.5 The following compound is a:

(a) Monoterpene  (b) Sesquiterpene  (c) Diterpene

(d) Triterpene  (e) Tetraterpene

23.6 Mark off the isoprene units in the previous compound.

23.7 Which is a systematic name for the steroid shown here?

(a) 5α-Androstan-3α-ol

(b) 5β-Androstan-3β-ol

(c) 5α-Pregnan-3α-ol

(d) 5β-Pregnan-3β-ol

(e) 5α-Estran-3α-ol
AMINO ACIDS AND PROTEINS

SOLUTIONS TO PROBLEMS

24.1 (a) \( \text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H} \)  (b) \( \text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}^- \)

(c) \( \text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2^- \) predominates at the isoelectric point rather than \( \text{NH}_3^+ \) \( \text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H} \) because of the acid-strengthening inductive effect of the \( \alpha \)-ammonium group.

(d) Since glutamic acid is a dicarboxylic acid, acid must be added (i.e., the pH must be made lower) to suppress the ionization of the second carboxyl group and thus achieve the isoelectric point. Glutamine, with only one carboxyl group, is similar to glycine or phenylalanine and has its isoelectric point at a higher pH.

24.2 The conjugate acid is highly stabilized by resonance.

\[
\text{R-}\text{NH-C}^\text{=NH,} \quad \text{R-}\text{NH-C}^\text{=NH,}
\]

24.3 (a) \( \text{HCO}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \) + \( \text{H}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \) \( \text{NaOH} \) heat

24.4 (a) \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \) \( \text{H}_2\text{O} \) \( \text{HCN} \) base \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+ \)

(b) \( \text{CH}_3\text{SH} + \text{CH}_2=\text{CH}-\text{CH} \) base \( \text{CN} \) \( \text{CH}_3\text{SCH}_2\text{CH}_{3} \) \( \text{H}_2\text{O} \) \( \text{NH}_3^+ \)

24.5 Because of the presence of an electron-withdrawing 2,4-dinitrophenyl group, the labeled amino acid is relatively nonbasic and is, therefore, insoluble in dilute aqueous acid. The other amino acids (those that are not labeled) dissolve in dilute aqueous acid.
24.6 (a) $\text{H}_2\text{NCHCONHCHCONHCH}_2\text{CO}_2^- \xrightarrow{\text{O}_2^-} \text{HCO}_3^-$

Val+Ala+Gly

24.7 $\text{N=C=S} + \text{H}_2\text{N}-\text{CHCH=NH}-\text{CHCH=NH}-\text{CHCH=NH}_3^-$

Phenyl isothiocyanate

24.8 (a) Two structures are possible with the sequence Glu+Cys+Gly. Glutamic acid may be linked to cysteine through its $\alpha$-carboxyl group,

$$\text{HO}_2\text{CCH}_3\text{CH}_2\text{CHCO}^- - \text{NHCHCO}^- - \text{NHCH}_2\text{CO}_2^-$$

or through its $\gamma$-carboxyl group,

$$\text{H}_2\text{NCHCHCH}_2\text{CO}^- - \text{NHCHCO}^- - \text{NHCH}_2\text{CO}_2^-$$

(b) This result shows that the second structure is correct, that in glutathione the $\gamma$-carboxyl group is linked to cysteine.
24.9 We look for points of overlap to determine the amino acid sequence in each case.
(a) Ser • Thr
Pro • Ser
Thr • Hyp
Pro • Ser • Thr • Hyp
(b) Ala • Cys
Cys • Arg • Val
Leu • Ala
Leu • Ala • Cys • Arg • Val

24.10 Sodium in liquid ammonia brings about reductive cleavage of the disulfide linkage of oxytocin to two thiol groups; then air oxidizes the two thiol groups back to a disulfide linkage.

24.11 \( \text{H}_{3}\text{NCH}_{2}\text{CO}_{2}^- + (\text{CH}_3\text{CO})\text{COO}(\text{CH}_3)_3 \rightarrow \text{OH}^- \)

\( \text{Boc-Gly} \)

\( \text{Valine} \)

\( \text{Boc-Gly} + \text{Val} \)

24.12 (a) \( 2\text{C}_2\text{H}_5\text{CH}_2\text{OCCl} + \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2^- \rightarrow \text{OH}^- \)

\( \text{Lysine} \text{NH}_2 \)

\( \text{Boc-Gly+Val} \text{Ala} \)

\( \text{Lys+Ile} \text{CH}_3 \)
The weakness of the benzyl-oxygen bond allows these groups to be removed by catalytic hydrogenolysis.

An electrophilic substitution reaction:

[b] The linkage between the resin and the polypeptide is a benzyl ester. It is cleaved by HBr in CF₃CO₂H at room temperature because the carbocation that is formed initially is the relatively stable, benzyl cation.
24.16 (a) Isoleucine, threonine, hydroxyproline, and cystine.

(b) Serine: 
\[
\begin{align*}
\text{H}_3\text{N}^+ & \quad \text{CO}_2^- \\
\text{H} & \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]
and
\[
\begin{align*}
\text{H}_3\text{N}^+ & \quad \text{CO}_2^- \\
\text{H} & \quad \text{H} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

24.17 (a) Alanine

\[
\text{CH}_3\text{CH}_2\text{CO}_2^- + \text{HONO} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{N}_2\text{O}
\]

(b) Proline and hydroxyproline. All of the other amino acids have at least one primary amine group.

(c) Diastereomers

24.18 (a) (-)-Serine

\[
\text{H}_3\text{N}^+ \quad \text{CO}_2^- + \text{HCl} \rightarrow \text{H}_3\text{N}^+ \quad \text{CO}_2\text{H} + \text{Cl}^-
\]

(b) HCl

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CH}_2\text{Cl} \\
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{Cl}^-
\end{align*}
\]

(c) NaHg

\[
\begin{align*}
\text{H}_3\text{N}^+ \quad \text{CO}_2^- & \rightarrow \text{H}_3\text{N}^+ \quad \text{CO}_2^- + \text{H}_2\text{O} \\
\text{H}_3\text{N}^+ \quad \text{CO}_2^- & \rightarrow \text{H}_3\text{N}^+ \quad \text{CO}_2^- + \text{H}_2\text{O}
\end{align*}
\]

(d) L-(+)-Alanine
24.20 We look for points of overlap:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arg + Pro + Gly + Phe</td>
<td>Pro + Gly + Phe</td>
</tr>
<tr>
<td>Arg + Pro + Gly + Phe</td>
<td>Pro + Phe</td>
</tr>
</tbody>
</table>

Bradykinin

24.21 1. This experiment shows that valine is the N-terminal amino acid and that valine is attached to leucine. (Lysine labeled at the e-amino group is to be expected if lysine is not the N-terminal amino acid and if it is linked in the polypeptide through its e-amino group.)

2. This experiment shows that alanine is the C-terminal amino acid and that it is linked to glutamic acid.

At this point, then, we have the following information about the structure of the heptapeptide:

Val + Leu (Ala, Lys, Phe) Glu + Ala

The sequence here is unknown.

3. (a) This experiment shows that the dipeptide, A, is Leu + Lys

(b) The carboxypeptidase reaction shows that the C-terminal amino acid of the tripeptide, B, is glutamic acid; the DNP labeling experiment shows that the N-terminal amino acid is phenylalanine. Thus, the tripeptide B is Phe + Ala + Glu

Putting these pieces together in the only way possible, we arrive at the following amino acid sequence for the heptapeptide:

Val + Leu + Lys

Phe + Ala + Glu

24.22 At pH 2-3 the γ-carboxyl groups of polymalic acid are uncharged. (They are present as CO₂⁻ groups.) At pH 5 the γ-carboxyl groups ionize and become negatively charged. (They become CO₂⁻ groups.) The repulsive forces between these negatively charged groups cause an unwinding of the α helix and the formation of a random coil.
The observation that the $^1$H NMR spectrum taken at room temperature shows two different signals for the methyl groups suggests that they are in different environments. This would be true if rotation about the carbon-nitrogen bond was not taking place.

\[
\begin{align*}
\delta & = 8.05 & \text{HCH,} & \delta & = 2.95 & \text{HCH,} & \delta & = 2.80
\end{align*}
\]

We assign the $\delta 2.80$ signal to the methyl group that is on the same side as the electronegative oxygen atom.

The fact that the methyl signals appear as doublets (and that the formyl proton signal is a multiplet) indicates that long-range coupling is taking place between the methyl protons and the formyl proton.

That the two doublets are not simply the result of spin-spin coupling is indicated by the observation that the distance that separates one doublet from the other changes when the applied magnetic field strength is lowered. [Remember! The magnitude of a chemical shift is proportional to the strength of the applied magnetic field, while the magnitude of a coupling constant is not.]

That raising the temperature (to 11°C) causes the doublets to coalesce into a single signal indicates that at higher temperatures the molecules have enough energy to surmount the energy barrier of the carbon-nitrogen bond. Above 11°C, rotation is taking place so rapidly that the spectrometer is unable to discriminate between the two methyl groups.

\[
\begin{align*}
\text{(a) } & \text{HO-} & \text{+H}_2\text{O, and } & \text{+H}^+ \\
\text{H}_2\text{N:} & \text{HO-C-CH(CH}_2)_n-S-\text{etc.} & \text{+H}^+ & \text{etc.} \\
\end{align*}
\]
25 NUCLEIC ACIDS AND PROTEIN SYNTHESIS

SOLUTIONS TO PROBLEMS

25.1 Adenine:

Guanine:

Cytosine:

Thymine (R=CH₃) or Uracil (R=H):

25.2 (a) The nucleosides have an ₩-glycosidic linkage that (like an O-glycosidic linkage) is rapidly hydrolyzed by aqueous acid but is one that is stable in aqueous base.
25.3 The reaction appears to take place through an $S_{N}2$ mechanism. Attack occurs preferentially at the primary 5'-carbon atom rather than at the secondary 3'-carbon atom.

25.5 (a) The isopropylidene group is part of a cyclic acetal and is thus susceptible to hydrolysis by mild acid.
(b) It can be installed by treating the nucleoside with acetone and a trace of acid and by simultaneously removing the water that is produced.

25.6 (a) Cordycepin is (3'-Deoxyadenosine)
(b) It can be installed by treating the nucleoside with acetone and a trace of acid and by simultaneously removing the water that is produced.
25.7 (a) \[ 6 \times 10^9 \text{ base pairs} \times \frac{34 \text{ Å}}{10 \text{ base pairs}} \times \frac{10^{-10} \text{ m}}{\text{Å}} = 2 \text{ m} \]

(b) \[ 6 \times 10^{-12} \text{ ovum} \times 3 \times 10^9 \text{ ova} = 1.8 \times 10^{-2} \text{ g} \]

25.8 (a)

[Diagram of lactim form of guanine and thymine]

(b) Thymine would pair with adenine and thus adenine would be introduced into the complementary strand where guanine should occur.

25.9 (a) A diazonium salt and a heterocyclic analog of a phenol.

25.10

(c) Original double strand

First replication

Second replication

No errors in daughter strands

25.11 (a) UGG GGG UUU UAC AGC mRNA

(b) Tyr Gly Phe Tyr Ser Amino acids

(c) ACC CCC AAA AUG UCG Anticodons

25.12 (a) AGA AUA Cys Tyr Val Amino acids

(b) TCT TAT ACC CAT DNA

(c) UCU UAU AGC CAU Anticodons

25.13 A change from C-T-T to C-A-T or a change from C-T-C to C-A-C.
APPENDIX
Empirical and Molecular Formulas

In Section 1.2B, we discussed briefly the pioneering work of Berzelius, Dumas, Liebig, and Cannizzaro in devising methods for determining the formulas of organic compounds. Although the experimental procedures for these analyses have been refined, the basic methods for determining the elemental composition of an organic compound today are not substantially different from those used in the nineteenth century. A carefully weighed quantity of the compound to be analyzed is oxidized completely to carbon dioxide and water. The weights of carbon dioxide and water are carefully measured and used to find the percentages of carbon and hydrogen in the compound. The percentage of nitrogen is usually determined by measuring the volume of nitrogen (N₂) produced in a separate procedure.

Special techniques for determining the percentage composition of other elements typically found in organic compounds have also been developed, but the direct determination of the percentage of oxygen is difficult. However, if the percentage composition of all the other elements is known, then the percentage of oxygen can be determined by difference. The following examples will illustrate how these calculations can be carried out.

EXAMPLE A

A new organic compound is found to have the following elemental analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>67.95%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.69%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>26.20%</td>
</tr>
</tbody>
</table>

Total: 100.84%

Since the total of these percentages is very close to 100% (within experimental error), we can assume that no other element is present. For the purpose of our calculation it is convenient to assume that we have a 100-g sample. If we did, it would contain the following:

- 67.95 g of carbon
- 5.69 g of hydrogen
- 26.20 g of nitrogen

In other words, we use percentages by weight to give us the ratios by weight of the elements in the substance. To write a formula for the substance, however, we need ratios by moles.

We now divide each of these weight-ratio numbers by the atomic weight of the particular element and obtain the number of moles of each element, respectively, in 100 g of the compound. This operation gives us the ratios by moles of the elements in the substance:

- C: \( \frac{67.95 \text{ g}}{12.01 \text{ g mol}^{-1}} = 5.66 \text{ mol} \)
- H: \( \frac{5.69 \text{ g}}{1.008 \text{ g mol}^{-1}} = 5.64 \text{ mol} \)
- N: \( \frac{26.20 \text{ g}}{14.01 \text{ g mol}^{-1}} = 1.87 \text{ mol} \)

One possible formula for the compound, therefore, is \( C_{56.6}H_{56.4}N_{1.87} \).

By convention, however, we use whole numbers in formulas. Therefore, we convert these fractional numbers of moles to whole numbers by dividing each by 1.87, the smallest number.

- C: \( \frac{5.66}{1.87} = 3.03 \text{ which is } -3 \)
- H: \( \frac{5.64}{1.87} = 3.02 \text{ which is } -3 \)
- N: \( \frac{1.87}{1.87} = 1.00 \)

Thus, within experimental error, the ratios by moles are 3 C to 3 H to 1 N, and \( C_3H_3N \) is the empirical formula. By empirical formula, we mean the formula in which the subscripts are the smallest integers that give the ratio of atoms in the compound. In contrast, a molecular formula discloses the complete composition of one molecule. The molecular formula of this particular compound could be \( C_3H_3N₂ \) or some whole number multiple of \( C_3H_3N \); that is, \( C_6H_6N_2 \), \( C_9H_9N_3 \), \( C_{12}H_{12}N_4 \), and so on. If, in a separate determination, we find that the molecular weight of the compound is 108 ± 3, we can be certain that the molecular formula of the compound is \( C_3H_3N₂ \).

**FORMULA**

**MOLECULAR WEIGHT**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3H_3N )</td>
<td>53.06</td>
</tr>
<tr>
<td>( C_3H_3N₂ )</td>
<td>106.13 (which is within the range 108 ± 3)</td>
</tr>
<tr>
<td>( C_6H_6N_2 )</td>
<td>159.19</td>
</tr>
<tr>
<td>( C_9H_9N_3 )</td>
<td>212.26</td>
</tr>
</tbody>
</table>

The most accurate method for determining molecular weights is by mass spectrometry. A variety of other methods based on freezing point depression, boiling point elevation, osmotic pressure, and vapor density can also be used to determine molecular weights.
EXAMPLE B

Histidine, an amino acid isolated from protein, has the following elemental analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>46.38%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.90</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>27.01</td>
</tr>
</tbody>
</table>

Total: 79.29%

Difference: 20.71% (assumed to be oxygen)

Since no elements other than carbon, hydrogen, and nitrogen are found to be present in histidine, the difference is assumed to be oxygen. Again, we assume a 100-gram sample and divide the weight of each element by its gram-atomic weight. This gives us the ratio of moles (A).

\[
\begin{align*}
\text{(A)} & = \frac{46.38}{12.01} = 3.86 \\
\text{(B)} & = \frac{5.90}{1.008} = 5.85 \\
\text{(C)} & = \frac{27.01}{1.004} = 27.01 \\
\end{align*}
\]

Dividing each of the moles (A) by the smallest of them does not give a set of numbers (B) that is close to a set of whole numbers. Multiplying each of the numbers in column (B) by 2 does, however, as seen in column (C). The empirical formula of histidine is, therefore, \( \text{C}_6\text{H}_5\text{N}_2\text{O}_3 \).

In a separate determination, the molecular weight of histidine was found to be 158 ± 5. The empirical formula weight of \( \text{C}_6\text{H}_5\text{N}_2\text{O}_3 \) (153.15) is within this range; thus, the molecular formula of histidine is the same as the empirical formula.

PROBLEMS

A.1 What is the empirical formula of each of the following compounds?

(a) Hydrazine, \( \text{N}_2\text{H}_4 \)
(b) Benzene, \( \text{C}_6\text{H}_6 \)
(c) Dioxane, \( \text{C}_4\text{H}_8\text{O}_2 \)
(d) Nicotinic acid, \( \text{C}_9\text{H}_7\text{O}_4\text{N} \)
(e) Cyclooctane, \( \text{C}_{10}\text{H}_{20} \)
(f) Acetylene, \( \text{C}_2\text{H}_2 \)

A.2 The empirical formulas and molecular weights of several compounds are given next. In each case, calculate the molecular formula for the compound.

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2 )</td>
<td>179 ± 5</td>
</tr>
<tr>
<td>( \text{CH}_3\text{N} )</td>
<td>80 ± 5</td>
</tr>
<tr>
<td>( \text{CCl}_2 )</td>
<td>410 ± 10</td>
</tr>
</tbody>
</table>

A.3 The widely used antibiotic, penicillin G, gave the following elemental analysis: C, 57.43%; H, 5.40%; N, 8.45%; S, 9.61%. The molecular weight of penicillin G is 330 ± 10. Assume that no other elements except oxygen are present and calculate the empirical and molecular formulas for penicillin G.

A.4 Calculate the percentage composition of each of the following compounds.

(a) \( \text{C}_2\text{H}_2\text{O}_5 \)
(b) \( \text{CH}_3\text{CH}_2\text{NO}_2 \)
(c) \( \text{CH}_3\text{CH}_2\text{CBr}_3 \)

A.5 An organometallic compound called ferrocene contains 30.02% iron. What is the minimum molecular weight of ferrocene?

A.6 A gaseous compound gave the following analysis: C, 40.04%; H, 6.69%. At standard temperature and pressure, 1.00 g of the gas occupied a volume of 746 mL. What is the molecular formula of the compound?

A.7 A gaseous hydrocarbon has a density of 1.251 g L\(^{-1}\) at standard temperature and pressure. When subjected to complete combustion, a 1.000-L sample of the hydrocarbon gave 3.926 g of carbon dioxide and 1.608 g of water. What is the molecular formula for the hydrocarbon?

A.8 Nicotinamide, a vitamin that prevents the occurrence of pellagra, gave the following analysis: C, 59.10%; H, 4.92%; N, 22.91%. The molecular weight of nicotinamide was shown in a separate determination to be 120 ± 2. What is the molecular formula for nicotinamide?

A.9 The antibiotic chloromphenicol gave the following analysis: C, 40.88%; H, 3.74%; Cl, 21.95%; N, 8.67%. The molecular weight was found to be 300 ± 30. What is the molecular formula for chloromphenicol?
SOLUTIONS TO PROBLEMS OF APPENDIX A

A.1 (a) NH₂ (b) CH (c) C₂H₅O (d) C₇H₇N (e) CH₃ (f) CH

A.2

<table>
<thead>
<tr>
<th>EMPirical Formula</th>
<th>EMPIRICAL FORMULA</th>
<th>MOLECULAR WEIGHT</th>
<th>MOLECULAR FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CH₃O</td>
<td>30</td>
<td>179 / 30 = 6</td>
<td>C₇H₅O₆</td>
</tr>
<tr>
<td>(b) CHN</td>
<td>27</td>
<td>80 / 27 = 3</td>
<td>C₂H₆N₂</td>
</tr>
<tr>
<td>(c) CCl₂</td>
<td>83</td>
<td>410 / 83 = 5</td>
<td>C₇Cl₆</td>
</tr>
</tbody>
</table>

A.3 If we assume that we have a 100-g sample, the amounts of the elements are:

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT</th>
<th>Moles (A)</th>
<th>( \text{Mol (A)} )</th>
<th>( % \text{MW} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>57.45</td>
<td>57.45 / 12.01 = 4.78</td>
<td>0.300</td>
<td>15.9 = 16</td>
</tr>
<tr>
<td>H</td>
<td>5.40</td>
<td>5.40 / 1.008 = 5.36</td>
<td>0.300</td>
<td>17.9 = 18</td>
</tr>
<tr>
<td>N</td>
<td>8.45</td>
<td>8.45 / 14.01 = 0.603</td>
<td>0.300</td>
<td>2.01 = 2</td>
</tr>
<tr>
<td>S</td>
<td>9.61</td>
<td>9.61 / 32.06 = 0.300</td>
<td>0.300</td>
<td>1.00 = 1</td>
</tr>
<tr>
<td>O</td>
<td>19.09</td>
<td>19.09 / 16.00 = 1.19</td>
<td>0.300</td>
<td>3.97 = 4</td>
</tr>
</tbody>
</table>

(* by difference from 100)

The empirical formula is thus C₆H₅N₂S₂O₂. The empirical formula weight (334.4) is within the range given for the molecular weight (330 ± 10). Thus, the molecular formula for penicillin G is the same as the empirical formula.

A.4 (a) To calculate the percentage composition from the molecular formula, first determine the weight of each element in 1 mol of the compound. For C₇H₅O₆:

\[ \text{C}_6 = 6 \times 12.01 = 72.06 \]

\[ \frac{72.06}{180.2} = 0.400 = 40.0\% \]

\[ \text{H}_{12} = 12 \times 1.008 = 12.10 \]

\[ \frac{12.10}{18.02} = 0.671 = 6.7\% \]

\[ \text{O}_6 = 6 \times 16.00 = 96.00 \]

\[ \frac{96.00}{180.16} = 0.533 = 53.3\% \]

Then determine the percentage of each element using the formula

\[ \text{Percentage of A} = \left( \frac{\text{Weight of A}}{\text{Molecular Weight}} \right) \times 100 \]

(b) C₂ = 2 \times 12.01 = 24.02

\[ \frac{24.02}{75.07} = 0.320 = 32.0\% \]

H₂ = 5 \times 1.008 = 5.04

\[ \frac{5.04}{75.07} = 0.067 = 6.7\% \]

N = 1 \times 14.01 = 14.01

\[ \frac{14.01}{75.07} = 0.187 = 18.7\% \]

O₂ = 2 \times 16.00 = 32.00

\[ \frac{32.00}{75.07} = 0.426 = 42.6\% \]

Total = 75.07

(c) C₃ = 3 \times 12.01 = 36.03

\[ \frac{36.03}{280.77} = 0.128 = 12.8\% \]

H₃ = 5 \times 1.008 = 5.04

\[ \frac{5.04}{280.77} = 0.018 = 1.8\% \]

Br₃ = 3 \times 79.90 = 239.70

\[ \frac{239.70}{280.77} = 0.854 = 45.4\% \]

Total = 280.77

A.5 If the compound contains iron, each molecule must contain at least one atom of iron, and 1 mol of the compound must contain at least 55.85 g of iron. Therefore,

\[ \text{MW of ferrocene} = 55.85 \times \left( \frac{8 \text{ Fe}}{\text{mol}} \right) \times \left( \frac{1000 \text{ g}}{\text{mol}} \right) \]

\[ = 186.0 \text{ g/mol} \]

A.6 First, we must determine the empirical formula. Assuming that the difference between the percentages given and 100% is due to oxygen, we calculate:

\[ \text{C} = \frac{40.04}{12.01} = 3.33 \]

\[ \text{H} = \frac{6.69}{1.008} = 6.64 \approx 2 \]

\[ \text{O} = \frac{53.22}{100.00} = 0.53 \]

The empirical formula is thus CH₂O.
To determine the molecular formula, we must first determine the molecular weight. At standard temperature and pressure, the volume of 1 mol of an ideal gas is 22.4 L. Assuming ideal behavior,

\[ \frac{1.00 \text{ g}}{0.746 \text{ L}} = \frac{\text{MW}}{22.4 \text{ L}} \text{ where MW = molecular weight} \]

\[ \text{MW} = \frac{(1.00)(22.4)}{0.746} = 30.0 \text{ g} \]

The empirical formula weight (30.0) equals the molecular weight; thus, the molecular formula is the same as the empirical formula.

A.7 As in Problem A.6, the molecular weight is found by the equation

\[ \frac{1.251 \text{ g}}{1.00 \text{ L}} = \frac{\text{MW}}{22.4 \text{ L}} \]

\[ \text{MW} = (1.251)(22.4) \]

\[ \text{MW} = 28.02 \]

To determine the empirical formula, we must determine the amount of carbon in 3.926 g of carbon dioxide, and the amount of hydrogen in 1.608 g of water.

\[
\begin{align*}
\text{C} & \left( \frac{3.926 \text{ g CO}_2}{44.01 \text{ g CO}_2} \right) \left( \frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2} \right) = 1.071 \text{ g carbon} \\
\text{H} & \left( \frac{1.608 \text{ g H}_2\text{O}}{18.016 \text{ g H}_2\text{O}} \right) \left( \frac{2.016 \text{ g H}}{18.016 \text{ g H}_2\text{O}} \right) = 0.180 \text{ g hydrogen} \\
& \left( \frac{1.251 \text{ g sample}}{1.008 \text{ g sample}} \right)
\end{align*}
\]

The weight of C and H in a 1.251-g sample is 1.251 g. Therefore, there are no other elements present.

To determine the empirical formula, we proceed as in Problem A.6 except that the sample size is 1.251 g instead of 100 g.

\[
\begin{align*}
\text{C} & \left( \frac{1.071}{12.01} \right) = 0.0892 \\
& = 0.0892 \text{ mol C} \\
& = 1 \text{ mol C} \\
\text{H} & \left( \frac{0.180}{1.008} \right) = 0.179 \\
& = 0.179 \text{ mol H} \\
& = 2 \text{ mol H}
\end{align*}
\]

The empirical formula is thus CH. The empirical formula weight (14) is one-half the molecular weight. Thus, the molecular formula is C$_2$H$_2$.

A.8 Use the procedure of Problem A.3.

\[
\begin{align*}
\text{C} & \left( \frac{59.10}{12.01} \right) = 4.92 \\
& = 6.02 \text{ mol C} \\
& = 6 \text{ mol C}
\end{align*}
\]

APPENDIX A EMPIRICAL AND MOLECULAR FORMULAS

The empirical formula is thus C$_2$H. The empirical formula weight is 28.02, which is equal to the molecular weight within experimental error. The molecular formula is thus the same as the empirical formula.

A.9

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass (g)</th>
<th>Empirical Formula</th>
<th>Empirical Formula Weight</th>
</tr>
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<tr>
<td>C</td>
<td>21.95</td>
<td>C</td>
<td>12.01</td>
</tr>
<tr>
<td>H</td>
<td>8.67</td>
<td>H</td>
<td>1.008</td>
</tr>
<tr>
<td>Cl</td>
<td>3.74</td>
<td>Cl</td>
<td>35.45</td>
</tr>
<tr>
<td>N</td>
<td>22.91</td>
<td>N</td>
<td>14.01</td>
</tr>
<tr>
<td>O</td>
<td>13.07</td>
<td>O</td>
<td>16.00</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The empirical formula is thus C$_3$H$_4$ClN$_2$O. The empirical formula weight (323) is equal to the molecular weight; therefore, the molecular formula is the same as the empirical formula.
APPENDIX
Answers to Quizzes

CHAPTER 1

1.1 (d), 1.2 (a), 1.3 (e), 1.4 (d), 1.5 (c), 1.6 H—C

1.7 CH₃CH₂CH₂CH₃ and CH₃C—CH₃

1.8

1.9 (a) sp² (b) sp³ (c) 0 (d) trigonal planar (e) 0

1.10 (a) +1 (b) 0 (c) -1

1.11 H

CHAPTER 2

2.1 (c) 2.2 (a) 2.3 (e)

2.4 (a) CH₃CH₂C—OH (b) CH₃C—NCH₃ (c) Cl—C=Cl

2.5 

2.6 (a) CH₃CH₂CH₂OH (b) (c) CH₃CH₂COH

2.7 (a) Isopropyl phenyl ether (b) Ethylmethylyphenylamine (c) Isopropylamine

CHAPTER 3

3.1 (a) 3.2 (c) 3.3 (b) 3.4 (e) 3.5 (b) 3.6 (b)

3.7 H₂SO₄ + Na⁺ → NaHSO₄ + HF

3.8 (CH₃)₂NH

3.9 (a) CH₃Li (b) D₂O (c) CH₃

3.10 (a) CH₃Li (b) CH₃CH₂OH (c) CH₃CH₂OLi

CHAPTER 4

4.1 (c) 4.2 (c) 4.3 (b) 4.4 (a) 4.5 (b) 4.6 (a) 4.7 (a)
4.8 (a) \[ \begin{array}{c} \text{Cl} \\
\text{H} \\
\text{Cl} \\
\text{H} \\
\text{H} \\
\text{Br} \end{array} \] (b) \[ \begin{array}{c} \text{Br} \end{array} \] or \[ \begin{array}{c} \text{Br} \end{array} \] (c) \[ \begin{array}{c} \text{Br} \end{array} \]

4.9 (a) \( \text{H}_2, \text{Pt} \) or \( \text{H}_2, \text{Ni} \) (b) \( \text{Zn}, \text{H}^+ \)

4.10 \( \text{CH}_3 \text{CH} \equiv \text{CH} \text{CH}_3 \)

CHAPTER 5

5.1 (a) 5.2 (b) 5.3 (b) 5.4 (c) 5.5 (b)

5.6 \( \text{H}_3 \text{C} \equiv \text{C} \text{CH}_3 \) and \( \text{H}_3 \text{C} \equiv \text{C} \text{CH}_3 \)

5.7 \( \text{H}_3 \text{C} \equiv \text{C} \text{CH}_3 \) 5.8 \( \text{CH}_3 \text{CH} \equiv \text{CH} \text{CH}_2 \text{CH}_3 \)

CHAPTER 6

6.1 (b) 6.2 (b) 6.3 (a)

6.4 \( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{Br} \) > \( \text{CH}_3 \text{CH} \equiv \text{CH} \text{Br} \) > \( \text{CH}_3 \text{CH} \equiv \text{CH} \text{Br} \) > \( \text{CH}_3 \text{C} \equiv \text{Br} \)

6.5 (a) \[ \begin{array}{c} \text{Br} \\
\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3 \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{H} \end{array} \] B = \( \text{CH}_3 \text{CH} \equiv \text{CH}_2 \)

C = \( \begin{array}{c} \text{H} \\
\text{CH}_3 \\
\text{CH}_3 \end{array} \) D = \( \begin{array}{c} \text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CN} \\
\text{H} \\
\text{H} \end{array} \)

6.6 (b)

6.7 \( \text{A} = \text{CH}_3 \text{C} \equiv \text{CH} \)

6.8 \( \text{CH}_3 \text{Br} \) B = \( \text{CH}_3 \text{CH} \equiv \text{CH}_2 \)

C = \( \begin{array}{c} \text{H} \\
\text{CH}_3 \end{array} \) D = \( \begin{array}{c} \text{C} \\
\text{CH}_3 \end{array} \)

6.9 A = \( \begin{array}{c} \text{C} \\
\text{CH}_3 \end{array} \) B = \( \begin{array}{c} \text{C} \\
\text{CH}_3 \end{array} \)

CHAPTER 7

7.1 (c) 7.2 (d) 7.3 (a)

7.4 (a) \( \text{Li}, \text{C}_2 \text{H}_5 \text{NH}_2 \), \(-78^\circ \text{C}, \) then \( \text{NH}_3 \text{Cl} \)
(b) \( \text{H}_2/\text{Ni} \text{B(P-2)} \) or \( \text{H}_2/\text{Pd/CaCO}_3 \) (Lindlar's catalyst)
(c) \( \text{H}_2/\text{Ni} \) or \( \text{H}_2/\text{Pt} \) using at least 2 molar equivalents of \( \text{H}_2 \)
(d) \( \text{C}_2 \text{H}_5 \text{ONa}/\text{C}_2 \text{H}_5 \text{OH} \)
(e) \( \text{CH}_2 \text{COK} / \text{CH}_2 \text{COH} \)
(f) \( \text{Zn/C}_2 \text{H}_5 \text{CO}_2 \text{H} \) or \( \text{Na/acetone} \)

7.5 \( \text{CH}_3 \text{C} \equiv \text{CH} \text{CH}_3 \) > \( \text{H} \text{C} \equiv \text{C} \text{CH}_3 \) > \( \text{H} \text{C} \equiv \text{C} \text{CH}_3 \) > \( \text{H} \text{C} \equiv \text{C} \text{CH}_3 \) > \( \text{CH}_3 \text{C} \equiv \text{C} \text{CH}_3 \)

7.6 (a) \( \text{CH}_3 \text{C} \equiv \text{CH} \text{Br} \) (b) \( \text{CH}_3 \text{C} \equiv \text{CNa} \) (c) \( \text{CH}_3 \text{C} \equiv \text{CH} \)
(d) \( \text{CH}_3 \text{C} \equiv \text{CNa} \) (e) \( \text{CH}_3 \text{CH}_2 \text{Br} \)
CHAPTER 8
8.1 (c)  8.2 (c)  8.3 (e)  8.4 (a)  8.5 (d)  8.6 (c)
8.7 (c)  8.8 (b)

CHAPTER 9
9.1  (a) CH₃CCH₃  (b) BrCH₂CH₂Br  (c) CH₂=CH₂CH₂CH₂
    (d) CH₂⁻CH₂CH₂  (e) CH₃C≡CH₂NO₂
9.2  (c)  9.3 (a)

CHAPTER 10
10.1 (d)  10.2 (b)  10.3 (c)  10.4 (b)  10.5 (c)
10.6 CH₃CH₂CH₂CH₃
10.7 Six
10.8 (d)

CHAPTER 11
11.1 (d)  11.2 (a)  11.3 (a)
11.4 A = C₆H₅CH₂ONa  B = C₆H₅CH₂OCH₂CH₂OH
    C = C₆H₅CH₂OCH₂CH₂OSO₂CH₃  D = C₆H₅CH₂OCH₂CH₂OCH₂CH₃

CHAPTER 12
12.1 (b)  12.2 (a)
12.3  (a) CH₃C≡CH₂Li  or  CH₃C≡CMgBr
    B = NaH
    C = CH₃I

CHAPTER 13
13.1 (d)  13.2 (c)  13.3 (c)  13.4 (c)  13.5 (b)

CHAPTER 14
14.1 (c)  14.2 (a)  14.3 (b)  14.4 (b)
14.5 Azulene

CHAPTER 15
15.1 (a)  15.2 (a)  15.3 (b)
15.4 (a) A = SO₃/H₂SO₄  B = 
    C = H₂O, H₂SO₄, heat
    (b) A = SOCl₂ or PCl₅  B = 
    C = Zn(Hg), HCl, reflux  D = Br₂/FeBr₃
CHAPTER 16

16.1 (d) 16.2 (b) 16.3 (b)

16.4 (a) \( A = \text{Ph} - \text{CH}_2 \text{Br} \quad B = \text{NaCN} \)

\quad (1) DIBAL-H, hexane, -78°C; (2) \( \text{H}_2 \text{O} \)

(b) \( A = \text{PCC}, \text{CH}_2\text{Cl}_2 \quad B = \text{HOCH}_2\text{CH}_2\text{OH}, \text{H}^+ \quad C = \text{H}_2\text{O}, \text{H}_3\text{O}^+ \)

(c) \( A = (\text{C}_3\text{H}_2)\text{P} \quad B = \text{CH}_3\text{CH}_2\text{CH}=\text{P}[(\text{C}_6\text{H}_5)_2\text{Br}]^- \quad C = \) \( \text{C} \)

(d) \( A = (\text{CH}_3)_2\text{CuLi} \quad B = \text{HCN} \quad C = (1) \text{LiAlH}_4 \quad (2) \text{H}_2\text{O} \)

CHAPTER 17

17.1 (a) \( \text{CH}_3\text{CH}_2\text{CHCHCH}_{\text{CH}_3} \)

(b) \( \text{CH}_3\text{CH}_2\text{CHCHCH}_{\text{CH}_3}\text{OH} \)

(c) \( \text{CH}_2\text{CH}_2\text{CH} = \text{CHCH}_3 \)

(d) \( \text{LiAlH}_4 \)

(e) \( \text{H}_2, \text{Ni} \)

(f) \( \text{CH}_2\text{OH} \text{ (excess), H}^+ \)

(g) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}(_\text{CH}_3)\text{OCH}_3 \)

(h) \( \text{CH}_3\text{CH}_2\text{CHCH}(_\text{CH}_3)\text{H} \)

(i) \( (1) \text{CH}_3\text{CHBrCO}_2\text{CH}_2\text{CH}_3, \text{Zn} \quad (2) \text{H}_2\text{O}^+ \)

17.2 (a) \( \text{HC} = \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} \)

(b) \( \text{HC} = \text{CH} = \text{CH} - \text{CH} = \text{CH} = \text{CH} \)

(c) \( \text{HCN} \)

17.3 (a) \( \text{CH}_3\text{Br} \quad (b) \text{CH}_3\text{CH} = \text{CH} \quad (c) (\text{CH}_3)_2\text{CuLi} \)

(d) \( \text{CH}_3\text{CH}_2\text{CH} \quad (e) \text{Zn(Hg)/HCl} \)

17.4 (e) 17.5 (a)

CHAPTER 18

18.1 (b) 18.2 (d) 18.3 (d)

18.4 \( A = \text{3-Chlorobutanoic acid} \quad B = \text{Methyl-4-nitrobenzoate} \quad C = \text{N-Methylamine} \)

18.5 (a) \( A = (1) \text{KMnO}_4, \text{OH}, \text{heat} \quad (2) \text{H}_3\text{O}^+ \)

(b) \( A = \text{CH}_3\text{CO}_2\text{CH}_3 \quad B = \text{CH}_3\text{OH} \)

(c) \( \text{C} \quad (\text{D}) \quad (\text{E}) \quad (\text{F}) \)

18.6 (a) \( A = \text{(C}_6\text{H}_5\text{)_3P} \quad B = \text{CH}_3\text{CH}_2\text{CH}_2\text{P}[(\text{C}_6\text{H}_5)_2\text{Cl}]^- \quad C = \) \( \text{C} \)

(d) \( A = (\text{CH}_3)\text{CuLi} \quad B = \text{HCN} \quad C = (1) \text{LiAlH}_4 \quad (2) \text{H}_2\text{O} \)

CHAPTER 19

19.1 (c) 19.2 (e) 19.3 (b)

19.4 (a) \( A = \text{CH}_3\text{CH}_2\text{CH} \quad B = \text{CH}_2\text{CHCO}_2\text{K} \)

19.5 (a) \( A = \text{CH}_3\text{CH}_2\text{CH} \quad B = \text{CH}_2\text{CHCO}_2\text{K} \)

19.6 (a) \( A = \text{CH}_3\text{CH}_2\text{CH} \quad B = \text{CH}_2\text{CHCO}_2\text{K} \)
APPENDIX B ANSWERS TO QUIZZES

20.4 (a) A = HNO₃/H₂SO₄    B = H₃C—CH=CH—NO₂    C = NaNO₂, HCl
     D = CuCN    E = LiAlH₄    F = (CH₃)₂N—(C₆H₄)₂

(b) A = Na₂S₂O₃    B = (CH₃)₃—N=N—N=N    C = NO—NH₂

D = Br—NH₂    E = H₃PO₄

20.5 (a) (2)    (b) (2)    (c) (1)

CHAPTER 21

21.1 (a)    21.2 (b)    21.3 (b)    21.4 (c)

21.5 (a) A = Br—OH    B = K NH₃, NH₂, -33°C

21.6 Br—OH + CH₃Br

21.7 (a) (1)    (b) (1)

CHAPTER 22

22.1 (a)
     (b) (CHOH)ₙ CH₃OH
     (c) (CHOH)ₙ CH₃OH

22.2 (d) CHO
     (CH(OH))ₙ CH₃OH
     n = 1, 2, 3...
APPENDIX B ANSWERS TO QUIZZES

22.2 (a) CHO
(b) CHO
H-OH
H-OH
H-OH
H-OH
H-OH
H-OH
CH₂OH

22.3 CHO
H-OH
H-OH
CH₂OH

22.4 (a) CHO
(b) CHO
CO₂H
H-OH
H-OH
H-OH
H-OH
H-OH
H-OH
CH₂OH
CO₂H

22.5

22.6 (a) Reducing
(d) Active
(e) Aldonic
(f) Active
(g) Aldonic

22.7 (a) Galactose → optically inactive alditol
(b) HIO₄ oxidation → different products:
   Fructose → 2 mol H₂O + CO₂ + 3 HO⁻OH
   Glucose → 1 mol H₂O + 5 HO⁻OH

22.8 (e) 22.9 (d)

CHAPTER 23

23.1 (a) CH₂(CH₃)₃CO₂H
(b) CH₂(CH₃)₃C=ONa
(c) CH₂OC(CH₃)₂CH₃
(d) CH₂OC(CH₃)₂CH=CH(CH₂)₃CH₃
(e) CH₂OC(CH₃)₂CH=CH(C₂H₅)₂CH₂
(f) CH₂OC(CH₃)₂CH=CH(C₂H₅)₂CH₂

23.2 (a) 1₂OH⁻ (iodoform test)
(b) Br₂/CCI₄
(c) Ethynylestradiol only shows IR absorption at ~3300 cm⁻¹

23.3 5α-Aandrostan

23.4 (a) CH₂(CH₃)₂CH=C=CH
(b) CH₂(CH₃)₂C=CNa
(c) CH₂(CH₃)₂C=CCl(CH₂)₃CH₂
(d) KCN
(e) CH₂(CH₃)₂C=CCl(CH₂)₃CO₂H
(f) H₂/Pd

23.5 Sesquiterpene

23.6

23.7 (e)
APPENDIX B  ANSWERS TO QUIZZES

CHAPTER 24

24.1  (a)  \[ \text{CH}_3 \text{CH}_2 \text{CHCHCO}_2^{-} \]
      (b)  \[ \text{CH}_3 \text{CH}_2 \text{CHCHCO}_2^{-} \]
      (c)  \[ \text{CH}_3 \text{CH}_2 \text{CHCHCO}_2^{-} \]

24.2  Pro-Leu-Gly-Phe-Gly-Tyr

APPENDIX

Molecular Model Set Exercises

The exercises in this appendix are designed to help you gain an understanding of the three-dimensional nature of molecules. You are encouraged to perform these exercises with a model set as described.

These exercises should be performed as part of the study of the chapters shown below.

<table>
<thead>
<tr>
<th>Chapter in Text</th>
<th>Accompanying Exercises</th>
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<td>2, 7, 9, 13, 24, 25, 26, 27</td>
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<td>6</td>
<td>9, 19, 22, 28</td>
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<td>7</td>
<td>31</td>
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<td>8</td>
<td>23</td>
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<td>10</td>
<td>30</td>
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<tr>
<td>11</td>
<td>31</td>
</tr>
</tbody>
</table>

The following molecular model set exercises were originally developed by Ronald Starkey.

Refer to the instruction booklet that accompanies your model set for details of molecular model assembly.

EXERCISE 1 (Chapter 4)

Assemble a molecular model of methane, \( \text{CH}_4 \). Note that the hydrogen atoms describe the apexes of a regular tetrahedron with the carbon atom at the center of the tetrahedron. Demonstrate by attempted superposition that two models of methane are identical.

Replace any one hydrogen atom on each of the two methane models with a halogen to form two molecules of \( \text{CH}_3X \). Are the two structures identical? Does it make a difference which of the four hydrogen atoms on a methane molecular you replace? How many different configurations of \( \text{CH}_3X \) are possible?