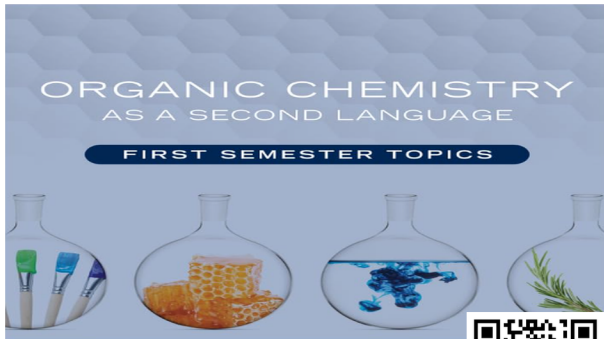


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# ORGANIC CHEMISTRY

AS A SECOND LANGUAGE

FIRST SEMESTER TOPICS



DAVID KLEIN

SIXTH EDITION

WILEY



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*ORGANIC CHEMISTRY AS A  
SECOND LANGUAGE, 6e*



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*ORGANIC CHEMISTRY AS A  
SECOND LANGUAGE, 6e*

**First Semester Topics**

**DAVID KLEIN**

*Johns Hopkins University*

**WILEY**

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# INTRODUCTION

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## IS ORGANIC CHEMISTRY REALLY ALL ABOUT MEMORIZATION?

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Is organic chemistry really as tough as everyone says it is? The answer is yes and no. Yes, because you will spend more time on organic chemistry than you would spend in a course on underwater basket weaving. And no, because those who say it's so tough have studied inefficiently. Ask around, and you will find that most students think of organic chemistry as a memorization game. *This is not true!* Former organic chemistry students perpetuate the false rumor that organic chemistry is the toughest class on campus, because it makes them feel better about the poor grades that they received.

If it's not about memorizing, then what is it? To answer this question, let's compare organic chemistry to a movie. Picture in your mind a movie where the plot changes every second. If you're in a movie theatre watching a movie like that, you can't leave even for a second because you would miss something important to the plot. So you try your hardest to wait until the movie is over before going to the bathroom. Sounds familiar?

Organic chemistry is very much the same. It is one long story, and the story actually makes sense if you pay attention. The plot constantly develops, and everything ties into the plot. If your attention wanders for too long, you could easily get lost.

You probably know at least one person who has seen one movie more than five times and can quote every line by heart. How can this person do that? It's *not* because he or she tried to memorize the movie. The first time you watch a movie, you learn the plot. After the second time, you understand why individual scenes are necessary to develop the plot. After the third time, you understand why the dialogue was necessary to develop each scene. After the fourth time, you are quoting many of the lines by heart. *Never at any time did you make an effort to memorize the lines.* You know them *because they make sense* in the grand scheme of the plot. If I were to give you a screenplay for a movie and ask you to memorize as much as you can in 10 hours, you would probably not get very far into it. If, instead, I put you in a room for 10 hours and played the same movie over again five times, you would know most of the movie by heart, without even trying. You would know everyone's names, the order of the scenes, much of the dialogue, and so on.

Organic chemistry is exactly the same. It's not about memorization. It's all about making sense of the plot, the scenes, and the individual concepts that make up our story. Of course you will need to remember all of the terminology, but with enough practice, the terminology will become second nature to you. So here's a brief preview of the plot.

---

## THE PLOT

---

The first half of our story builds up to reactions, and we learn about the characteristics of molecules that help us understand reactions. We begin by looking at atoms, the building blocks of molecules, and what happens when they combine to form bonds. We focus on special bonds between certain atoms, and we see how the nature of bonds can affect the shape and stability of molecules. Then, we need a vocabulary to start talking about molecules, so we learn how to draw and name molecules. We see how molecules move around in space, and we explore the relationships between similar types of molecules. At this point, we know the important characteristics of molecules, and we are ready to use our knowledge to explore reactions.

Reactions take up the rest of the course, and they are typically broken down into chapters based on categories. Within each of these chapters, there is actually a subplot that fits into the grand story.

---

## HOW TO USE THIS BOOK

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This book will help you study more efficiently so that you can avoid wasting countless hours. It will point out the major scenes in the plot of organic chemistry. The book will review the critical principles and explain why they are relevant to the rest of the course. In each section, you will be given the tools to better understand your textbook and lectures, as well as plenty of opportunities to practice the key

skills that you will need to solve problems on exams. In other words, you will learn the language of organic chemistry. *This book cannot replace your textbook, your lectures, or other forms of studying.* This book is not the Cliff Notes of Organic Chemistry. It focuses on the basic concepts that will empower you to do well if you go to lectures and study in addition to using this book. To best use this book, you need to know how to study in this course.

## HOW TO STUDY

---

There are two separate aspects to this course:

1. Understanding principles
2. Solving problems

Although these two aspects are completely different, instructors will typically gauge your understanding of the principles by testing your ability to solve problems. So you must master both aspects of the course. The principles are in your lecture notes, but *you* must discover how to solve problems. Most students have a difficult time with this task. In this book, we explore some step-by-step processes for analyzing problems. There is a very simple habit that you must form immediately: *learn to ask the right questions.*

If you go to a doctor with a pain in your stomach, you will get a series of questions: How long have you had the pain? Where is the pain? Does it come and go, or is it constant? What was the last thing you ate? and so on. The doctor is doing two very important and very different things: 1) asking the right questions, and 2) arriving at a diagnosis based on the answers to those questions.

Let's imagine that you want to sue McDonald's because you spilled hot coffee in your lap. You go to an attorney who asks you a series of questions. Once again, the lawyer is doing two very important and very different things: 1) asking the right questions, and 2) formulating an opinion based on the answers to those questions. Once again, the first step is asking questions.

In fact, in any profession or trade, the first step of diagnosing a problem is always to ask questions. The same is true with solving problems in this course. Unfortunately, you are expected to learn how to do this on your own. In this book, we will look at some common types of problems and we will see what questions you should be asking in those circumstances. More importantly, we will also be developing skills that will allow you to figure out what questions you should be asking for a problem that you have never seen before.

Many students freak out on exams when they see a problem that they can't do. If you could hear what was going on in their minds, it would sound something like this: "I can't do it ... I'm gonna flunk." These thoughts are counterproductive and a waste of precious time. Remember that when all else fails, there is always one question that you can ask yourself: "What questions should I be asking right now?"

The only way to truly master problem-solving is to practice problems every day, consistently. You will never learn how to solve problems by just reading a book. You must try, and fail, and try again. You must learn from your mistakes. You must get frustrated when you can't solve a problem. That's the learning process. Whenever you encounter an exercise in this book, pick up a pencil and work on it. Don't skip over the problems! They are designed to foster skills necessary for problem-solving.

The worst thing you can do is to read the solutions and think that you now know how to solve problems. It doesn't work that way. If you want an A, you will need to sweat a little (no pain, no gain). And that doesn't mean that you should spend day and night memorizing. Students who focus on memorizing will experience the pain, but few of them will get an A.

The simple formula: Review the principles until you understand how each of them fits into the plot; then *focus all of your remaining time on solving problems.* Don't worry. The course is not that bad if you approach it with the right attitude. This book will act as a road map for your studying efforts.

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# CONTENTS

---

## CHAPTER 1 BOND-LINE DRAWINGS 1

- 1.1 How to Read Bond-Line Drawings 1
- 1.2 How to Draw Bond-Line Drawings 4
- 1.3 Mistakes to Avoid 6
- 1.4 More Exercises 6
- 1.5 Identifying Formal Charges 8
- 1.6 Finding Lone Pairs that Are Not Drawn 11
- End-of-Chapter Problems 15

---

## CHAPTER 2 RESONANCE 19

- 2.1 What Is Resonance? 19
- 2.2 Curved Arrows: The Tools for Drawing Resonance Structures 20
- 2.3 The Two Commandments 21
- 2.4 Drawing Good Arrows 24
- 2.5 Formal Charges in Resonance Structures 26
- 2.6 Drawing Resonance Structures—Step By Step 29
- 2.7 Drawing Resonance Structures—By Recognizing Patterns 33
- 2.8 Assessing the Relative Importance of Resonance Structures 40
- End-of-Chapter Problems 45

---

## CHAPTER 3 ACID–BASE REACTIONS 48

- 3.1 Factor 1—What Atom Is the Charge On? 48
- 3.2 Factor 2—Resonance 51
- 3.3 Factor 3—Induction 54
- 3.4 Factor 4—Orbitals 56
- 3.5 Ranking the Four Factors 57
- 3.6 Other Factors 60
- 3.7 Quantitative Measurement ( $pK_a$  Values) 61
- 3.8 Predicting the Position of Equilibrium 61
- 3.9 Showing a Mechanism 62
- End-of-Chapter Problems 64

---

## CHAPTER 4 GEOMETRY 68

- 4.1 Orbitals and Hybridization States 68
- 4.2 Geometry 71
- 4.3 Lone Pairs 73
- End-of-Chapter Problems 75

**CHAPTER 5** *NOMENCLATURE* **77**

---

- 5.1 Functional Group **78**
- 5.2 Unsaturation **79**
- 5.3 Naming the Parent Chain **80**
- 5.4 Naming Substituents **83**
- 5.5 Stereoisomerism **85**
- 5.6 Numbering **87**
- 5.7 Common Names **91**
- 5.8 Going from a Name to a Structure **92**
- End-of-Chapter Problems **92**

**CHAPTER 6** *CONFORMATIONS* **95**

---

- 6.1 How to Draw a Newman Projection **95**
- 6.2 Ranking the Stability of Newman Projections **99**
- 6.3 Drawing Chair Conformations **101**
- 6.4 Placing Groups on the Chair **105**
- 6.5 Ring Flipping **108**
- 6.6 Comparing the stability of Chairs **114**
- 6.7 Don't Be Confused by The Nomenclature **117**
- End-of-Chapter Problems **117**

**CHAPTER 7** *CONFIGURATIONS* **121**

---

- 7.1 Locating Chiral Centers **121**
- 7.2 Determining the Configuration of a Chiral Center **124**
- 7.3 Nomenclature **131**
- 7.4 Drawing Enantiomers **134**
- 7.5 Diastereomers **138**
- 7.6 *MESO* Compounds **139**
- 7.7 Drawing Fischer Projections **141**
- 7.8 Optical Activity **145**
- End-of-Chapter Problems **146**

**CHAPTER 8** *MECHANISMS* **149**

---

- 8.1 Introduction to Mechanisms **149**
- 8.2 Nucleophiles and Electrophiles **149**
- 8.3 Basicity vs. Nucleophilicity **151**
- 8.4 Arrow-Pushing Patterns for Ionic Mechanisms **153**
- 8.5 Carbocation Rearrangements **158**
- 8.6 Information Contained in a Mechanism **162**
- End-of-Chapter Problems **164**

**CHAPTER 9** *SUBSTITUTION REACTIONS* **168**

---

- 9.1 The Mechanisms **168**
- 9.2 Factor 1—The Electrophile (Substrate) **170**
- 9.3 Factor 2—The Nucleophile **172**
- 9.4 Factor 3—The Leaving Group **174**

9.5 Factor 4—The Solvent	176
9.6 Using All Four Factors	177
9.7 Drawing a Substitution Product and the Mechanism of Its Formation	178
End-of-Chapter Problems	182

---

**CHAPTER 10 ELIMINATION REACTIONS 185**

---

10.1 The E2 Mechanism	185
10.2 The Regiochemical Outcome of an E2 Reaction	186
10.3 The Stereochemical Outcome of an E2 Reaction	187
10.4 The E1 Mechanism	190
10.5 The Regiochemical Outcome of an E1 Reaction	192
10.6 The Stereochemical Outcome of an E1 Reaction	192
10.7 Substitution vs. Elimination	193
10.8 Determining the Function of the Reagent	193
10.9 Identifying the Mechanism(s)	195
10.10 Predicting the Products	197
End-of-Chapter Problems	200

---

**CHAPTER 11 ADDITION REACTIONS 204**

---

11.1 Terminology Describing Regiochemistry	204
11.2 Terminology Describing Stereochemistry	206
11.3 Adding H and H	212
11.4 Adding H and X, Markovnikov	215
11.5 Adding H and Br, <i>Anti</i> -Markovnikov	220
11.6 Adding H and OH, Markovnikov	224
11.7 Adding H and OH, <i>Anti</i> -Markovnikov	226
11.8 Synthesis Techniques	230
11.9 Adding Br and Br; Adding Br and OH	236
11.10 Adding OH and OH, <i>Anti</i>	241
11.11 Adding OH and OH, <i>syn</i>	243
11.12 Oxidative Cleavage of an Alkene	245
End-of-Chapter Problems	248

---

**CHAPTER 12 ALKYNES 253**

---

12.1 Structure and Properties of Alkynes	253
12.2 Preparation of Alkynes	255
12.3 Alkylation of Terminal Alkynes	256
12.4 Reduction of Alkynes	258
12.5 Hydration of Alkynes	261
12.6 Keto-Enol Tautomerization	264
12.7 Ozonolysis of Alkynes	269
End-of-Chapter Problems	270

---

**CHAPTER 13 ALCOHOLS 274**

---

13.1 Naming and Designating Alcohols	274
13.2 Predicting Solubility of Alcohols	275
13.3 Predicting Relative Acidity of Alcohols	276

**X CONTENTS**

13.4 Preparing Alcohols: A Review	<b>279</b>
13.5 Preparing Alcohols via Reduction	<b>280</b>
13.6 Preparing Alcohols via Grignard Reactions	<b>286</b>
13.7 Summary of Methods for Preparing Alcohols	<b>289</b>
13.8 Reactions of Alcohols: Substitution and Elimination	<b>290</b>
13.9 Reactions of Alcohols: Oxidation	<b>294</b>
13.10 Converting an Alcohol into an Ether	<b>297</b>
End-of-Chapter Problems	<b>298</b>

**CHAPTER 14 ETHERS AND EPOXIDES 300**

---

14.1 Introduction to Ethers	<b>300</b>
14.2 Preparation of Ethers	<b>302</b>
14.3 Reactions of Ethers	<b>304</b>
14.4 Preparation of Epoxides	<b>305</b>
14.5 Ring-Opening Reactions of Epoxides	<b>307</b>
End-of-Chapter Problems	<b>313</b>

**CHAPTER 15 SYNTHESIS 316**

---

15.1 Functional Group Interconversion	<b>316</b>
15.2 Changing the Carbon Skeleton	<b>317</b>
15.3 Two Questions to Ask in Every Synthesis Problem	<b>318</b>
15.4 Retrosynthetic Analysis	<b>320</b>
15.5 Creating Your Own Problems	<b>323</b>
End-of-Chapter Problems	<b>324</b>

Detailed Solutions **S-1**

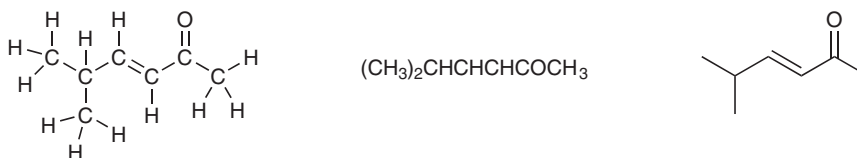
Index **I-1**

# CHAPTER 1

## BOND-LINE DRAWINGS

To do well in organic chemistry, you must first learn to interpret the drawings that organic chemists use. When you see a drawing of a molecule, it is absolutely critical that you can read all of the information contained in that drawing. Without this skill, it will be impossible to master even the most basic reactions and concepts.

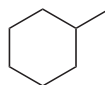
Molecules can be drawn in many ways. For example, below are three different ways of drawing the same molecule:



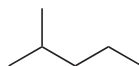
Without a doubt, the last structure (bond-line drawing) is the quickest to draw, the quickest to read, and the best way to communicate. Open to any page in the second half of your textbook and you will find that every page is plastered with bond-line drawings. It is essential that you learn to read these drawings fluently. This chapter will help you develop the skills that you will need to read these drawings quickly and fluently.

### 1.1 HOW TO READ BOND-LINE DRAWINGS

Bond-line drawings show the carbon skeleton (the connections of all the carbon atoms that build up the backbone, or skeleton, of the molecule) with any functional groups that are attached, such as  $\text{—OH}$  or  $\text{—Br}$ . Lines are drawn in a zigzag format, where each corner or endpoint represents a carbon atom. For example, the following compound has seven carbon atoms:



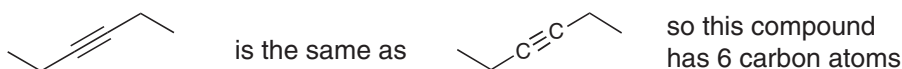
Don't forget that the ends of lines represent carbon atoms as well. For example, the following molecule has six carbon atoms (make sure you can count them):



Double bonds are shown with two lines, and triple bonds are shown with three lines:

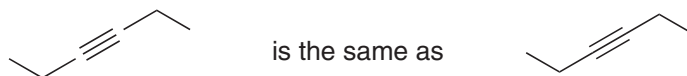


When drawing triple bonds, be sure to draw them in a straight line rather than zigzag, because triple bonds are linear (there will be more about this in the chapter on geometry). This can be quite confusing at first, because it can get hard to see just how many carbon atoms are in a triple bond, so let's make it clear:

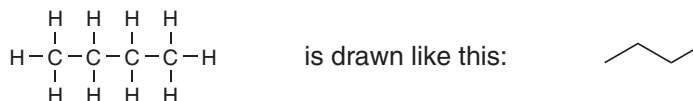


## 2 CHAPTER 1 BOND-LINE DRAWINGS

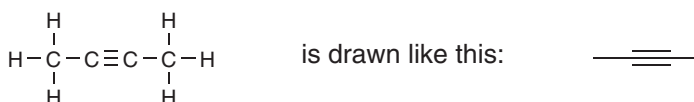
It is common to see a small gap on either side of a triple bond, like this:



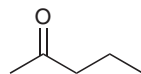
Both drawings above are commonly used, and you should train your eyes to see triple bonds either way. Don't let triple bonds confuse you. The two carbon atoms of the triple bond and the two carbons connected to them are drawn in a straight line. All other bonds are drawn as a zigzag:



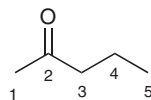
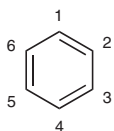
BUT



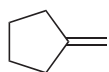
**EXERCISE 1.1** Count the number of carbon atoms in each of the following drawings:



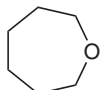
**Answer** The first compound has six carbon atoms, and the second compound has five carbon atoms:



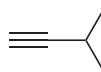
**PROBLEMS** Count the number of carbon atoms in each of the following drawings.



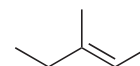
**1.2** Answer: \_\_\_\_\_



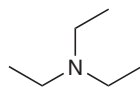
**1.3** Answer: \_\_\_\_\_



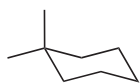
**1.4** Answer: \_\_\_\_\_



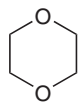
**1.5** Answer: \_\_\_\_\_



**1.6** Answer: \_\_\_\_\_



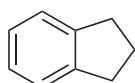
**1.7** Answer: \_\_\_\_\_



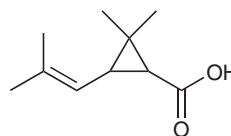
**1.8** Answer: \_\_\_\_\_



**1.9** Answer: \_\_\_\_\_

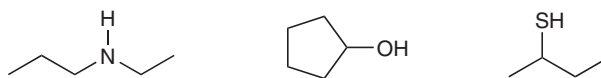


**1.10** Answer: \_\_\_\_\_

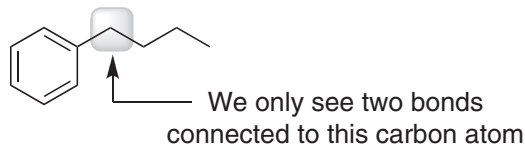


**1.11** Answer: \_\_\_\_\_

Now that we know how to count carbon atoms, we must learn how to count the hydrogen atoms in a bond-line drawing. Most hydrogen atoms are not shown, so bond-line drawings can be drawn very quickly. Hydrogen atoms connected to atoms other than carbon (such as nitrogen or oxygen) must be drawn:



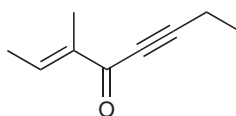
But hydrogen atoms connected to carbon are not drawn. Here is the rule for determining how many hydrogen atoms are connected to each carbon atom: *uncharged carbon atoms have a total of four bonds*. In the following drawing, the highlighted carbon atom is showing only two bonds:



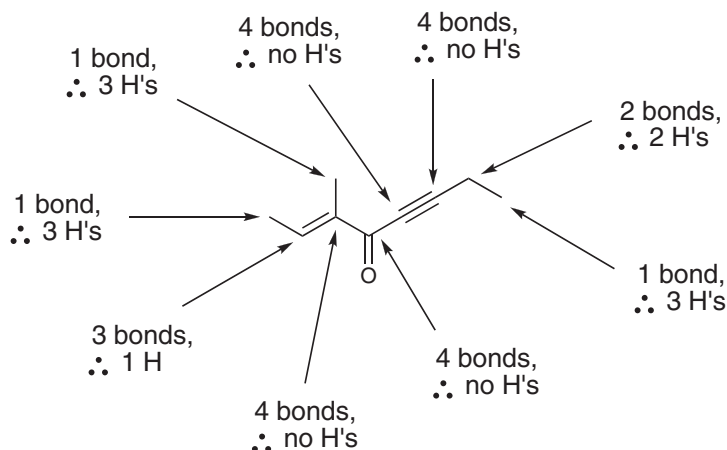
Therefore, it is assumed that there are two more bonds to hydrogen atoms (to give a total of four bonds). This is what allows us to avoid drawing the hydrogen atoms and to save so much time when drawing molecules. It is assumed that the average person knows how to count to four, and therefore is capable of determining the number of hydrogen atoms even though they are not shown.

So you only need to count the number of bonds that you can see on a carbon atom, and then you know that there should be enough hydrogen atoms to give a total of four bonds to the carbon atom. After doing this many times, you will get to a point where you do not need to count anymore. You will simply get accustomed to seeing these types of drawings, and you will be able to instantly “see” all of the hydrogen atoms without counting them. Now we will do some exercises that will help you get to that point.

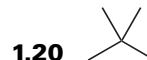
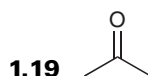
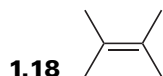
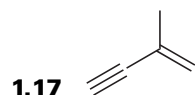
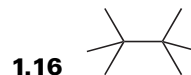
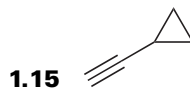
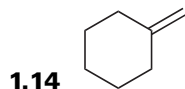
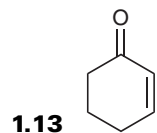
**EXERCISE 1.12** The following molecule has nine carbon atoms. Count the number of hydrogen atoms connected to each carbon atom.



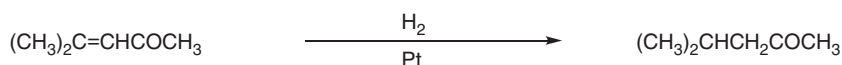
**Answer**



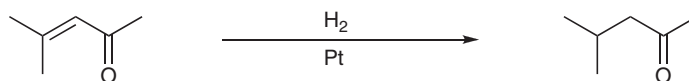
**PROBLEMS** For each of the following molecules, count the number of hydrogen atoms connected to each carbon atom.



Now we can understand why we save so much time by using bond-line drawings. Of course, we save time by not drawing every C and H. But, there is an even larger benefit to using these drawings. Not only are they easier to draw, but they are easier to read as well. Take the following reaction for example:



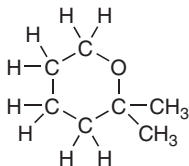
It is somewhat difficult to see what is happening in the reaction. You need to stare at it for a while to see the change that took place. However, when we redraw the reaction using bond-line drawings, the reaction becomes very easy to read immediately:



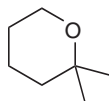
As soon as you see the reaction, you immediately know what is happening. In this reaction we are converting a double bond into a single bond by adding two hydrogen atoms across the double bond. Once you get comfortable reading these drawings, you will be better equipped to see the changes taking place in reactions.

## 1.2 HOW TO DRAW BOND-LINE DRAWINGS

Now that we know how to read these drawings, we need to learn how to draw them. Take the following molecule as an example:

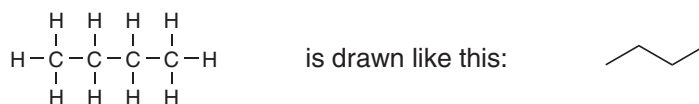


To draw this as a bond-line drawing, we focus on the carbon skeleton, making sure to draw any atoms other than C and H. All atoms other than carbon and hydrogen *must* be drawn. So the example above would look like this:

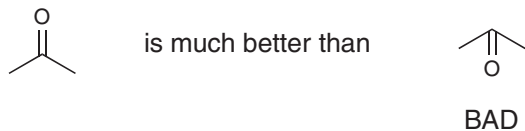


A few pointers may be helpful before you do some problems.

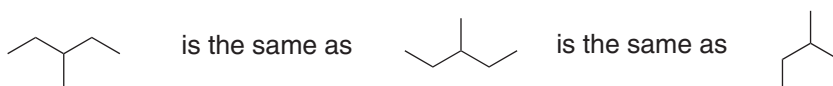
1. Don't forget that carbon atoms in a straight chain are drawn in a zigzag format:



2. When drawing double bonds, try to draw the other bonds as far away from the double bond as possible:

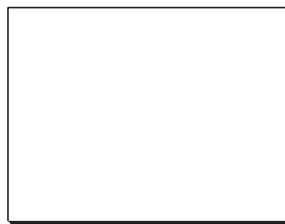
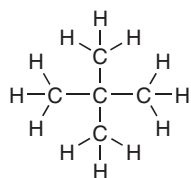


3. When drawing zigzags, it does not matter in which direction you start drawing:

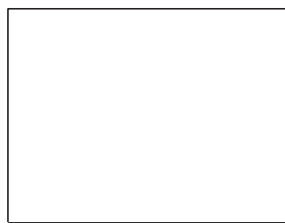
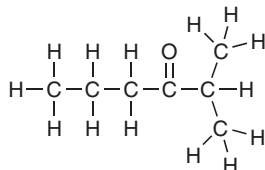


**PROBLEMS** For each structure below, draw a bond-line drawing in the box provided.

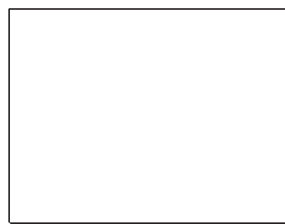
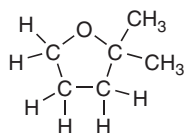
1.21



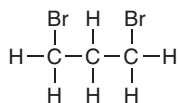
1.22



1.23



1.24

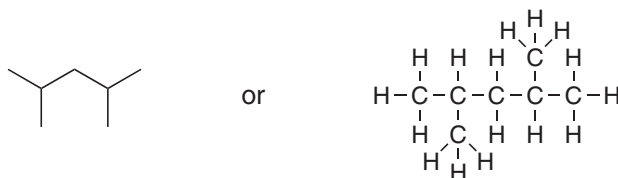


### 1.3 MISTAKES TO AVOID

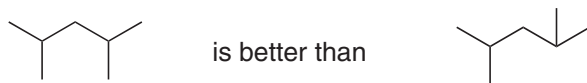
1. *Never* draw a carbon atom with more than four bonds. This is a big no-no. Carbon atoms only have four orbitals; therefore, carbon atoms can form only four bonds (bonds are formed when orbitals of one atom overlap with orbitals of another atom). This is true of all second-row elements, and we will discuss this in more detail in the upcoming chapter.
2. When drawing a molecule, you should either show all of the H's and all of the C's, or draw a bond-line drawing where the C's and H's are not drawn. You *cannot* draw the C's without also drawing the H's:



This drawing is insufficient. Either leave out the C's (which is preferable) or put in the H's:



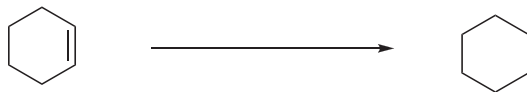
3. When drawing each carbon atom in a zigzag, try to draw all of the bonds as far apart as possible:



### 1.4 MORE EXERCISES

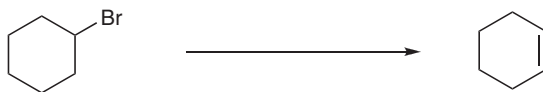
First, open your textbook and flip through the pages in the second half. Choose any bond-line drawing and make sure that you can say with confidence how many carbon atoms you see and how many hydrogen atoms are attached to each of those carbon atoms.

Now examine the following transformation, and think about the changes that are occurring:

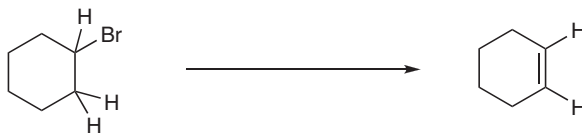


Don't worry about *how* these changes occur. That will be covered much later (in Chapter 11), when we explore this type of transformation in more detail. For now, just focus on describing the changes that you see. In this case, two hydrogen atoms have been installed, and a double bond has been converted into a single bond. It is certainly clear to see that the double bond has been converted into a single bond, but you should also clearly see that two hydrogen atoms have been installed during this process.

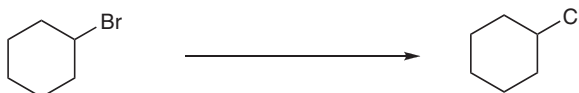
Consider another example:



In this example, H and Br have been removed, and a single bond has been converted into a double bond (we will see in Chapter 10 that it is actually  $\text{H}^+$  and  $\text{Br}^-$  that are removed). If you cannot see that an H was removed, then you will need to count the number of hydrogen atoms in the starting material and compare it with the product:

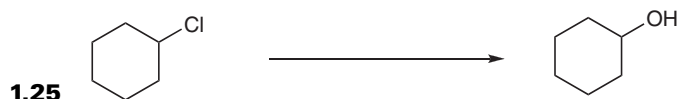


Now consider one more example:

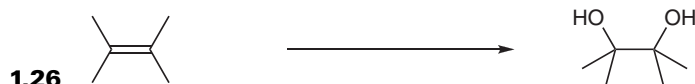


In this example, a bromine atom has been replaced with a chlorine atom (as we will see in Chapter 9). Inspection of the bond-line drawings clearly indicates that no other changes occurred in this case.

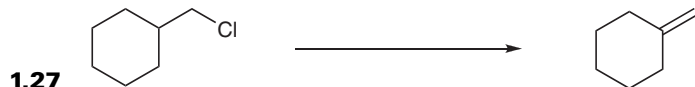
**PROBLEMS** For each of the following transformations, describe the changes that are occurring.



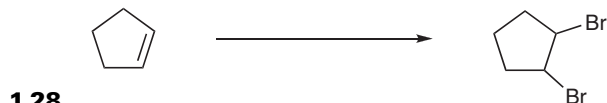
Answer: \_\_\_\_\_



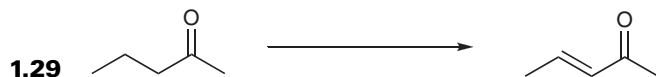
Answer: \_\_\_\_\_



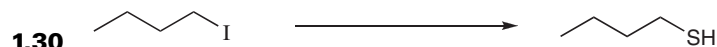
Answer: \_\_\_\_\_



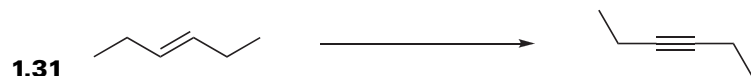
Answer: \_\_\_\_\_



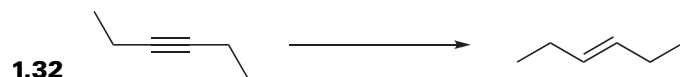
Answer: \_\_\_\_\_



Answer: \_\_\_\_\_



Answer: \_\_\_\_\_



Answer: \_\_\_\_\_

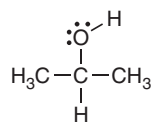
## 1.5 IDENTIFYING FORMAL CHARGES

Formal charges are charges (either positive or negative) that we must often include in our drawings. They are extremely important. If you don't draw a formal charge when it is supposed to be drawn, then your drawing will be incomplete (and wrong). So you must learn how to identify when you need formal charges and how to draw them. If you cannot do this, then you will not be able to draw resonance structures (which we will see in the next chapter), and if you can't do that, then you will have a very hard time passing this course.

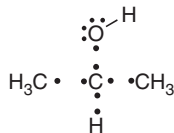
A formal charge is a charge associated with an atom that does not exhibit the expected number of valence electrons. When calculating the formal charge on an atom, we first need to know the number of valence electrons the atom is *supposed* to have. We can get this number by inspecting the periodic table, since each column of the periodic table indicates the number of expected valence electrons (valence electrons are the electrons in the valence shell, or the outermost shell of electrons—you probably remember this from high school chemistry). For example, carbon is in Column 4A, and therefore has four valence electrons. This is the number of valence electrons that a carbon atom is supposed to have.

Next we ask how many electrons are attributed to each atom in the Lewis structure. For each atom, if the electron count does not match the expected valence, then the atom bears a formal charge.

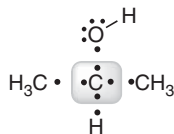
Let's see an example. Consider the central carbon atom in the compound below:



Remember that every bond represents two electrons being shared between two atoms. Begin by splitting each bond apart equally, like this:



Now count the number of electrons immediately surrounding the central carbon atom:



There are four electrons. This is the number of electrons that are attributed to this carbon atom.

In this case, the electron count matches the expected valence, so this carbon atom has no formal charge. This will be the case for most of the atoms in the structures you will draw in this course. But in some cases, there will be a difference between the electron count and the expected valence. In those cases, there will be a formal charge. So let's see an example of an atom that has a formal charge.

Consider the oxygen atom in the structure below:



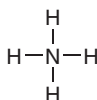
Let's begin by determining the number of valence electrons that are expected for an oxygen atom. Oxygen is in Column 6A of the periodic table, so oxygen should have six valence electrons. Next, we count the number of valence electrons that are attributed to this oxygen atom in the Lewis structure. To do this, we redraw the structure by splitting up the C—O bond equally, like this:



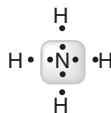
One electron of the C—O bond is attributed to the oxygen atom, and in addition, this oxygen atom also has three lone pairs. Recall that lone pairs are unshared electrons (electrons that are not being used to form bonds), and therefore, we attribute both electrons of each lone pair to the oxygen atom. As such, we attribute seven electrons to this oxygen atom (one from the C—O bond, and six more from the lone pairs). In this case, the electron count (seven) does NOT match the expected valence (six). This oxygen atom has one extra electron and will therefore bear a negative charge:



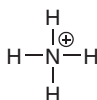
**EXERCISE 1.33** Consider the nitrogen atom in the structure below and determine if it has a formal charge:



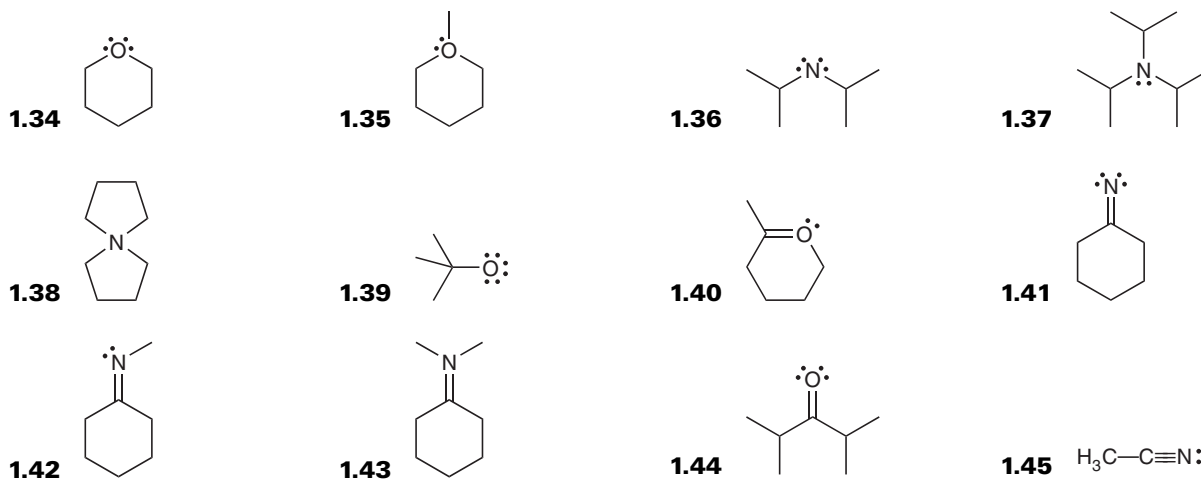
**Answer** Nitrogen is in Column 5A of the periodic table so it should have five valence electrons. Now we count the number of electrons that are attributed to the nitrogen atom in this structure:



There are only four electrons attributed to this nitrogen atom (one electron for each bond). This nitrogen atom appears to be missing an electron, and therefore, this nitrogen atom has a positive charge:



**PROBLEMS** For each of the structures below determine if the oxygen or nitrogen atom has a formal charge. If there is a charge, draw the charge.



This brings us to the most important atom of all: carbon. We saw before that carbon forms four bonds. This allows us to ignore the hydrogen atoms when drawing bond-line structures, because it is assumed that we know how to count to four and can figure out how many hydrogen atoms are there. When we said that, we were only talking about carbon atoms without formal charges (most carbon atoms in most structures will not have formal charges). But now that we have learned what a formal charge is, let's consider what happens when carbon has a formal charge.

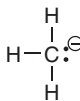
If carbon bears a formal charge, then we cannot just assume it will still have four bonds. In fact, it will have only three. Let's see why. Let's first consider  $\text{C}^+$ , and then we will move on to  $\text{C}^-$ .

If carbon has a *positive* formal charge, then it has only three valence electrons (it is supposed to have four valence electrons, because carbon is in Column 4A of the periodic table). Since it has only three valence electrons, it can form only three bonds. That's it. So, a carbon atom with a positive formal charge will have only three bonds, and you should keep this in mind when counting hydrogen atoms:



No hydrogen atoms  
on this  $\text{C}^+$

Now let's consider what happens when we have a carbon atom with a *negative* formal charge. The reason it has a negative formal charge is because it has one more electron than it is supposed to have. That is, it has five electrons attributed to it, rather than four. Two of these electrons form a lone pair, and the other three electrons are used to form bonds:



We have the lone pair, because we can't use each of the five electrons to form a bond. Carbon can *never* have five bonds. Why not? Electrons exist in regions of space called orbitals. These orbitals can overlap with orbitals from other atoms to form bonds, or the orbitals can contain two electrons (which is called a lone pair). Carbon has only four orbitals in its valence shell, so there is no way it could possibly form five bonds—it does not have five orbitals to use to form those bonds. This is why a carbon atom with a negative charge will have a lone pair (if you look at the drawing above, you will count four orbitals—one for the lone pair and then three more for the bonds).

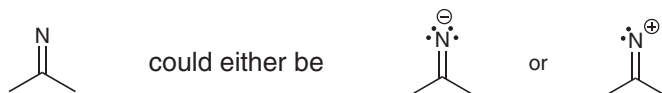
Therefore, a carbon atom with a negative charge can also form only three bonds (just like a carbon with a positive charge). When you count hydrogen atoms, you should keep this in mind:



No hydrogen atoms  
on this C<sup>-</sup>

## 1.6 FINDING LONE PAIRS THAT ARE NOT DRAWN

From all of the cases above (oxygen, nitrogen, and carbon), you can see why you have to know how many lone pairs there are on an atom in order to figure out the formal charge on that atom. Similarly, you have to know the formal charge to figure out how many lone pairs there are on an atom. Take the case below with the nitrogen atom shown:



If the lone pairs were drawn, then we would be able to figure out the charge (two lone pairs would mean a negative charge and one lone pair would mean a positive charge). Similarly, if the formal charge was drawn, we would be able to figure out how many lone pairs there are (a negative charge would mean two lone pairs and a positive charge would mean one lone pair). So you can see that drawings must include either lone pairs or formal charges. *The convention is to always show formal charges and to leave out the lone pairs.* This is much easier to draw, because you usually won't have more than one charge on a drawing (if even that), so you get to save time by not drawing every lone pair on every atom.

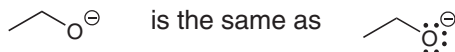
Now that we have established that formal charges must *always* be drawn and that lone pairs are usually *not* drawn, we need to get practice in how to see the lone pairs when they are not drawn. This is not much different from training yourself to see all the hydrogen atoms in a bond-line drawing even though they are not drawn. If you know how to count, then you should be able to figure out how many lone pairs are on an atom where the lone pairs are not drawn.

Let's see an example to demonstrate how you do this:



In this case, we are looking at an oxygen atom. Oxygen is in Column 6A of the periodic table, so it is supposed to have six valence electrons. Then, we need to take the formal charge into account. This oxygen atom has a negative charge, which means one extra electron. Therefore, we attribute  $6 + 1 = 7$  electrons to this oxygen atom. Now we can figure out how many lone pairs there are.

The oxygen atom has one bond, which means that it is using one of its seven electrons to form a bond. The other six must be in lone pairs. Since each lone pair is two electrons, this must mean that there are three lone pairs:

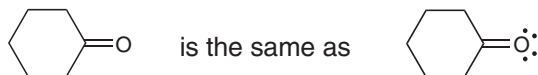
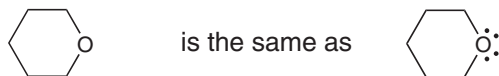
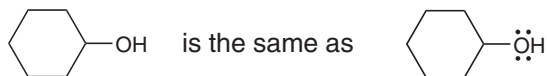


Let's review the process:

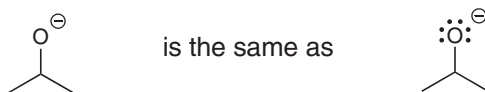
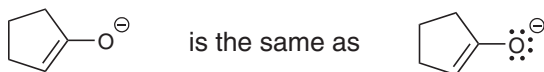
1. Identify the expected valence (using the periodic table).
2. Determine the number of electrons attributed to the atom in the Lewis structure. To do this, take the formal charge into account. A negative charge means one more electron, and a positive charge means one less electron.
3. Use this number to figure out how many lone pairs there are.

Now we need to get used to the common examples. Although it is important that you know how to count and determine numbers of lone pairs, it is actually much more important to get to a point where you don't have to waste time counting. You need to get familiar with the common situations you will encounter. Let's go through them methodically.

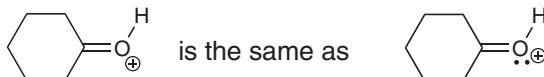
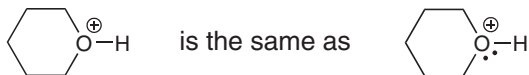
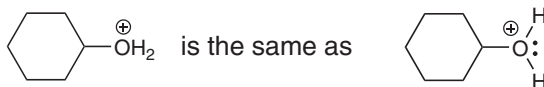
When oxygen has no formal charge, it will have two bonds and two lone pairs:



If oxygen has a negative formal charge, then it must have one bond and three lone pairs:



If oxygen has a positive charge, then it must have three bonds and one lone pair:



**EXERCISE 1.46** Draw all lone pairs in the following structure:



**Answer** The oxygen atom has a positive formal charge and three bonds. You should try to get to a point where you recognize that this must mean that the oxygen atom has one lone pair:

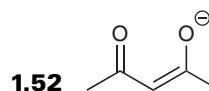
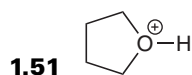
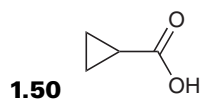
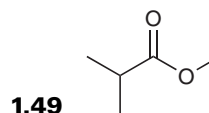
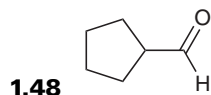
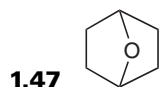


Until you get to the point where you can recognize this, you should be able to figure out the answer by counting.

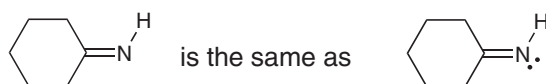
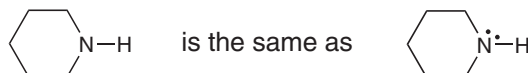
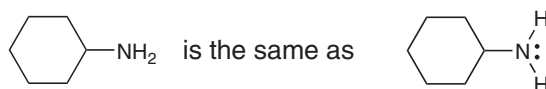
Oxygen is supposed to have six valence electrons. This oxygen atom has a positive charge, which means it is missing an electron. Therefore, we attribute  $6 - 1 = 5$  electrons to this oxygen atom. Now, we can figure out how many lone pairs there are.

The oxygen atom has three bonds, which means that it is using three of its five electrons to form bonds. The other two must be in a lone pair. So there is only one lone pair.

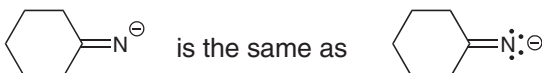
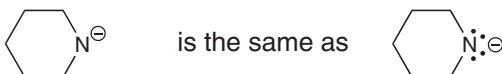
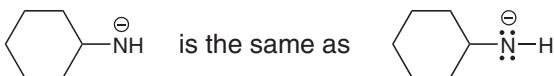
**PROBLEMS** Review the common situations above, and then come back to these problems. For each of the following structures, draw all lone pairs. Try to recognize how many lone pairs there are *without* having to count. Then count to see if you were right.



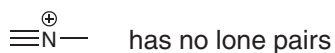
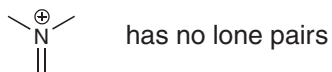
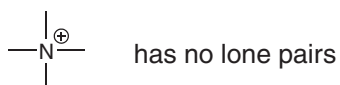
Now let's look at the common situations for nitrogen atoms. When nitrogen has no formal charge, it will have three bonds and one lone pair:



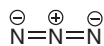
If nitrogen has a negative formal charge, then it must have two bonds and two lone pairs:



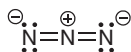
If nitrogen has a positive charge, then it must have four bonds and no lone pairs:



**EXERCISE 1.53** Draw all lone pairs in the following structure:



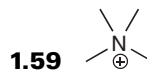
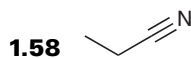
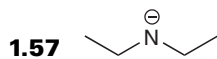
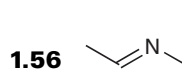
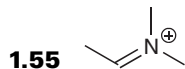
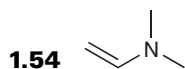
**Answer** The central nitrogen atom has a positive formal charge and four bonds. You should try to get to a point where you recognize that this nitrogen atom does not have any lone pairs. Each of the other nitrogen atoms has a negative formal charge and two bonds. You should try to get to a point where you recognize that each of these nitrogen atoms has two lone pairs:



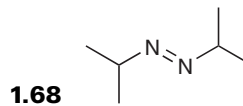
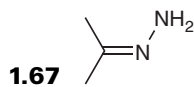
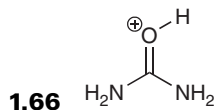
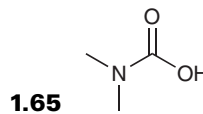
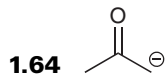
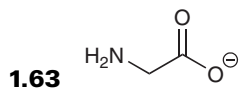
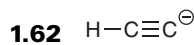
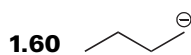
Until you get to the point where you can recognize this, you should be able to figure out the answer by counting. Nitrogen is supposed to have five valence electrons. The central nitrogen atom has a positive charge, which means it is missing an electron. In other words, we attribute  $5 - 1 = 4$  electrons to this nitrogen atom. Now, we can figure out how many lone pairs there are. Since it has four bonds, it is using all of its electrons to form bonds. So there is no lone pair on this nitrogen atom.

For each of the remaining nitrogen atoms, there is a negative formal charge. That means that each of those nitrogen atoms has one extra electron,  $5 + 1 = 6$  electrons. Each nitrogen atom has two bonds, which means that each nitrogen atom has four electrons left over, giving two lone pairs.

**PROBLEMS** Review the common situations for nitrogen, and then come back to these problems. For each of the following structures, draw all lone pairs. Try to recognize how many lone pairs there are *without* having to count. Then count to see if you were right.



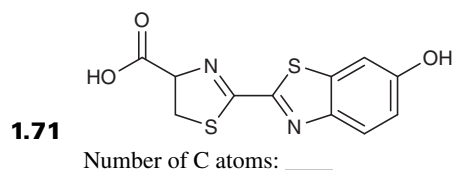
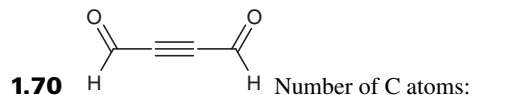
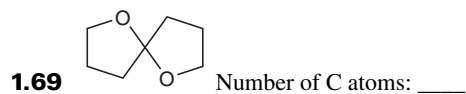
For each of the following structures, draw all lone pairs.



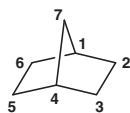
## END-OF-CHAPTER PROBLEMS

## PRACTICE PROBLEMS (Problems that involve only one skill)

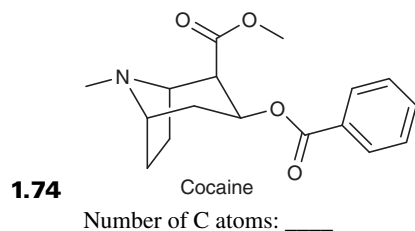
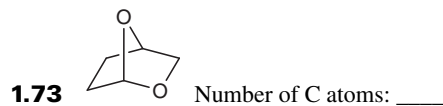
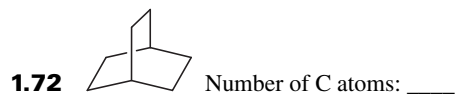
**Problems 1.69–1.71.** Count the number of carbon atoms in each of the following structures:



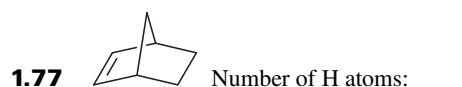
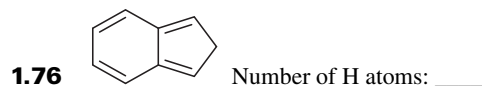
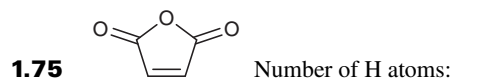
**Problems 1.72–1.74.** The structure below has seven carbon atoms and is said to be bicyclic (because converting this compound into an acyclic compound, with no ring at all, would require that we break two C—C bonds).



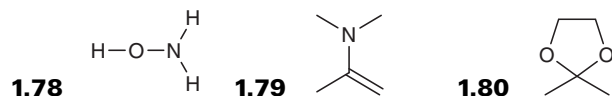
Notice that the bond between C1 and C6 is drawn with a gap to indicate that this bond is behind the bond between C4 and C7. Bicyclic compounds are drawn in this way (with one of the bonds drawn with a gap) to illustrate their three-dimensional nature. With this in mind, count the number of carbon atoms in each of the following structures:



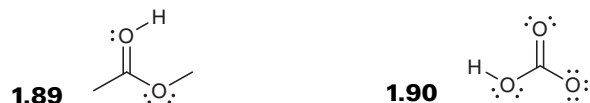
**Problems 1.75–1.77.** Count the number of hydrogen atoms in each of the following structures:



**Problems 1.78–1.80.** Each of the following structures has one or more atoms with lone pairs. We will encounter each of these structures as we study organic chemistry, and in each case, one of the lone pairs is responsible for the reactivity that we will see. For each of the following structures, identify all lone pairs:

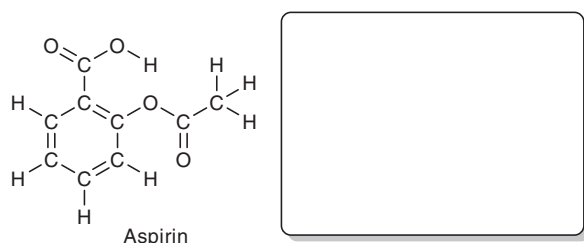


**Problems 1.81–1.90.** Draw any missing formal charges in each of the following structures. Also, determine the net (total) charge on each structure by adding together all the individual charges. For example, a structure will have a net charge of zero if the structure has one positive charge and one negative charge.

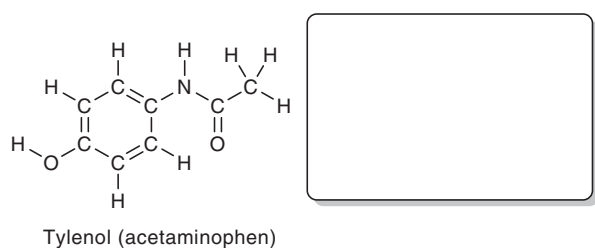


**Problems 1.91–1.93.** Below are the structures of three common analgesics (pain relievers). In each of the following cases, use the box provided to draw a bond-line structure for the compound shown.

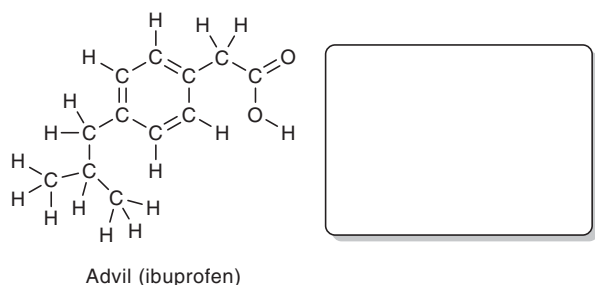
## 1.91



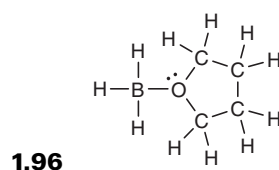
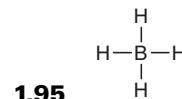
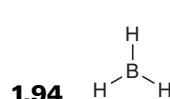
## 1.92



## 1.93



**Problems 1.94–1.96.** Boron is in column 3A of the periodic table and therefore has three valence electrons (as compared with carbon, which has four valence electrons). Based on this information, draw any missing formal charges in each of the following structures. Note: All lone pairs in the given structures are shown. Also, determine the net (total) charge on each structure, by adding together all the individual charges. For example, a structure will have a net charge of zero if the structure has one positive charge and one negative charge:

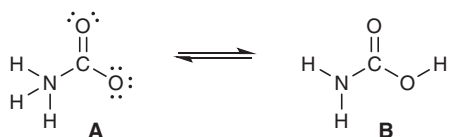


1.97 Below is the reaction between a ketone and HCl. The products are ionic, but the formal charges have not been shown. Draw the formal charges on the products.



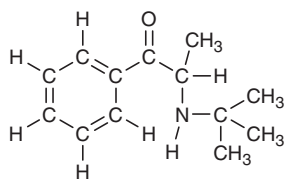
### INTEGRATED PROBLEMS (Problems that involve more than one skill)

1.98 Shown below is the amino acid called glycine. Notice that glycine exists as an equilibrium between two structures, labelled **A** and **B** below:



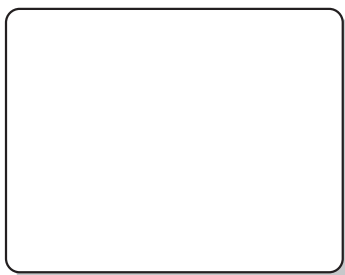
- Structure **A** has formal charges which have not been shown. Draw those formal charges.
- What is the net charge on structure **A**?
- Draw all lone pairs in structure **B**.
- Does structure **B** have any formal charges that need to be drawn?
- Does structure **B** have the same net charge as structure **A**?

**1.99** Marketed under the trade name Zyban, the drug below is used as a smoking cessation aid for people who want to quit smoking.

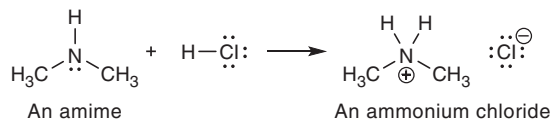


Zyban

- (a) In the box provided below, draw a bond-line structure for Zyban:



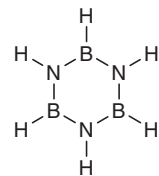
- (b) Zyban is described as an amine because of the part of its structure that contains a nitrogen atom. As we will see in an upcoming chapter, when an amine is treated with HCl, an acid–base reaction occurs in which  $H^+$  is transferred to the amine, thereby generating an ammonium ion and a chloride ion:



This product is an ionic species (much like NaCl), and is called an ammonium chloride. Zyban is actually sold as an ammonium chloride, rather than as an amine. In the box provided, draw the structure of this ammonium chloride:

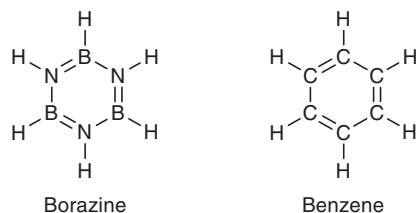


**1.100** The following compound, called borazine, is inorganic (it contains no carbon atoms).



Borazine

- (a) Boron is in column 3A of the periodic table and therefore has three valence electrons (as compared with carbon, which has four valence electrons). Based on this information, and assuming that none of the atoms bears a formal charge, draw all lone pairs in the structure above.
- (b) Borazine is remarkably stable, as it shares features with a very stable organic compound, called benzene (later in the course, we will see the source of this stability). Indeed, borazine can alternatively be drawn as shown below, which illustrates its structural similarity with benzene:

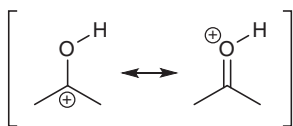


In this drawing of borazine (which has three double bonds, but no lone pairs), there are missing formal charges that have not been drawn. Draw these missing formal charges, and then indicate the net charge on this structure.

## CHALLENGE PROBLEM

**1.101** In the next chapter, we will see that some structures cannot be adequately represented with only one bond-line drawing, because it is difficult to pinpoint the exact location of some of the electrons. In such cases, we will see that we must draw more than one drawing (called resonance structures), and then meld those images together in our minds. For example, in the previous problem, we saw two different resonance structures for borazine (one resonance structure that had only single bonds, and another resonance structure that had three double bonds but no lone pairs). Neither of these structures alone can adequately represent the nature of the compound. That is, the B—N bonds are not purely single bonds, nor are they purely double bonds. Rather, the B—N bonds are somewhere in between these two extremes, having some double-bond character and some single-bond character.

With this in mind, consider the cation shown below, which has two resonance structures.



- (a) Draw all of the lone pairs in each of the resonance structures above.

- (b) The two resonance structures above are used to represent a single chemical entity, although these two resonance structures do not contribute equal character to the overall nature of this chemical entity. That is, one of these resonance structures contributes more character than the other resonance structure. For reasons that we will see in the next chapter, the resonance structure with fewer lone pairs is the structure that contributes more character. Based on this information, determine whether the C—O bond has more single-bond character or more double-bond character.
- (c) Let's explore the reason why one of these resonance structures contributes more character than the other. Recall that a lone pair is a pair of electrons that is NOT shared between atoms. Therefore, the resonance structure with fewer lone pairs (fewer unshared electrons) will be the resonance structure with more bonds (more shared electrons). With more shared electrons, it is more likely that all atoms will have filled octets (will be surrounded by eight electrons, which is one of the most important features for making a resonance structure stable). Indeed, one of the resonance structures shown above has an atom that is missing an octet of electrons, while the other resonance structure has filled octets for every atom. Identify the resonance structure with the unfilled octet, and identify which atom in that resonance structure lacks an octet of electrons.

# CHAPTER 2

## RESONANCE

In this chapter, you will learn the tools that you need to draw resonance structures with proficiency. I cannot adequately stress the importance of this skill. Resonance is the one topic that permeates the entire subject matter from start to finish. It finds its way into every chapter, into every reaction, and into your nightmares if you do not master the rules of resonance. You cannot get an A in this class without mastering resonance. So what is resonance? And why do we need it?

### 2.1 WHAT IS RESONANCE?

In Chapter 1, we introduced one of the best ways of drawing molecules, bond-line structures. They are fast to draw and easy to read, but they have one major deficiency: they do not describe molecules perfectly. In fact, no drawing method can completely describe a molecule using only a single drawing. Here is the problem.

Although our drawings are very good at showing which atoms are connected to each other, our drawings are not good at showing where all of the electrons are, because electrons aren't really solid particles that can be in one place at one time. All of our drawing methods treat electrons as particles that can be placed in specific locations. Instead, it is best to think of electrons as *clouds of electron density*. We don't mean that electrons fly around in clouds; we mean that electrons *are* clouds. These clouds often spread themselves across large regions of a molecule.

So how do we represent molecules if we can't draw where the electrons are? The answer is resonance. We use the term *resonance* to describe our solution to the problem: we use more than one drawing to represent a single molecule. We draw several drawings, and we call these drawings *resonance structures*. We meld these drawings into one image in our minds. To better understand how this works, consider the following analogy.

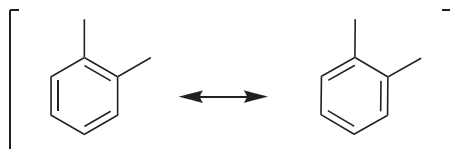
Your friend asks you to describe what a nectarine looks like, because he has never seen one. You aren't a very good artist so you say the following:

*Picture a peach in your mind, and now picture a plum in your mind. Well, a nectarine has features of both: the inside tastes like a peach, but the outside is smooth like a plum. So take your image of a peach together with your image of a plum and meld them together in your mind into one image. That's a nectarine.*

It is important to realize that a nectarine does not switch back and forth every second from being a peach to being a plum. A nectarine is a nectarine all of the time. The image of a peach is not adequate to describe a nectarine. Neither is the image of a plum. But by imagining both together at the same time, you can get a sense of what a nectarine looks like.

The problem with drawing molecules is similar to the problem above with the nectarine. No single drawing adequately describes the nature of the electron density spread out over the molecule. To solve this problem, we draw several drawings and then meld them together in our mind into one image. Just like the nectarine.

Let's see an example:



The compound above has two resonance structures. Notice that we separate resonance structures with a straight, two-headed arrow, and we place brackets around the structures. The arrow and brackets indicate that they are resonance structures *of one molecule*. The molecule is not flipping back and forth between the different resonance structures.

Now that we know why we need resonance, we can begin to understand why resonance structures are so important. Ninety-five percent of the reactions that you will see in this course occur because one molecule has a region of low electron density and the other molecule has a region of high electron density. They attract each other in space, which causes a reaction. So, to predict how and when two molecules will react with each other, we must first predict where there is low electron density and where there is high electron density. We need to have a firm grasp of resonance to do this. In this chapter, we will see many examples of how to predict the regions of low or high electron density by applying the rules of drawing resonance structures.

## 2.2 CURVED ARROWS: THE TOOLS FOR DRAWING RESONANCE STRUCTURES

In the beginning of the course, you might encounter problems like this: here is a drawing; now draw the other resonance structures. But later on in the course, it will be assumed and expected that you can draw all of the resonance structures of a compound. If you cannot actually do this, you will be in big trouble later on in the course. So how do you draw all of the resonance structures of a compound? To do this, you need to learn the tools that help you: curved arrows.

Here is where it can be confusing as to what is exactly going on. These arrows do NOT represent an actual process (such as electrons moving). This is an important point, because you will learn later about curved arrows used in drawing reaction mechanisms. Those arrows look exactly the same, but they actually do refer to the flow of electron density. In contrast, curved arrows here are used only as tools to help us draw all resonance structures of a molecule. The electrons are not actually moving. It can be tricky because we will say things like: "this arrow shows the electrons coming from here and going to there." But we don't actually mean that the electrons are moving; they are *not* moving. Since each drawing treats the electrons as particles stuck in one place, we will need to "move" the electrons to get from one drawing to another. Arrows are the tools that we use to make sure that we know how to draw all resonance structures for a compound. So, let's look at the features of these important curved arrows.

Every curved arrow has a *head* and a *tail*. It is essential that the head and tail of every arrow be drawn in precisely the proper place. *The tail shows where the electrons are coming from, and the head shows where the electrons are going* (remember that the electrons aren't really going anywhere, but we treat them as if they were so we can make sure to draw all resonance structures):



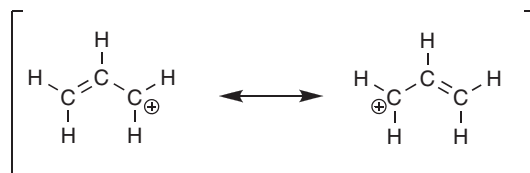
Therefore, there are only two things that you have to get right when drawing an arrow: the tail needs to be in the right place and the head needs to be in the right place. So we need to see rules about where you can and where you cannot draw arrows. But first we need to talk a little bit about electrons, since the arrows are describing the electrons.

Atomic orbitals can hold a maximum of two electrons. So, there are only three options for any atomic orbital:

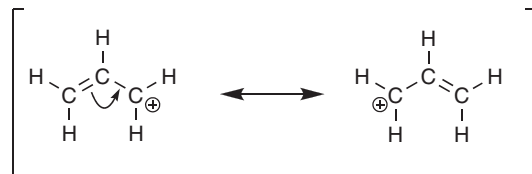
# of electrons in atomic orbital	Comments	Outcome
0	Nothing to talk about (no electrons)	-
1	Can overlap with another atomic orbital (also housing one electron) to form a bond with another atom	<b>bond</b>
2	The atomic orbital is filled and is called a lone pair	<b>lone pair</b>

So we see that electrons can be found in two places: in bonds or in lone pairs. Therefore, electrons can only come from either a bond or a lone pair. Similarly, electrons can only go to form either a bond or a lone pair.

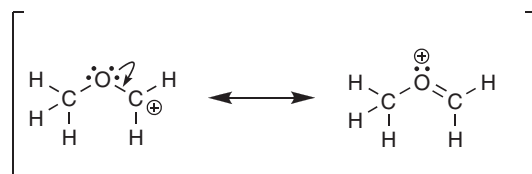
Let's focus on tails of arrows first. Remember that the tail of an arrow indicates where the electrons are coming from. So the tail has to come from a place that has electrons: either from a bond or from a lone pair. As an example, consider the following resonance structures:



How do we get from the first structure to the second one? Notice that the electrons that make up the double bond have been “moved.” This is an example of electrons coming from a bond. Let’s see the arrow showing the electrons coming from the bond and going to form another bond:

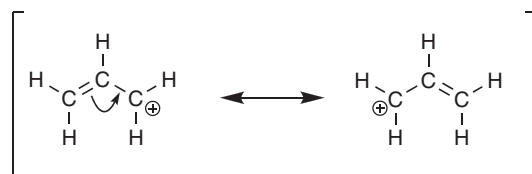


Now let’s see an example where electrons come from a lone pair:

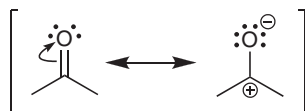


Never draw an arrow that comes from a positive charge. The tail of an arrow must come from a spot that has electrons.

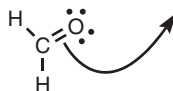
Heads of arrows are just as simple as tails. The head of an arrow shows where the electrons are going. So the head of an arrow must either point directly in between two atoms to form a bond, like this:



or it must point to an atom to form a lone pair, like this:



Never draw the head of an arrow going off into space, like this:



Bad arrow

Remember that the head of an arrow shows where the electrons are going. So the head of an arrow must point to a place where the electrons can go—either to form a bond or to form a lone pair.

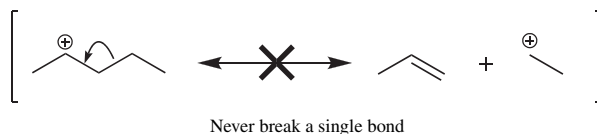
## 2.3 THE TWO COMMANDMENTS

Now we know what curved arrows are, but how do we know when to use curved arrows to push electrons and where to push them? First, we need to learn where we *cannot* push electrons. There are two important rules that you should *never* violate when pushing arrows. They are the “two commandments” of drawing resonance structures:

1. Thou shall not break a single bond.
2. Thou shall not exceed an octet for second-row elements.

Let's focus on one at a time.

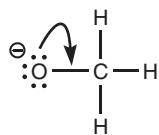
1. *Never break a single bond* when drawing resonance structures. By definition, resonance structures must have all the same atoms connected in the same order.



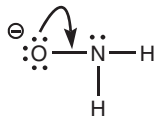
There are very few exceptions to this rule, and only a trained organic chemist can be expected to know when it is permissible to violate this rule. Some instructors might violate this rule one or two times (about half-way through the course). If this happens, you should recognize that you are seeing a very rare exception. In virtually every situation that you will encounter, you *cannot* violate this rule. Therefore, you must get into the habit of never breaking a single bond when drawing resonance structures.

There is a simple way to ensure that you never violate this rule. When drawing resonance structures, just make sure that you never draw the tail of an arrow on a single bond.

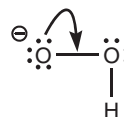
2. *Never exceed an octet for second-row elements.* Elements in the second row (C, N, O, F) have only four orbitals in their valence shell. Each of these four orbitals can be used either to form a bond or to hold a lone pair. Each bond requires the use of one orbital, and each lone pair requires the use of one orbital. So the second-row elements can never have five or six bonds; the most is four. Similarly, they can *never* have four bonds and a lone pair, because this would also require five orbitals. For the same reason, they can never have three bonds and two lone pairs. The sum of (bonds) + (lone pairs) for a second-row element can never exceed the number four. Let's see some examples of arrow pushing that violate this second commandment:



**BAD ARROW**



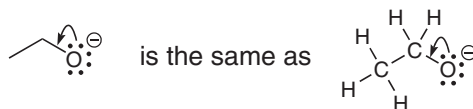
**BAD ARROW**



**BAD ARROW**

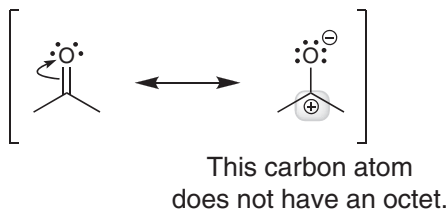
In each of these drawings, the central atom cannot form another bond because it does not have a fifth orbital that can be used. *This is impossible.* Don't ever do this.

The examples above are clear, but with bond-line drawings, it can be more difficult to see the violation because the hydrogen atoms are not drawn (and, very often, neither are the lone pairs). You have to train yourself to see the hydrogen atoms and to recognize when you are exceeding an octet:



At first it is difficult to see that the arrow on the left structure violates the second commandment. But when we count the hydrogen atoms, we can see that the arrow above would give a carbon atom with five bonds.

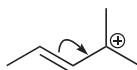
From now on, we will refer to the second commandment as "the octet rule." But be careful—for purposes of drawing resonance structures, it is only a violation if we *exceed* an octet for a second-row element. However, it is OK for carbon (which is a second-row element) to have *fewer* than an octet of electrons. For example:



This drawing is perfectly acceptable, even though the central carbon atom has only six electrons surrounding it. For our purposes, we will only consider the “octet rule” to be violated if we exceed an octet.

Our two commandments (never break a single bond, and never violate “the octet rule”) reflect the two parts of a curved arrow (the head and the tail). A bad tail violates the first commandment, and a bad head violates the second commandment.

**EXERCISE 2.1** Look at the arrow drawn on the following structure and determine whether it violates either of the two commandments for drawing resonance structures:

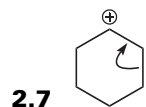
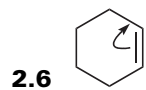
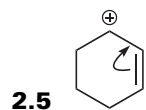
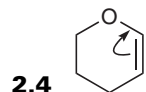
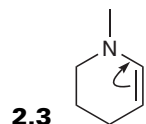
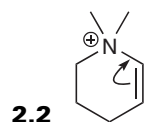


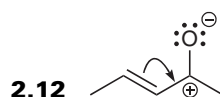
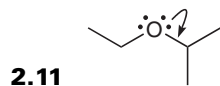
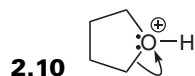
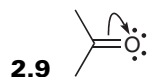
**Answer** First we need to ask if the first commandment has been violated: did we break a single bond? To determine this, we look at the *tail* of the arrow. If the tail of the arrow is coming from a single bond, then that means we are breaking that single bond. If the tail is coming from a double bond, then we have not violated the first commandment. In this example, the tail is on a double bond, so we did not violate the first commandment.

Now we need to ask if the second commandment has been violated: did we violate the octet rule? To determine this, we look at the *head* of the arrow. Are we forming a fifth bond? Remember that  $C^+$  only has three bonds, not four. When we push the electrons as shown above, the carbon atom will now get four bonds, and the second commandment has not been violated.

The arrow above is valid, because the two commandments were not violated.

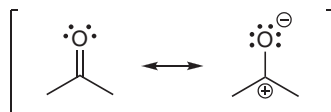
**PROBLEMS** For each of the problems below, determine which arrows violate either one of the two commandments, and explain why. (Don't forget to count all hydrogen atoms and all lone pairs.)





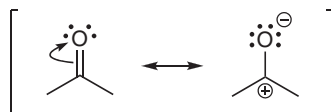
## 2.4 DRAWING GOOD ARROWS

Now that we know how to identify good arrows and bad arrows, we need to get some practice drawing arrows. We know that the tail of an arrow must come either from a bond or a lone pair, and that the head of an arrow must go to form a bond or a lone pair. If we are given two resonance structures and are asked to show the arrow(s) that get us from one resonance structure to the other, it makes sense that we need to look for any bonds or lone pairs that are appearing or disappearing when going from one structure to another. For example, consider the following resonance structures:



How would we figure out what curved arrow to draw to get us from the drawing on the left to the drawing on the right? We must look at the difference between the two structures and ask, "How should we push the electrons to get from the first structure to the second structure?" Begin by looking for any double bonds or lone pairs that are disappearing. That will tell us where to put the tail of our arrow. In this example, there are no lone pairs disappearing, but there is a double bond disappearing. So we know that we need to put the tail of our arrow on the double bond.

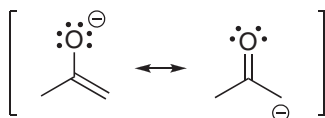
Now, we need to know where to put the head of the arrow. We look for any lone pairs or double bonds that are appearing. We see that there is a new lone pair appearing on the oxygen atom. This tells us where to put the head of the arrow:



Notice that when we move a double bond up onto an atom to form a lone pair, it creates two formal charges: a positive charge on the carbon atom that lost its bond, and a negative charge on the oxygen atom that got a lone pair. This is a very important issue. Formal charges were introduced in the previous chapter, and now they will become instrumental in drawing resonance structures. For the moment, let's just focus on pushing arrows, and in the next section of this chapter, we will come back to focus on these formal charges.

It is pretty straightforward to see how to push only one curved arrow that gets us from one resonance structure to another. But what about when we need to push more than one arrow to get from one resonance structure to another? Let's do an example.

**EXERCISE 2.13** Draw curved arrows that convert the first resonance structure into the second resonance structure below:



**Answer** Let's analyze the difference between these two drawings. We begin by looking for any double bonds or lone pairs that are disappearing. We see that oxygen is losing a lone pair, and the C=C bond on the bottom is also disappearing. This should automatically tell us that we need two curved arrows. To lose a lone pair and a double bond, we will need two tails.

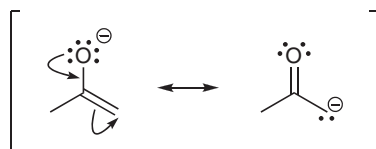
Now let's look for any double bonds or lone pairs that are appearing. We see that a C=O bond is appearing and a C with a negative charge is appearing (remember that a C<sup>-</sup> means a C with a lone pair). This tells us that we need two heads, which confirms that we need two curved arrows.

So we know we need two curved arrows. Let's start at the top. We lose a lone pair from the oxygen atom and form a C=O bond. Let's draw that curved arrow:



**CAN'T STOP HERE**

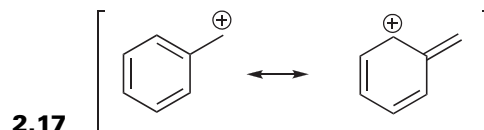
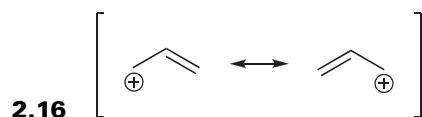
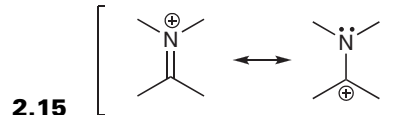
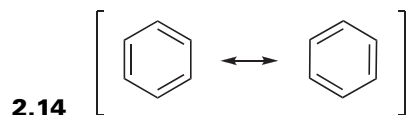
Notice that if we stopped here, we would be violating the second commandment. The central carbon atom is getting five bonds. To avoid this problem, we must also draw the second curved arrow. The C=C bond disappears (which solves our octet problem) and becomes a lone pair on carbon.

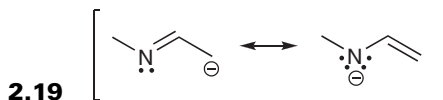
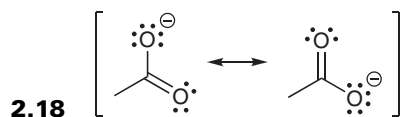


Arrow pushing is much like riding a bike. If you have never done it before, watching someone else will not make you an expert. You have to learn how to balance yourself. Watching someone else is a good start, but you have to get on the bike if you want to learn. You will probably fall a few times, but that's part of the learning process. The same is true with arrow pushing. The only way to learn is with practice.

Now it's time for you to get on the arrow-pushing bike. You would never be stupid enough to try riding a bike for the first time next to a steep cliff. Similarly, do not let your first arrow-pushing experience be during your exam. Practice right now!

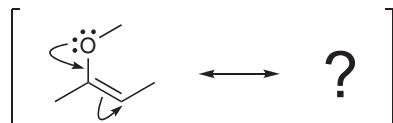
**PROBLEMS** Draw the curved arrows that convert one drawing to the next. In many cases you will need to draw more than one curved arrow.



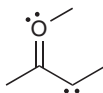


## 2.5 FORMAL CHARGES IN RESONANCE STRUCTURES

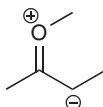
Now we know how to draw good arrows (and how to avoid drawing bad arrows). In the last section, we were given the resonance structures and just had to draw the arrows. Now we need to take this to the next level. We need to get practice drawing the resonance structures when they are not given. To ease into it, we will still show the arrows, and we will focus on drawing the resonance structures with proper formal charges. Consider the following example:



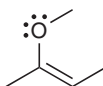
In this example, we can see that one of the lone pairs on oxygen is coming down to form a bond, and the C=C double bond is being pushed to form a lone pair on a carbon atom. When both arrows are pushed at the same time, we are not violating either of the two commandments. So, let's focus on how to draw the resonance structure. Since we know what arrows mean, it is easy to follow the arrows. We just get rid of one lone pair on oxygen, place a double bond between carbon and oxygen, get rid of the carbon-carbon double bond, and place a lone pair on carbon:



The arrows are really a language, and they tell us what to do. But here comes the tricky part: we cannot forget to put formal charges on the new drawing. If we apply the rules of assigning formal charges, we see that oxygen gets a positive charge and carbon gets a negative charge. As long as we draw these charges, it is not necessary to draw in the lone pairs:



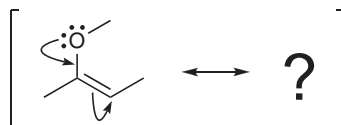
It is absolutely critical to draw these formal charges. Structures drawn without them are *wrong*. In fact, if you forget to draw the formal charges, then you are missing the whole point of resonance. Let's see why. Look at the resonance structure we just drew. Notice that there is a negative charge on a carbon atom. This tells us that this carbon atom is a site of high electron density. We would not know this by looking only at the first drawing of the molecule:



This is why we need resonance—it shows us where there are regions of high and low electron density in the resonance hybrid. If we draw resonance structures without formal charges, then what is the point in drawing the resonance structures at all?

Now that we see that proper formal charges are essential, we should make sure that we know how to draw them when drawing resonance structures. If you are a little bit shaky when it comes to formal charges, you can go back and review formal charges in the previous chapter. More importantly, you should be able to draw formal charges without having to count each time. We saw the common situations for oxygen, nitrogen, and carbon. It is important to remember those (go back and review those if you need to).

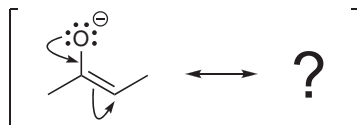
Another way to assign formal charges is to read the arrows properly. Let's look at our example again:



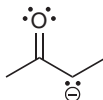
Notice what the arrows are telling us: oxygen is giving up a lone pair (two electrons entirely on oxygen) to form a bond (two electrons being shared: one for oxygen and one for carbon). So oxygen is losing an electron. This tells us that it must get a positive charge in the resonance structure. A similar analysis for the carbon atom on the bottom right shows that it will get a negative charge. Remember that the electrons are not really moving anywhere. Arrows are just tools that help us draw resonance structures. To use these tools properly, we imagine that the electrons are moving, but they are not.

Now let's practice.

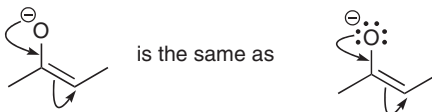
**EXERCISE 2.20** Draw the resonance structure that you get when you push the arrows shown below. Be sure to include formal charges.



**Answer** We read the curved arrows carefully. One of the lone pairs on oxygen is coming down to form a bond, and the C=C double bond is being pushed to form a lone pair on a carbon atom. This is very similar to the example we just saw. We just get rid of one lone pair on oxygen, place a double bond between carbon and oxygen, get rid of the carbon-carbon double bond, and place a lone pair on carbon. Finally, we must draw any formal charges:



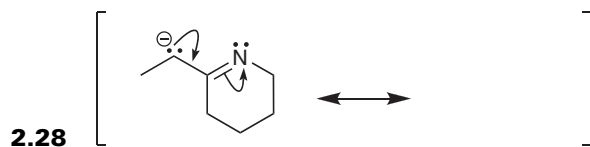
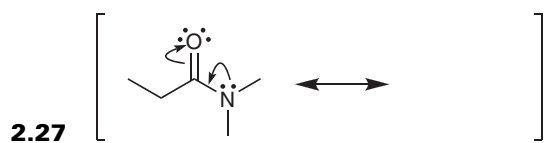
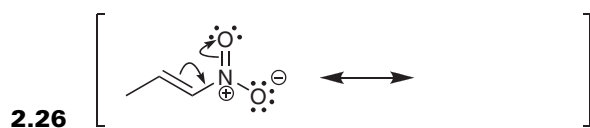
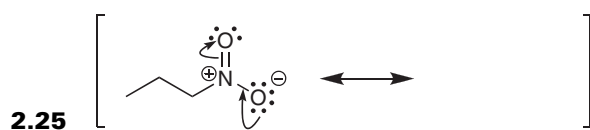
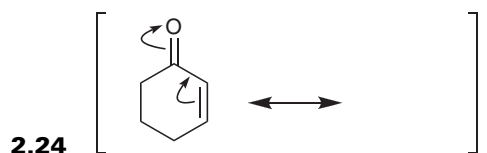
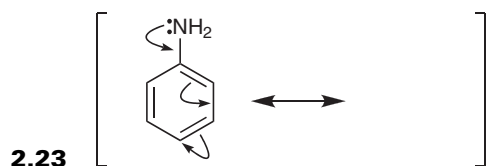
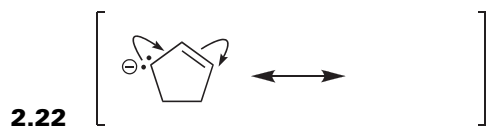
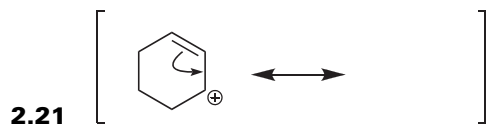
There is one subtle point that must be mentioned. We said that you do not need to draw lone pairs—you only need to draw formal charges. There will be times when you will see arrows being pushed on structures that do not have the lone pairs drawn. When this happens, you might see an arrow coming from a negative charge:



The drawing on the right is more accurate and complete, but the drawing on the left is often used by organic chemists. So, if you are reviewing your lecture notes and you find that your instructor drew the tail of a curved arrow on a negative charge, just don't forget that the electrons are really coming from a lone pair (as seen in the drawing on the right).

One way to double check your drawing when you are done is to count the total charge on the resonance structure that you draw. This total charge should be the same as the structure you started with. So if the first structure has a negative charge, then the resonance structure you draw should also have a negative charge. If it doesn't, then you know you did something wrong (this is known as *conservation of charge*). You cannot change the total charge when drawing resonance structures.

**PROBLEMS** For each of the structures below, draw the resonance structure that you get when you push the arrows shown. Be sure to include formal charges. (*Hint:* In some cases the lone pairs are drawn and in other cases they are not drawn. Be sure to take them into account even if they are not drawn—you need to train yourself to see lone pairs when they are not drawn.)



## 2.6 DRAWING RESONANCE STRUCTURES—STEP BY STEP

Now we have all the tools we need. We know why we need resonance structures and what they represent. We know what curved arrows represent. We know how to recognize bad arrows that violate the two commandments. We know how to draw arrows that get you from one structure to another, and we know how to draw formal charges. We are now ready to begin using curved arrows to draw resonance structures.

First we need to locate the part of the molecule where resonance is an issue. Remember that we can push electrons only from lone pairs or bonds. We don't need to worry about all bonds, because we can't push an arrow from a single bond (that would violate the first commandment). So we only care about double or triple bonds. Double and triple bonds are called *pi bonds*. So we need to look for lone pairs and pi bonds.

Once we have located the regions where resonance is an issue, now we need to ask if there is any way to push the electrons without violating the two commandments. Let's be methodical, and break this up into three questions:

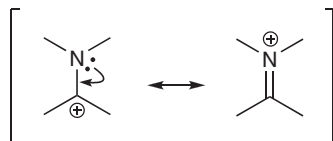
1. Can we convert any *lone pairs into pi bonds* without violating the two commandments?
2. Can we convert any *pi bonds into lone pairs* without violating the two commandments?
3. Can we convert any *pi bonds into pi bonds* without violating the two commandments?

We do not need to worry about the fourth possibility (converting a lone pair into a lone pair) because electrons cannot jump from one atom to another. Only the three possibilities above are acceptable.

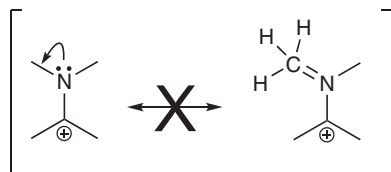
Let's go through these three steps, one at a time, starting with step 1, converting lone pairs into pi bonds. Consider the following example:



We ask if there are any lone pairs that we can move to form a pi bond. So we draw an arrow that brings the lone pair down to form a pi bond:



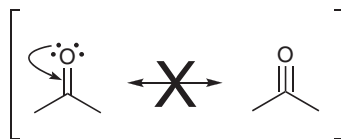
This does not violate either of the two commandments. We did not break any single bonds and we did not violate the octet rule. So this is a valid structure. Notice that we cannot move the lone pair in another direction, because then we would be violating the octet rule:



Let's try again with the following example:

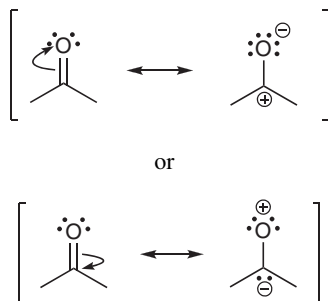


We ask if we can move one of the lone pairs down to form a pi bond, so we try to draw it:



This violates the octet rule—the carbon atom would end up with five bonds. So we cannot push the arrows that way. There is no way to turn a lone pair into a pi bond in this example.

Now let's move on to step 2, converting pi bonds into lone pairs. We try to move the double bond to form a lone pair and we see that we can move the bond in either direction:

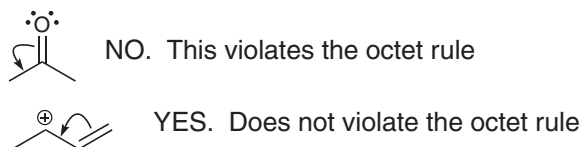


Neither of these structures violates the two commandments, so both structures above are valid resonance structures. (However, the bottom structure, although valid, is not a significant resonance structure. In the next section, we will see how to determine which resonance structures are significant and which are not.)

For step 3, converting pi bonds into pi bonds, let's consider the following examples:



If we try to push the pi bonds to form other pi bonds, we find



The arrow on the top structure violates the octet rule (giving carbon five bonds), and the arrow on the bottom structure does not violate the octet rule. The arrow on the bottom structure will therefore provide a valid resonance structure:



Now that we have learned all three steps, we need to consider that these steps can be combined. Sometimes we cannot do a step without violating the octet rule, but by doing two steps at the same time, we can avoid violating the octet rule. For example, if we try to turn a lone pair into a bond in the following structure, we see that this would violate the octet rule:



# INDEX

- A**  
Acetaldehyde, 91  
Acetic acid, 91  
Acetone, 176, 248  
Acetylene, 91, 257, 272, 273  
Acid-base reactions, 48–63  
  conjugate base in, 48  
  importance of, 48  
  induction in, 54–56  
  orbitals in, 56–57  
  predicting position of equilibrium in, 61–62  
  protons in, 48  
  relative importance of factors in, 57–60  
  resonance in, 51–54  
  showing mechanism of, 62–63  
Acid-catalyzed reactions, 224–226, 242  
Acid-catalyzed hydration, 224, 225, 261  
Acidity:  
  and conjugate base, 48  
  quantitative method of measuring, 61  
  relative, 276–279  
Acids, 48, 49  
Addition reactions, 204–247  
  of alcohols, 279–280  
  bond-line drawings for, 6  
  Br groups in, 212, 236–241  
  and cleavage of alkenes, 245–246  
  and elimination reactions, 232–235  
  hydrogen halides in, 215–223  
  OH groups in, 210–212, 231–245  
  regiochemistry of, 204–205  
  stereochemistry of, 206–212  
  summary of, 246–247  
  and synthesis techniques, 230–236  
  water in, 224–230  
Alcohols, 206, 274–298  
  elimination reactions with, 293–294  
  in E1 reactions, 190–191  
  into ether, 297–298  
  naming and designating, 274–275  
  preparation of, 279–290  
  reactions of, 290–296  
  relative acidity of, 276–279  
  solubility of, 275–276  
Aldehydes, 84, 263–264, 267, 268,  
  282–288, 290, 295, 296, 317, 321  
Alkanes, 235, 236, 258, 282, 300  
Alkenes:  
  acyclic, 208  
  cleavage of, 245–246  
  cyclic, 208  
  as nucleophile, 238  
  symmetrical, 204, 216  
Alkoxide ions, 195, 254, 297, 302, 307,  
  308  
Alkylation, of alkynes, 256–258  
Alkyl chloride, 265, 302, 303  
Alkyl groups, 84, 159, 170, 171, 186, 205,  
  221, 228, 263, 285, 300, 304  
Alkyl halides, 190, 191, 193  
Alkyl shift, 228  
Alkyl substituents, 83  
Alkyl tosylates, substitution reactions  
  with, 303–304  
Alkynes:  
  alkylation, 256–258  
  hydration, 261–264  
  keto-enol tautomerization, 264–269  
  ozonolysis, 269–270  
  preparation, 255–256  
  reduction, 258–260  
  structure and properties, 253–255  
Allylic carbocation, 159  
Allylic systems, 171  
Alpha ( $\alpha$ ) carbon, 274, 321  
-al suffix, 78  
Aluminum, 283, 284  
Amines, 78, 85, 277  
-amine suffix, 78  
-amino-, 84  
Ammonia, 70, 72, 165, 259  
*anti* addition, 174, 206–207, 210  
*anti* conformations, 99  
*anti*-Markovnikov addition:  
  *anti* addition vs., 206  
  definition of, 204, 205  
  of hydrogen chloride, 220–223  
  of water, 226–230  
Antiperiplanar positions, 188  
Aprotic solvents, 176–177  
ARIO of acid-base reactions, 60, 277, 278  
Arrow-pushing patterns:  
  carbocation rearrangement, 154  
  concerted process, 156  
  leaving group, loss of, 154  
  nucleophilic attack, 153  
  proton transfer, 153–155  
  rearrangement, 154  
  S<sub>N</sub>1 and S<sub>N</sub>2 processes, 156  
Arrows:  
  curved (*see* Curved arrows)  
  equilibrium, 225  
  fishhook, 221  
  straight, in resonance structures, 19  
Atomic orbitals, 20  
Atoms:  
  charge stability of, 48–51  
  electronegative, 38  
  geometry of (*see* Geometry)  
  hybridization state of, 68–70  
  periodic table and size of, 49  
  ranking, in configuration of chiral  
  center, 124–130  
Axial substituents, 103, 109–110
- B**  
Bad leaving groups, 174  
Base(s). *See also* Acid-base reactions  
  conjugate, 48, 50, 185, 277  
  for deprotonating alcohols, 297  
  in elimination reactions, 186–190  
  reagents as, 193–194

## I-2 INDEX

- Basicity, 193–194  
Bent geometry, 76  
Benzylic systems, 171  
Beta ( $\beta$ ) proton, 185, 187  
Bicyclic systems, 137  
Bimolecular elimination, 185. *See also* E2 reactions  
Bond(s), 280–281. *See also* Pi bond(s)  
  breaking single, 22, 62  
  and determining hybridization state, 68–70  
  formation of, 20, 21  
  geometry of, 71–73  
  homolytic breakage, 220  
  sharing electrons in, 8  
Bond-line drawings, 1–14  
  drawings, 4–8  
  finding undrawn lone pairs in, 11–14  
  identifying formal charges in, 8–11  
  mistakes to avoid in, 6  
  reading, 1–4  
  showing reactions with, 4  
Borane, 227  
Boron, 227, 228, 283, 284  
Branched substituents, 71  
Bromide, 158, 166, 175, 178, 237, 238, 291  
Bromination, radical, 235–236  
Bromine, 212, 220, 236–241  
  *-bromo-*, 84  
Bromonium ion, 237–238, 240  
1-Butanol, 276  
2-Butanol, 321, 322  
Butyl groups, 84
- C**  
Carbocationic character, 238  
Carbocation rearrangements:  
  allylic carbocation, 159  
  energy diagram, 158–159  
  hyperconjugation, 159  
  methyl and hydride shift, 159–161  
  stability, 159  
  steps in, 158  
Carbocations, 179, 180  
  in addition reactions, 215–217, 219–220  
  in E1 reactions, 190  
  in S<sub>N</sub>1 reactions, 169, 171  
Carbon atom(s)  
  alpha ( $\alpha$ ) carbon, 274  
  in bond-line drawings, 1–2  
  charge stability of, 49  
  with formal charge, 9, 10  
  hybridized orbitals of, 56–57, 68, 69  
  lone pairs in, 11  
  neutral, 3  
  orbitals of, 6, 10  
  resonance structures, 43  
  valence electrons of, 9  
Carbon dioxide, 270  
Carbon skeleton, 1, 4  
Carboxylic acids, 78, 82  
  acidity, 52  
  peroxy acid *vs.*, 241  
  synthesis of, 282, 295  
Catalysts:  
  acids as, 224–226, 242  
  for hydrogenation reactions, 213  
C–C bond-forming reactions, 288  
Center of inversion, 140  
Chair conformations, 95, 101–105, 108–116, 121, 136  
  comparing stability of, 114–116  
  drawing, 102–105  
  enantiomers of, 122  
  nomenclature for, 117  
  placing groups on, 105–108  
  and ring flipping, 108–114  
Charge(s):  
  in acid-base reactions, 48–51  
  in conjugate base, 48  
  conservation of, 27  
  delocalized, 51  
  formal (*see* Formal charges)  
  partial positive/negative, 54  
  and position of equilibrium, 61–62  
  and strength of nucleophile, 173  
Chiral centers, 90–91  
  definition of, 121  
  determining configuration of, 124–130  
  diastereomers, 138–139  
  enantiomers, 134–138  
  Fischer projections for depicting, 141–145  
  importance of, 121  
  locating, 121–123  
  *meso* compounds, 139–141  
  nomenclature for, 86, 89, 131–134  
  numbering groups in, 124–125, 131  
  and optical activity, 145–146  
  trick for determining configuration of, 129  
Chloride ion, 151, 154, 176, 216, 220  
  *-chloro-*, 89  
Chromic acid, 295  
*cis* configuration, 86–87, 89, 107, 117, 131–132, 162, 188, 192, 199  
Cleavage, of alkenes, 245–246  
Common names, 91–92, 300  
Concentration, 275  
Concerted process, 156, 244  
Configuration(s), 121–146  
  of chiral centers, 124–130  
  conformations *vs.*, 121  
  definition of, 121  
  of diastereomers, 138–139  
  of enantiomers, 134–138  
  Fischer projections, 141–145  
  inversion of, 169  
  of *meso* compounds, 139–141  
  nomenclature for, 131–134  
  and optical activity, 145–146  
  *R vs. S*, 121  
Conformations, 95–117  
  *anti*, 99  
  chair, 95, 101–105, 108–116, 121, 136  
  configurations *vs.*, 121  
  definition of, 95  
  eclipsed, 97, 99, 100  
  Newman projections, 95–98  
  staggered, 97, 99, 100  
Conjugate base, 48, 50, 185, 277  
Conjugated double bonds, 39  
Conservation of charge, 27  
Covalent bonds, 41, 237, 287  
Crown ethers, 301  
Curved arrows, 20–26  
  for acid-base reactions, 62  
  drawing, 21–24  
  head of, 20–24  
  multiple, 27  
  from a negative charge, 27  
  and octet rule, 22–23  
  tail of, 20, 23  
  two commandments for pushing, 21–24  
Cyclic alkenes, 208  
Cyclic ether, 301  
Cyclic polyether, 301

Cyclic systems, enantiomers of, 136  
 -*cyclo*-, 81  
 -*cyclohex*-, 81  
 Cyclohexane, 101, 109, 113, 114, 136,  
 140, 249  
 Cyclohexanol, 277  
 -*cyclopent*-, 81

**D**

Dashes:  
 for chiral centers, 122, 128  
 in Newman projections, 95–98, 105,  
 107  
 -*decyl*-, 83  
 Delocalized charges, 51  
 Deprotonation, 48  
 of alcohols, 297  
 of beta positions, 187  
 of carbocations, 224  
 of hydrogen peroxide, 228  
 with water, 239, 241–242  
 Deuterium, 214  
 -*di*-, 80, 84, 89  
 Dialkyl borane, 263  
 Diastereomers, 138–139  
 Diborane, 227  
 -*dien*-, 80  
 Diethyl ether, 92, 300, 301  
 Dimethoxyethane (DME), 176  
 Dimethyl ether, 92  
 Dimethylformamide (DMF), 176  
 Dimethyl sulfide (DMS), 245–246  
 Dimethylsulphoxide (DMSO),  
 176, 177  
 Dipole moments, 237  
 Disubstituted alkenes, 86, 186  
 -*diyn*-, 80  
 DME (dimethoxyethane), 176  
 DMF (dimethylformamide), 176  
 DMS (dimethyl sulfide), 245–246  
 DMSO (dimethylsulphoxide), 176, 177  
 DNA, 275  
 Double bonds, 33. *See also* Pi bond(s)  
 in bond-line drawings, 1, 5  
 and configurations of chiral center,  
 124–130  
 conjugated, 39  
 drawings, 1, 5  
 nomenclature for, 86

in numbering, 87–91  
 and parent chain, 80–82  
 and  $sp^2$  orbitals, 57, 70  
 and stereoisomerism, 85–87  
 in stereoisomers, 131  
*Z vs. E*, 132–133

**E**

Eclipsed conformations, 97, 99, 100  
*E* configuration, 132–133  
 Electron density, 19, 20, 55, 149, 150,  
 168, 173, 194, 227, 237,  
 280, 309  
 Electronegativity:  
 and partial charges, 54  
 in periodic table, 57  
 and pi bonds, 38  
 and resonance structures, 42  
 Electronics, 171  
 Electrons. *See also* Orbitals  
 bond as sharing of, 8  
 as clouds of electron density, 19  
 and curved arrows, 20–21  
 in lone pairs, 9, 21  
 valence, 8, 9  
 Electrophile (substrate)  
 in addition reactions, 237  
 carbon atom, 150  
 in elimination reactions, 185, 187–188,  
 192, 196  
 poor electron density, 150  
 in substitution reactions, 170–172  
 Elements, second-row, 6, 22–23. *See also*  
 Periodic table  
 Elimination reactions, 185–200. *See also*  
 E1 reactions; E2 reactions  
 and addition reactions, 232–234  
 of alcohols, 290–294  
 analyzing mechanisms of, 195–197  
 base in, 186–187, 230  
 bond-line drawings for, 7  
 electrophile (substrate) in, 185,  
 187–188, 192, 196  
 function of reagent in, 193–195  
 Hofmann product in, 187  
 leaving group in, 185  
 predicting products of, 197–200  
 regiochemistry of, 186–187, 192, 198  
 stereochemistry of, 187–190, 192, 198

substitution *vs.*, 185, 190, 193–200  
 Zaitsev product in, 186, 192

## Enantiomers:

from addition of Br groups, 237  
 of chair configurations, 136  
 definition of, 121–122  
 diastereomers *vs.*, 138–139  
 drawing, 134–138  
 E1 reactions, 190–192  
 of alcohols, 290  
 mechanism of, 190–192  
 regiochemistry of, 192  
 stereochemistry, 192  
 substitution reactions *vs.*, 195, 196, 198

## Epoxides, 241, 242

preparation, 305–307  
 ring-opening reactions, 307–313

Equatorial substituents, 104, 105,  
109–110, 114

## Equilibrium:

predicting position of, 61–62  
 reagents controlling, 225

## Equilibrium arrows, 225

## Esters, 287

## Ethanal, 91

## Ethanoic acid, 91

## Ethene, 91

## Ethers, 92, 297–298

preparation, 302–304  
 reactions, 304–305

-*ethyl*-, 83, 87, 89

## Ethylene, 91

## Ethyl groups, 83

## Ethyl methyl ether, 300

## Ethyne, 91

## E2 reactions, 185–190

of alcohols, 290  
 mechanism, 185  
 regiochemistry of, 186–187  
 stereochemistry of, 187–190  
 substitution reactions *vs.*, 193,  
 196, 198

**F**

## Fischer projections, 141–145

## Fishhook arrows, 221, 259

## Fluoride, 49, 301

## Fluorine, 49

-*fluoro*-, 84, 89

Formal charges:

- and electron density, 280
- and finding lone pairs, 11–14
- identifying, 8–11
- in resonance structures, 26–28

Formaldehyde, 91

Formic acid, 91

Functional groups, 77–79, 84, 87

- and parent chain, 78
- as substituents, 83–85
- syntheses without, 235–236

## G

Gauche interactions, 99

Geometry, 71–73

- of bonds, 69
- of hybridization states, 68–70
- importance of, 68
- and lone pairs, 73–74
- of orbitals, 68–70

Good leaving groups, 154, 174, 291

Grignard reactions, 286–289, 321, 322

## H

Halides, 175, 190, 191, 194, 215, 257, 291, 292

Halogens, 78, 84

Halohydrins, 239

HBr (hydrogen bromide), 220–223

*-heptyl-*, 83

*-hexyl-*, 83

Hofmann product, 186, 187, 232, 233, 235, 293, 295

Homolytic bond breakage, 220–221

Hybridization states, geometry of, 68–70

Hybridized orbitals, 56–57, 67–74

Hydration reactions:

- alkynes, 261–264
- Markovnikov addition, 224–230

Hydride ion, 152, 195, 297

Hydride shifts, 159, 219, 227

Hydroboration, 163, 228, 263

Hydroboration–oxidation, 229, 262–264, 266, 279, 300, 319

Hydrogenation reactions, 212–213, 224–230

Hydrogen atoms, 22, 23

- in addition of HBr, 221
- in bond-line drawings, 3, 4, 6, 7, 10, 11

Hydrogen bonding, 275–276

Hydrogen bromide (HBr), 220–223

Hydrogen halides, 215–216, 277

Hydrogen peroxide, 228

Hydrohalogenation, 224

Hydroperoxide anion, 228

Hydrophilic region, of alcohol, 275

Hydrophobic region, of  
alcohol, 275

Hydroxide ion, 307

- in addition reactions, 209–211, 228, 233, 241–245
- in elimination reactions, 193, 195
- in substitution reactions, 173, 174

*-hydroxy-*, 84

Hydroxylation, 243–245

Hyperconjugation, 159

## I

Induction, 54–56, 309

Intermediates

- ionic vs. radical, 221, 222
- in  $S_N1$  reaction, 169

Inversion, centers of, 140

Inversion of configuration, 162

Iodide, 174, 194

Iodine, 173

*-iodo-*, 84

Ionic bonds, 287

Ionic intermediates, 221, 222

Isopropyl groups, 83

IUPAC nomenclature, *see* Nomenclature

## K

*-keto-*, 84

Keto-enol tautomerization, of alkynes,  
264–269

Ketones, 78, 84, 282–284, 295, 307–308

Kinetics, 168

## L

Leaving groups (LG), 168–170

- in benzylic vs. allylic position, 171
- categories of, 174
- changing position of, 232–234
- in elimination reactions, 174–176
- as factor in substitution reactions,  
174–176
- hydroxide as, 233

Le Chatelier's principle, 225

Lewis structures, 42

LG, *see* Leaving groups (LG)

$LiAlH_4$  (lithium aluminum hydride),  
294–295, 309

Lindlar's catalyst, 258, 260

Linear structure, 71

Lithium aluminum hydride ( $LiAlH_4$ ),  
294–295, 309

Lone pair(s), 11–14

- in carbon atoms, 11
- and determining hybridization state,  
73–74
- electrons in, 9, 20, 21
- and formal charges, 9–14
- and geometry of orbitals, 69–70
- next to  $C^+$  (in resonance structures),  
35–37
- next to pi bonds (in resonance  
structures), 33–35
- in nitrogen atom, 11, 13–14
- in oxygen atom, 9, 11–12
- undrawn, 11–14

## M

Magnesium, in Grignard reagents, 286

Markovnikov addition

- definition of, 204, 205
- of hydrogen halides, 215–220
- of water, 224–226

Markovnikov, Vladimir, 217

MCPBA (*meta*-Chloroperoxybenzoic  
acid), 241, 306

Mechanisms, 149–164

- in acid-base reactions, 62–63
- anti* addition, 163
- arrow-pushing patterns
  - carbocation rearrangement, 154
  - concerted process, 156
  - leaving group, loss of, 154
  - nucleophilic attack, 153
  - proton transfer, 153–155
  - rearrangement, 154
  - $S_N1$  and  $S_N2$  processes, 156
- basicity vs. nucleophilicity, 151–153
- carbocation rearrangements
  - allylic carbocation, 159
  - energy diagram, 158–159
  - hyperconjugation, 159

methyl and hydride shift, 156–161  
 stability, 159  
 steps in, 158  
 double bond, 163  
 electrophiles  
   carbon atom, 150  
   poor electron density, 150  
 of elimination reactions, 185, 187–188,  
   192, 196  
 hydroboration, 163  
 nucleophiles  
   lone pair of electrons, 149  
   nitrogen atoms, 150  
   Pi bonds, 149, 150  
 stereochemical and regiochemical  
   outcome, 162  
 of substitution reactions, 176–177,  
   193–195  
*syn* addition, 163  
*trans* isomer, 162  
*meso* compounds, 139–141, 145,  
   212, 214  
 Mesylate group, 175  
*meta*-Chloroperoxybenzoic acid  
   (MCPBA), 241, 306  
 Metal catalysts, 213  
 Methanal, 91  
 Methanoic acid, 91  
*-methyl-*, 83  
 Methyl groups, 83  
 Methyl shifts, 159–161, 219  
 Miscibility, 279  
 Molozonide, 245  
 Monosubstituted alkenes, 186  
 Multistep syntheses, 288

## N

Naming, *see* Nomenclature  
 Negative charge(s):  
   partial, 54  
   and position of equilibrium, 61–62  
   stability of, in conjugate base, 48  
 Negative formal charge, 83–85  
 Neutral carbon atoms, 3  
 Newman projections, 83–101  
   drawing, 95–98  
   and E2 reactions, 189  
   ranking the stability of, 99–101  
   wedges and dashes in, 95–98, 105, 107

Nitrogen atom:  
   with formal charge, 13, 14  
   lone pairs in, 9, 11, 13–14  
   nucleophilicity and basicity of, 194  
   valence electrons of, 9  
 Nitro group, 36, 42  
 Nomenclature, 77–92  
   of alcohols, 274–275  
   for chiral center, 131–134  
   *cis* and *trans*, 131–132, 138  
   common names, 91–92  
   components of, 77  
   deriving structure from, 92  
   functional group, 78–79  
   and numbering, 87–91  
   parent chain, 80–82  
   stereoisomerism component of, 85–87  
   substituents, 83–85  
   unsaturation component of, 79–80  
 Nonpolar solvents, 176

## Nucleophiles:

alkenes as, 238  
 definition of, 168  
 lone pair of electrons, 149  
 nitrogen atoms, 150  
 Pi bonds, 149, 150  
 reagents as, 193–195  
 and solvent shell, 177–178  
 strength of, 173  
 in substitution reactions, 168–170,  
   172–173

Nucleophilic attack, 179–181, 215

Nucleophilicity, 284

  basicity *vs.* 151–153, 194

Numbering, in molecule names, 87–91

## O

*-oate* suffix, 78  
 Octet rule, 22–23, 29–32  
*-octyl-*, 83  
*-oic* acids, 78  
*-ol* suffix, 78, 79  
 One-step syntheses, 230–232  
*-one* suffix, 78  
 Orbitals:  
   in acid-base reactions, 56–57  
   of carbon atom, 6, 10  
   geometry of, 71–73  
   hybridized, 56–57, 68–70

  number of electrons in, 20  
   of second-row elements, 22  
 Osmium tetroxide, 244  
*-o* suffix, 84  
 Oxidation reactions:  
   alcohol, 282, 294–296  
   trialkylborane, 228  
 Oxidation state, 280–282  
 Oxidizing agents, 241, 282, 295–296  
 Oxygen atom:  
   basicity and nucleophilicity of,  
     151–153  
   charge stability for, 49  
   with formal charge, 12  
   lone pairs in, 9, 11–12  
   valence electrons of, 9  
 Ozone, 245–246  
 Ozonolysis:  
   alkynes, 269–270  
   oxidative cleavage, of alkene, 245–246

## P

Parent chain, 78, 80–82, 87–89, 92  
 PCC (pyridinium chlorochromate),  
   295–296  
*-penta-*, 80, 84  
*-pentachloro-*, 84  
*-pentyl-*, 83  
 Periodic table:  
   and atom size, 49  
   and basicity, 194  
   and electronegativity, 49, 50  
   and nucleophilicity, 194  
 Peroxide, 220, 221, 234–235  
 Peroxyacetic acid, 306  
 Peroxyacid, 241  
 Phenol, 277–278  
 Pi bond(s), 29–30  
   attack of p orbital by, 227  
   changing position of, 234–235  
   going around in a ring, 39–40  
   lone pair next to, 33–35  
   next to C<sup>+</sup>, 37–38  
   between two atoms, 38–39  
 p*K<sub>a</sub>*, 61, 277  
 Polarizability, 173, 194, 284  
 Polarized light, 145–146  
 Polar solvents, 176–177  
 p orbitals, 68, 69, 227, 228

- Positive charge(s), 9, 11, 21, 35, 37, 42, 224, 227, 238, 304, 309, 310  
 nitrogen, 13, 14  
 oxygen, 12, 158  
 partial, 54  
 in resonance structure, 27
- Positive formal charge, 10, 12, 14
- Preparation:  
 alkynes, 255–256  
 epoxides, 305–307  
 ethers, 302–304
- Preparation of alcohols, 279–290  
 Grignard reactions, 286–289  
 reduction reactions, 280–285  
 substitution and addition reactions, 279–280  
 summary of, 289–290
- Primary alcohols, 274, 282, 289, 291, 292, 295, 296
- Primary substrates, 169, 185
- Problems, creating your own, 323
- Products:  
 predicting, 197–200  
 of substitution *vs.* elimination reactions, 197–200
- propyl-*, 83
- Propyl groups, 83
- Protic solvents, 176, 177
- Protons:  
 in acid-base reactions, 48  
 beta ( $\beta$ ), 185, 187  
 and  $pK_a$ , 61
- Proton transfer, 153–155, 215–217, 221, 242, 259, 270
- Pyridinium chlorochromate (PCC), 295–296
- Q**
- Qualitative method, 61
- Quantitative method, 61
- R**
- Racemic mixtures, 122, 145, 162, 169, 179, 210, 217, 225, 306
- Radical bromination, 235–236
- Radical intermediates, 220, 221
- Rate of reaction, 168–169
- R* configuration, 77, 86, 89, 131, 146  
 determining configuration for, 145–146  
 Fischer projections of, 142–143  
 and multiple chiral centers, 143  
 nomenclature, 131  
 and optical activity, 145–146
- Reagents:  
 for *anti*-Markovnikov hydration, 227–229  
 for changing position of leaving group, 231  
 in control of equilibrium, 225  
 for Markovnikov hydration, 224  
 for ozonolysis, 245–246  
 in substitution *vs.* elimination reactions, 193–195  
 in synthesis problems, 316
- Reducing agents, 246, 283
- Reduction, 258–260, 283, 285
- Reduction reactions:  
 alcohol preparation, 280–285  
 alkynes, 258–264
- Regiochemistry:  
 of addition reactions, 204–205, 238–239  
 of elimination reactions, 186–187, 192, 198  
 of substitution reactions, 198
- Relative acidity, of alcohols, 276–279
- Resonance, 19–20, 278
- Resonance structure(s), 19–44  
 assessing relative significance of, 40–44  
 brackets in, 19  
 curved arrows in, 20–26  
 double-checking drawings of, 27  
 drawing, 29–40  
 drawing arrows in, 24–26  
 formal charges in, 26–28  
 lone pair next to  $C^+$  in, 35–37  
 lone pair next to pi bond in, 33–35  
 pi bond between two atoms (one atom electronegative), 38–39  
 pi bond next to  $C^+$  in, 37–38  
 pi bonds going around a ring in, 39–40  
 pi bonds in, 29–32  
 and reactions, 20
- recognizing patterns in, 33–40
- resonance as term, 20–21
- straight arrows in, 19
- two commandments for pushing arrows in, 22–24
- Retrosynthetic analysis, 297, 320–323
- Ring flipping, 108–114
- Ring-opening reactions, 307–312
- S**
- S* configuration, 77, 86, 89  
 determining configuration for, 145–146  
 Fischer projections of, 142–143  
 and multiple chiral centers, 143  
 nomenclature, 124  
 and optical activity, 145–146
- Secondary alcohols, 274, 282, 289, 291, 292, 294, 295
- Secondary carbocation, 291
- Secondary radicals, 221
- Secondary substrates, 196, 197, 291
- Second order reactions, 168
- Second-row elements, 6, 21–22
- Single bonds:  
 breaking, 22, 62  
 and  $sp^3$  orbitals, 57, 68, 69
- $S_N1$  substitution reactions:  
 of alcohols, 290  
 analyzing, 171  
 electrophile as factor in, 169, 172  
 elimination reactions *vs.*, 82, 195, 196  
 leaving group as factor in, 174  
 nucleophile as factor in, 172–173  
 solvent as factor in, 176, 177
- $S_N2$  substitution reactions, 168–170  
 of alcohols, 291, 292  
 alkoxide ions in, 267  
 analyzing, 177–178  
 electrophile as factor in, 169  
 elimination reactions *vs.*, 195, 196, 198  
 nucleophile as factor in, 7, 196  
 solvent as factor in, 176–178  
 Williamson ether synthesis, 303
- Sodium, 297
- Sodium amide, 254, 256–258, 273

- Sodium borohydride, 283–284  
 Sodium hydride, 284  
 Solubility, of alcohols, 275–276  
 Solvents, 176–177, 301  
 Solvent shell, 177  
*s* orbitals, 68, 69  
*sp* orbitals, 56, 57, 68, 69  
*sp*<sup>2</sup> orbitals, 56, 57, 68, 69  
*sp*<sup>3</sup> orbitals, 56–58, 68–72, 74  
 Staggered conformations, 99, 100  
 Stereochemistry:  
   of addition reactions, 206–212, 225, 239, 244  
   of elimination reactions, 187–190, 192, 198  
   of substitution reactions, 169, 198  
 Stereoisomerism, 77, 85–87, 89, 90, 131, 134  
 Stereoisomers, 121  
   naming double bonds in, 131–134  
   optical properties of, 145–146  
 Stereoselectivity, 188  
 Stereospecificity, 188  
 Steric hindrance, 171, 186–187, 197, 199, 233, 308  
 Steric interaction, 114  
 Sterics, 68, 170, 185, 192  
 Straight arrows, in resonance structures, 19  
 Strong bases, 152, 154, 174, 187, 191, 193, 195, 196, 233, 234, 255, 297, 309  
 Strong nucleophiles, 151, 152, 173, 177, 193, 195, 196, 256, 292, 297, 307–309  
 Substituents, 77–79, 83–85, 87–91  
   axial, 103, 109–111  
   branched, 83  
   equatorial, 104, 105, 109–111  
   numbering of, 87–91  
 Substitution reactions, 168–181  
   of alcohols, 279–280, 290–292  
   of alkyl tosylates, 303–304  
   alkoxide ions in, 297  
   analyzing mechanisms in, 177–178  
   bond-line drawings for, 7  
   electrophile in, 170–172  
   elimination *vs.*, 185, 190, 193–200  
   function of reagent in, 193–195  
   identifying mechanisms, 195–197  
   leaving group in, 168–169, 174–176  
   mechanism, 168–170  
   nucleophile in, 172–173  
   one-step synthesis with, 230–232  
   predicting products, 197–200  
   S<sub>N</sub>1 *vs.* S<sub>N</sub>2, 168–170  
   solvent in, 176–177  
   substitution product and formation, 178–181  
 Substrate, *see* Electrophile (substrate)  
 Sulfonate ions, 175  
 Sulfur, 173, 194–195  
 Sulfuric acid, 195  
 Symmetrical alkenes, 204  
   *anti*-Markovnikov hydration reaction, 227  
   definition of, 204  
   hydrogenation reactions, 212–215  
   hydroxylation, 243–245  
 Symmetry, of *meso* compounds, 139–141  
*syn* addition, 163  
   *anti*-Markovnikov hydration reaction, 227  
   definition of, 206  
   hydrogenation reactions, 212–215  
 Synthesis(-es), 316–323  
   and addition reactions, 230–236  
   carbon skeleton, changes in, 317–320  
   for changing position of leaving group, 232–234  
   for changing position of pi bond, 234–235  
   creating synthesis problems, 323  
   functional group interconversion, 316, 318–320  
   multistep, 288  
   one-step, 230–232  
   and retrosynthetic analysis, 320–323  
   Williamson ether, 297  
   without functional groups, 235–236  
 Systematic names, 300
- ## T
- Tail (curved arrows), 20, 23–25  
 Tautomerization, 261–263  
 Tautomers, 261  
 Terminal alkynes, alkylation of, 255–258  
 -*tert*-, 84  
*tert*-Butoxide, 195  
*tert*-Butyl group, 84, 114, 115  
 Tertiary alcohols, 274, 289–293  
 Tertiary alkyl halides, 193, 290, 297, 304  
 Tertiary carbocations, 159, 161, 166, 190, 217, 219–221, 291  
 Tertiary radicals, 221  
 Tertiary substrates, 170, 177, 185, 195, 196, 292, 310  
 -*tetra*-, 80, 84  
 Tetrahedral structure, 71, 72  
 Tetrahydrofuran (THF), 227, 301  
 Tetrasubstituted alkenes, 186  
 THF (tetrahydrofuran), 227, 301  
 Thionyl chloride, 292  
 Tosylates, 175, 233, 234, 292–293  
*trans* configuration, 86–87, 89, 107, 117, 142, 160, 164  
 -*tri*-, 80, 84  
 Trialkylborane, 228  
 -*trien*-, 80  
 Triflate group, 175  
 Trigonal planar structure, 71, 87, 169, 171, 206, 239–240, 310  
 Trigonal pyramidal structure, 72, 74  
 Triple bonds, 70  
   in bond-line drawings, 1, 2  
   nomenclature for, 79–80  
   in numbering, 87–88  
   and parent chain, 80–82  
   and *sp* orbitals, 57, 68, 69  
 Trisubstituted alkenes, 186  
 -*triy*n-, 80

- U**  
Unimolecular elimination, 190  
Unsaturation, 77, 79–80, 83, 85, 87, 89
- V**  
Valence electrons, 9  
Valence shell, 8, 10, 22, 68, 71  
Vinyllic positions, 205, 206  
VSEPR theory, 72, 74
- W**  
Water:  
  in addition reactions, 224–226,  
  238–239  
  deprotonation of carbocation with, 224,  
  226  
  in elimination reactions, 196  
  in epoxide ring opening, 241  
  geometry, 72  
  as nucleophile, 173  
Weak bases, 193  
Weak nucleophiles, 151, 152, 172, 173,  
  181, 193, 195, 310  
Wedges:  
  for chiral center, 134–135  
  in Newman projections, 95–98, 105,  
  107  
Williamson ether synthesis, 297,  
  302–303
- Y**  
-yn-, 79
- Z**  
Zaitsev product, 186–188, 192, 198, 199,  
  232, 235, 293, 294  
Zigzag format, 1, 2, 5, 6, 142  
Z configuration, 132–133, 138