DAVID KLEIN

ORGANIC Chemistry

AS A SECOND LANGUAGE

First Semester Topics

4E

WILEY

ORGANIC CHEMISTRY AS A SECOND LANGUAGE, 4e

ORGANIC CHEMISTRY AS A SECOND LANGUAGE, 4e

First Semester Topics

DAVID KLEIN
Johns Hopkins University

WILEY

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INTRODUCTION

IS ORGANIC CHEMISTRY REALLY ALL ABOUT MEMORIZATION?

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

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 base 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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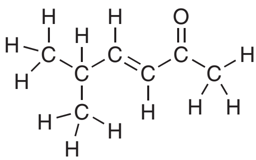
CHAPTER 1

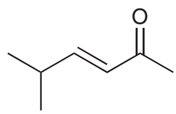
BOND-LINE DRAWINGS

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:



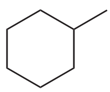
$(CH_3)_2CHCH{=}CHCOCH_3$



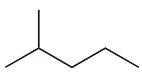
Without a doubt, the last structure (bond-line drawing) is the quickest to draw, the quickest to read, and the best way to communicate. Open to any page in the second half of your textbook and you will find that every page is plastered with bond-line drawings. Most students will gain a familiarity with these drawings over time, not realizing how absolutely critical it is to be able to read these drawings fluently. This chapter will help you develop your skills in reading these drawings quickly and fluently.

1.1 HOW TO READ BOND-LINE DRAWINGS

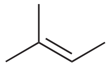
Bond-line drawings show the carbon skeleton (the connections of all the carbon atoms that build up the backbone, or skeleton, of the molecule) with any functional groups that are attached, such as –OH or –Br. Lines are drawn in a zigzag format, where each corner or endpoint represents a carbon atom.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

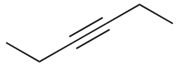


It is a common mistake to forget that the ends of lines represent carbon atoms as well. For example, the following molecule has six carbon atoms (make sure you can count them):

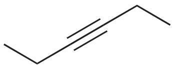


Double bonds are shown with two lines, and triple bonds are shown with three lines:

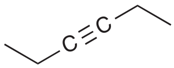




When drawing triple bonds, be sure to draw them in a straight line rather than zigzag, because triple bonds are linear (there will be more about this in the chapter on geometry). This can be quite confusing at first, because it can get hard to see just how many carbon atoms are in a triple bond, so let's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

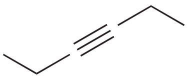


is the same as

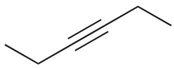


so this compound has 6 carbon atoms

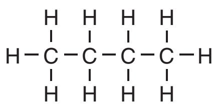
It is common to see a small gap on either side of a triple bond, like this:



is the same as

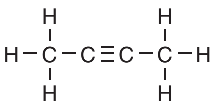


Both drawings above are commonly used, and you should train your eyes to see triple bonds either way. Don't let triple bonds confuse you. The two carbon atoms of the triple bond and the two carbons connected to them are drawn in a straight line. All other bonds are drawn as a zigzag:



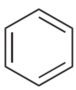
is drawn like this:

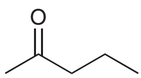
BUT



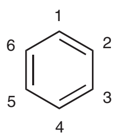
is drawn like this:

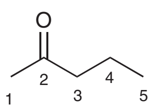
EXERCISE 1.1 Count the number of carbon atoms in each of the following drawings:



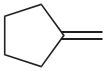


Answer The first compound has six carbon atoms, and the second compound has five carbon atoms:

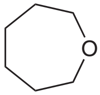




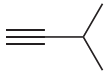
PROBLEMS Count the number of carbon atoms in each of the following drawings.



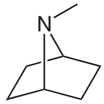
1.2 Answer: ______



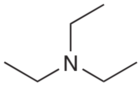
1.3 Answer: ______



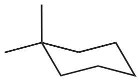
1.4 Answer: ______



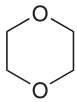
1.5 Answer: ______



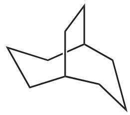
1.6 Answer: ______



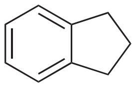
1.7 Answer: ______



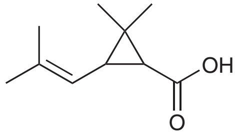
1.8 Answer: ______



1.9 Answer: ______

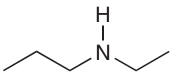


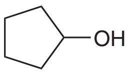
1.10 Answer: ______

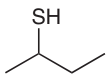


1.11 Answer: ______

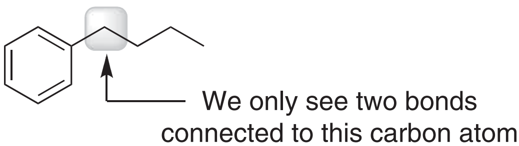
Now that we know how to count carbon atoms, we must learn how to count the hydrogen atoms in a bond-line drawing. Most hydrogen atoms are not shown, so bond-line drawings can be drawn very quickly. Hydrogen atoms connected to atoms other carbon (such as nitrogen or oxygen) must be drawn:







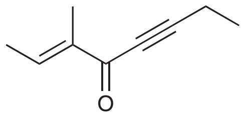
But hydrogen atoms connected to carbon are not drawn. Here is the rule for determining how many hydrogen atoms there are on each carbon atom: *uncharged carbon atoms have a total of four bonds*. In the following drawing, the highlighted carbon atom is showing only two bonds:



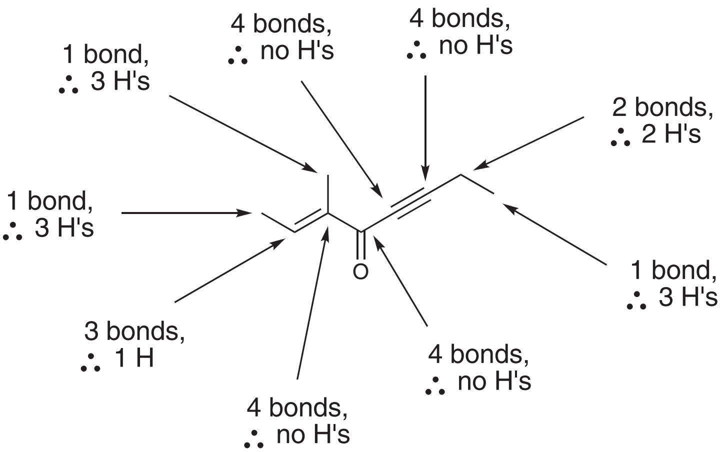
Therefore, it is assumed that there are two more bonds to hydrogen atoms (to give a total of four bonds). This is what allows us to avoid drawing the hydrogen atoms and to save so much time when drawing molecules. It is assumed that the average person knows how to count to four, and therefore is capable 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. The first problem has been solved for you (the numbers indicate how many hydrogen atoms are attached to each carbon).

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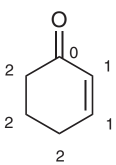

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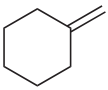

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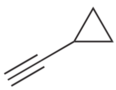

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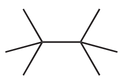

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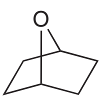

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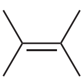

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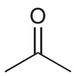


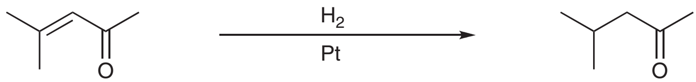
1.20


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:

$$(CH_3)_2C{=}CHCOCH_3 \xrightarrow[\text{Pt}]{H_2} (CH_3)_2CHCH_2COCH_3$$

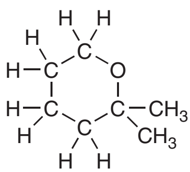
It is somewhat difficult to see what is happening in the reaction. You need to stare at it for a while to see the change that took place. However, when we redraw the reaction using bond-line drawings, the reaction becomes very easy to read immediately:



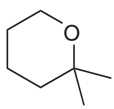
As soon as you see the reaction, you immediately know what is happening. In this reaction we are converting a double bond into a single bond by adding two hydrogen atoms across the double bond. Once you get comfortable reading these drawings, you will be better equipped to see the changes taking place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

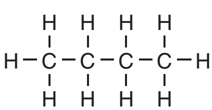


To draw this as a bond-line drawing, we focus on the carbon skeleton, making sure to draw any atoms other than C and H. All atoms other than carbon and hydrogen *must* be drawn. So the example above would look like this:

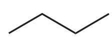


A few pointers may be helpful before you do some problems.

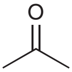
1. Don't forget that carbon atoms in a straight chain are drawn in a zigzag format:



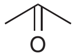
is drawn like this:



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

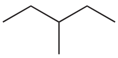


is much better than

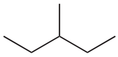


BAD

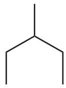
3. When drawing zigzags, it does not matter in which direction you start drawing:



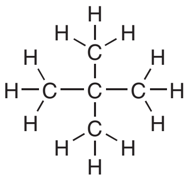
is the same as



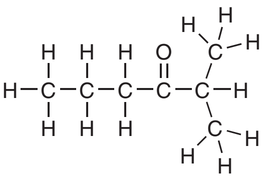
is the same as



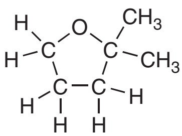
PROBLEMS For each structure below, draw a bond-line drawing in the box provided.



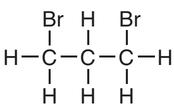
1.21



1.22



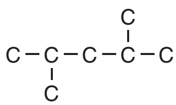
1.23



1.24

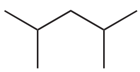
1.3 MISTAKES TO AVOID

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:

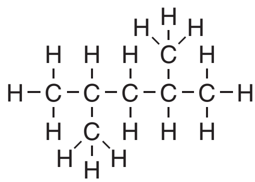


NEVER DO THIS

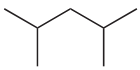
This drawing is no good. Either leave out the C's (which is preferable) or put in the H's:



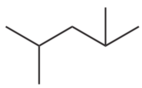
or



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



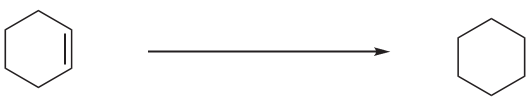
is better than



1.4 MORE EXERCISES

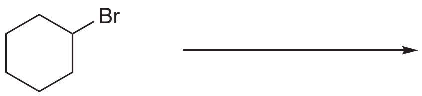
First, open your textbook and flip through the pages in the second half. Choose any bondline drawing and make sure that you can say with confidence how many carbon atoms you see and how many hydrogen atoms are attached to each of those carbon atoms.

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

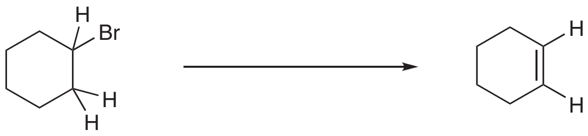


Don't worry about *how* these changes occur. That will be covered much later (in Chapter 11), when we explore this type of transformation in more detail. For now, just focus on describing the changes that you see. In this case, two hydrogen atoms have been installed, and a double bond has been converted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



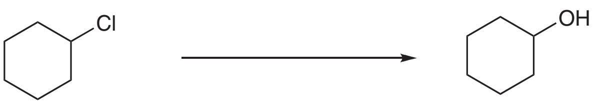
In this example, H and Br have been removed, and a single bond has been converted into a double bond (we will see in Chapter 10 that it is actually H^+ and Br^- that are removed). If you cannot see that an H was removed, then you will need to count the number of hydrogen atoms in the starting material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



1.25
Answer: ____

____

1.26
Answer: ____

____

1.27
Answer: ____

____

1.28
Answer:

1.29
Answer:

1.30
Answer:

1.31
Answer:

1.32
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 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 the atom *actually has* in the drawing. But how do we count this?