

STUDY GUIDE AND SOLUTIONS MANUAL
TO ACCOMPANY

Organic Chemistry

SECOND EDITION

G. Marc Loudon Joseph G. Stowell

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Purdue University



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How to Study Organic Chemistry

"You must be brilliant!" This is sometimes the response one gets on revealing to an acquaintance that one is studying chemistry and, specifically, organic chemistry. It may come as a surprise that many highly successful students of organic chemistry are not brilliant but of average intelligence. Why do they succeed? The answer is that they know how to organize, study, and learn organic chemistry efficiently, and they are interested enough in the subject to expend the effort required.

Our teaching experience has shown us that although many students want to learn organic chemistry, they do not know how to study the subject properly. Studying and learning a technical subject such as organic chemistry is very different from studying, say, world history. In this preface, we present some suggestions — some *detailed* suggestions — for developing productive study skills in organic chemistry. One benefit of learning and applying these skills is that they can be used, with slight modification, with virtually *any* technical subject. We believe that these skills should have lasting value for dealing with an increasingly technological world.

Here are the general guidelines for proper study; we'll discuss each one below:

1. Read and use the text *properly*.
2. Work problems.
3. Keep up with the assigned material.
4. Seek assistance when necessary.

Reading the Textbook It seems obvious that one should read the text for a course. We have found in our teaching, however, that many students do not know how to read and use a science textbook *properly*. Reading an organic chemistry text is very different from reading a novel or a history book. In reading a novel, one can frequently skim words and paragraphs and get a good sense of the whole. If one cannot define a word, further reading makes the meaning clear in context. In contrast, a science text must be read *in detail*. One term must be clearly understood

before the reader moves on to the next term. Another difference is that reading literature is in some respects a *passive* process. That is, the book speaks to the reader, who lies back and "listens;" the reader is entertained and enlightened. Reading a scientific or technical text, in contrast, must be an *active* process. One must interact with the text during the reading process in order to remain attentive and incorporate the material effectively into one's own knowledge base. Is a computer manual best read by taking it to bed and reading it like a novel? No. The best way is to turn on the computer and try each command as it is encountered. One doesn't go to page 2 until one masters page 1. Organic chemistry should be approached in the same way.

Let's go through one section of the text to illustrate the active-learning approach. Open your text to Section 5.1 on page 135. This section deals with a chemical reaction. Since *most* sections of the text deal with reactions, this section is fairly typical. It is not important that you understand the chemical terms at this point. Instead, focus on the study techniques. (We suggest that you re-read this discussion again when you get to Chapter 5.)

First, let's see how the section is organized. One or two examples (in this case, two examples) of the reaction to be studied are presented first (Eqs. 5.1 and 5.2). Then there are a few practical facts about the reaction in the first full paragraph on page 136, beginning "Bromine and chlorine. . ." There follows in Eqs. 5.3–5.6 a *mechanism* of the reaction — a stepwise description of how the reaction proceeds. Section 5.1B gives some further applications of the reaction that follow directly from the mechanism. Finally, there are some in-text problems on page 138. Let's summarize the organization:

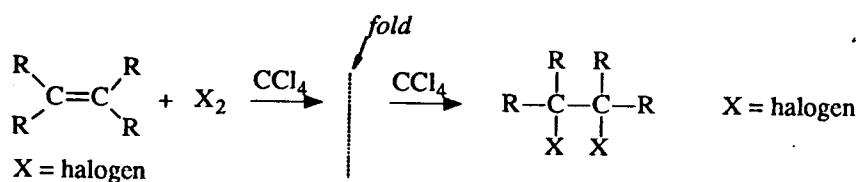
1. The reaction to be studied
2. Practical facts about the reaction
3. The mechanism of the reaction
4. Further applications
5. Problems

Now let's read the section. The first sentence contains no fewer than three chemical terms: *halogens*, *electrophilic addition*, and *alkenes*. You *must* understand these terms before reading on. We hope that the meaning of the word *halogens* is clear from your freshman chemistry course. If not, you must get a freshman chemistry text and review it. The term *electrophilic addition* is introduced in the previous chapter. When you read this section, you will probably remember seeing the term, but if not, you *must* go to the index, look it up, and review it. Finally, the term *alkenes* will probably present little difficulty, since you will find that this is the subject of the entire previous chapter. The point is that you *must understand each term before proceeding to the next*.

Notice the importance of continued review! Many students and professors alike suffer from their apparent adherence to a fallacious idea about learning, which one of our colleagues calls the "immunization theory of learning." Students would state the theory as follows: "If I've seen it once, I should never have to see it again...ever." Professors would modify the theory to read, "If I've taught it once, I should never have to teach it again, and students should remember everything I taught." This theory negates a fundamental caveat about learning: *Continued reinforcement is one of the best ways to learn.* When you learn, you should expect to forget something after the first exposure, and you should expect to have to re-learn it, probably more than once. Each relearning, however, takes less time and generally brings with it deeper understanding.

Whew! We've covered one sentence. Let's go on to the reaction. Look at the relationship of the reactants and products. From which parts of the reactants do the different atoms in the product originate? In this case the answer is fairly obvious from the simplicity of the reaction and the use of color in the text. In some cases the answer will be less obvious. In those cases you should *formulate a hypothesis* about the origin of the atoms in the product. (The *mechanism* will tell you whether your hypothesis is correct.) Developing your hypothesis forces you to *think* about the reaction.

Now take a sheet of paper and fold it lengthwise in half. Write this reaction on the paper with the reactants on the left and the products on the right. Write the reaction using the R-group notation in as general a form as possible. (You will learn about the R-group notation in Section 3.8 beginning on text page 81.) The reaction arrow should be duplicated on the left and right sides of the fold. Thus, your folded sheet should look as follows:



This sheet will become your *reaction review sheet*. After you have completed your first assignment you may have three or four such reactions on your sheet. Review them by folding the sheet over so that only the reactants are visible, and write the products. Then fold the sheet over so that only the products are visible and *write the reactants*. The ability to give the starting materials required to form a product will be particularly valuable when you learn about *organic synthesis* — how to prepare one organic compound from another. This is one aspect of learning reactions that some students either neglect or don't think about. Finally, write one or more examples of the reaction other than the ones shown in the text using particular R groups of your own choosing. Using these techniques, review the reactions from your first assignment during two subsequent

study sessions; notice the reinforcement involved in this review. Then drop them from your review. In other words, you will be constantly reviewing reactions from three consecutive assignments. Before a quiz or examination, go back and review all reactions to be covered. You'll be amazed that you'll remember most of them, and the ones you don't remember will come back very quickly!

Back to the text! In the first sentence on page 136 is a new term, *vicinal dihalides*, shown in boldface. Write this term on a sheet of paper, and opposite the term write the page number. For three consecutive periods, *write* on scratch paper the meaning of this as well as other terms you collect. (Writing the definition rather than speaking it forces you to use more precise language.) Write an example, if appropriate.

The practical facts about the reaction are next. These tell you, for example, what the CCl_4 is doing over the reaction arrow: It is an inert solvent.

Our next stop in the reading is the reaction mechanism embodied in Eqs. 5.3–5.6 and the accompanying discussion. You should follow each step in detail and try to relate each step of the mechanism to a simple reaction you have seen before. As you study the mechanism, write the mechanism of one of the example reactions in the text — for example, the reaction in Eq. 5.1. When you feel that you understand the mechanism, write the mechanism of the reaction in Eq. 5.2.

There are three purposes to studying mechanisms. First, mechanisms show why a reaction is reasonable by demonstrating that an overall reaction is a sequence of simple fundamental processes that are already familiar. Second, mechanisms show the relationship between reactions. By seeing the mechanistic similarities among seemingly different reactions, the reactions become easier to learn. Finally, mechanistic thinking allows one to *predict* the products of new reactions.

Mechanisms are not to be memorized! They are to be studied and *understood*.

The reading continues in a similar vein up to Problems 1 and 2 on text page 138. Work these problems when you come to them. (We'll have more to say about problem solving below.)

Notice how you are almost always writing something as you read. You are forcing yourself to *think* about the material. You are constantly turning back in the text to review material that you have seen before but have forgotten. Notice that we have *not* suggested highlighting the text or outlining the chapter. *These can easily become passive activities* because they don't force you to think about the material. Keep your learning *active*.

Once you finish reading a chapter, you will find the Study Guide sections of this manual to be useful. Each of these sections contains a glossary of terms with appropriate text references. Since these lists are alphabetized, they allow you to look at the terms out of the order in which they occur in the text and thus test whether you really do understand what they mean. As with your own sheet of terms, *write* a definition of each term and an example, if appropriate. The Study Guide also contains a *conceptual* outline of each chapter and a *reaction* outline. These make useful "quick reviews" of the material that can be used instead of a detailed re-reading of the chapter. They will not, however, substitute for proper reading of the text. If something is unfamiliar in these outlines, go back to the text and re-read it.

You should also correlate your lecture notes with material in the text. What part of the reading has the professor emphasized? Has the professor presented the material in a different manner from the text? Are there any inconsistencies? If so, do not hesitate to ask the professor or an assistant to help you resolve them.

Working Problems What is it that you are asked to do on an examination? Work problems! Thus, it stands to reason that working problems is one of the best ways to prepare for an examination. It is also one of the best ways to learn organic chemistry. You should work as many problems as you can. However, *how* you work them is much more important than *how many* you work.

Work the in-text problems as you come to them in your reading. Work though an entire set, if possible, without looking at the answer book. Then open this Solutions Guide and check your answers. There are three reasons why your answer might differ from that in the Solutions Guide. First, your answer may be wrong. Be sure you understand why your answer is wrong by reading the solution carefully. The second reason that your answer may differ from the one in the Solutions Guide is that there are more than one correct answer. Many problems, particularly problems in organic synthesis, have more than one acceptable answer. A third and less likely reason that your answer may differ is that there is an error in the Solutions Guide. Although we have endeavored to produce an accurate Solutions Guide, it is possible that it contains an occasional error. If you feel that you understand a problem, do not hesitate to ask for assistance if you feel your answer is correct.

Many students leave the Solutions Guide open in front of them when they "work" problems. If the answer does not come to them immediately, they read the Solutions Guide and say, "Oh, I knew that." This is not the proper approach to problem solving. Consult the Solutions Guide only after you have gone as far as you can with reasonable effort.

Many problems have several parts. Work one or two parts. If you have no difficulty, move on to the next problem.

After completing a chapter, work as many problems at the end of the chapter as possible. These problems are arranged in order of increasing sophistication. Many of these problems require material from earlier chapters. Do not hesitate to review this material when necessary. The continued reinforcement will pay handsome dividends. See how far into the assigned problem set you can work. Finally, do not be distressed if you do not have time to attempt every assigned problem. Decide how much time you can devote to problems, and (to quote a famous sports-caster) make that time Q.T. (*quality time*).

Old examinations make excellent sources of problems and also provide a sense of the style and level of difficulty that will be used by your professor in asking questions. Do not hesitate to use them if they are available. Work these examinations after you feel that you have done all you can to master the material. Let these be a final practice for the real thing — an intellectual "final scrimmage."

Keeping Up Organic chemistry is cumulative, like mathematics. Each concept and each reaction builds on the last. Individual assignments in organic chemistry are not generally difficult to cover, but it is very difficult to catch up once you are behind. Decide how much time you can afford to spend on organic chemistry and spend it *regularly and productively*. An analogy we like to use with our students is that studying organic chemistry is akin to playing a sport or practicing a musical instrument. Do you practice for the big game only once for fifteen hours? Or do you practice each day for a much shorter time? The mind reacts toward intellectual activity much like the body does toward physical activity. Many short, intense, productive sessions are preferable to one long, exhausting session (known in student parlance as a "cram").

Another useful technique that has an analogy in the worlds of sports and performance is to put the material away for a few days before an examination. Use your study time to keep up with new material. This technique serves two purposes: First, it keeps you from getting behind. But, even better, something mysterious happens when your mind is allowed to reflect unconsciously on the old material. When you return to this material for a final review, you will have a deeper understanding of it and a sense of perspective about it of which you were not previously aware!

Seeking Assistance Do not hesitate to seek assistance if you have continuing difficulty with some aspect of organic chemistry. Although many students feel intimidated by their professors, the fact is that most professors enjoy assisting students who have made a serious effort to master the material. Do not be afraid to seem ignorant in front of your professor. His or her job is to take you from ignorance to understanding.

Furthermore, good questions from confused students can help a professor become a better teacher!

Remember, you do not have to be brilliant to succeed in organic chemistry. You do have to be, or learn to be, disciplined, industrious, and organized. We hope you will use the text and this manual to best advantage, and that you find organic chemistry to be interesting and intellectually stimulating.

West Lafayette, Indiana
May 1988

G.M.L.
J.G.S.

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Chapter 1 / Introduction to Structure and Bonding

CHAPTER 1 TERMS

arrow formalism	1.3,1.5	halogen	1.2A
atomic number	1.2A	ion	1.2A
bond angle	1.6B	ionic bond	1.2A
bond dipole	1.2C	ionic compound	1.2A
bond length	1.6B	isoelectronic	1.2A
Brønsted acid	1.4	Lewis acid	1.3
Brønsted base	1.4	Lewis base	1.3
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chemical bond	1.2	molecular model	1.6B
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conjugate acid	1.4	nonbonding electron pair	1.2B
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curved–arrow formalism	1.3,1.5	polar bond	1.2C
debye	1.2C	polar molecule	1.2C
dielectric constant	1.2A	polarized	1.2C
dihedral angle	1.6B	pyramidal geometry	1.6B
dipole	1.2C	regular tetrahedron	1.6B
dipole moment	1.2C	resonance hybrid	1.7
dissociate	1.2A	resonance structures	1.7
double bond	1.2B	serendipity	1.1B
electrolysis	1.2	single bond	1.2B
electron diffraction	1.6A	tetrahedron	1.6B
electron shell	1.2A	trigonal geometry	1.6B
electronegativity	1.2C	triple bond	1.2B
electrophile	1.3	unshared electron pair	1.2B
electrostatic law	1.2A	valence electron	1.2A
formal charge	1.2B	valence shell	1.2A

The glossary in this and subsequent chapters is a list of the key terms and concepts contained in the chapter. These terms and concepts will be used throughout the text. It probably will not help you to memorize the exact definition given in the text; rather, define each of these terms and concepts in your own words and give an example if appropriate.

CHAPTER 1 CONCEPTS

I. Chemical Bonds:

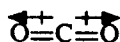
A. Ionic Bonds:

1. **Ionic bonds** are formed between ions of different charges.
2. They can be dissociated by solvent into free ions.

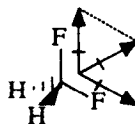


B. Covalent Bonds:

1. **Covalent bonds** are formed between atoms by sharing electrons.
2. All organic compounds contain covalent bonds.
3. Covalent bonds are **polarized** when the atoms have different electronegativities.
 - a) Electrons are attracted to the more **electronegative** atom.
 - b) The more electronegative atom has a partial negative charge.
 - c) The less electronegative (more electropositive) atom has a partial positive charge.
4. Polarized bonds have **dipole moments** called **bond dipoles**.
5. Bond dipoles add vectorially to give the permanent dipole moment.



$$\mu = 0 \text{ D}$$



$$\mu = 1.97 \text{ D}$$

C. Octet Rule:

1. Atoms gain or lose valence electrons to form ions that are **isoelectronic** with the noble gases (Group VIIIA elements).
2. If we count all bonding electrons and all **unshared electron pairs**, the **octet rule** is usually obeyed by atoms involved in covalent bonding.

D. Lewis Structures:

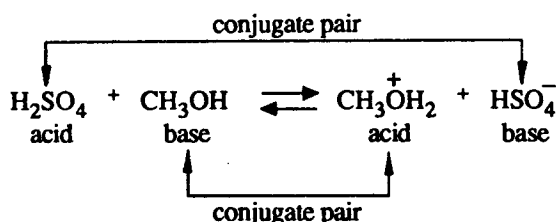
1. In **Lewis Structures**:
 - a) A single bond is represented by a pair of dots (:) or a single line (—).
 - b) A double bond is represented by two pairs of dots (::) or a double line (=).
 - c) A triple bond is represented by three pairs of dots (:::) or a triple line (≡).
 - d) A pair of unshared electrons is represented by two dots (:).
2. **Formal charges** can be assigned to individual atoms in a molecule or ion by:
 - a) Counting the number of unshared electrons on the atom of interest.
 - b) Adding half of the electrons shared by the atom.
 - c) Subtracting the result from the group number of the atom.



II. Acids and Bases:

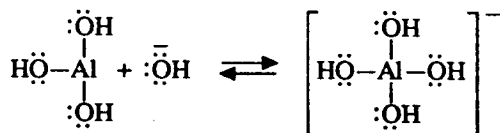
A. Brønsted-Lowry Acids and Bases:

1. A **Brønsted-Lowry acid** is a molecule or ion that can donate a proton (H^+).
2. A **Brønsted-Lowry base** is a molecule or ion that can accept a proton (H^+).
3. Members of a **conjugate acid-base pair** differ by only *one* proton (H^+).



B. Lewis Acids and Bases:

1. A **Lewis acid** is a molecule or ion that is at least two electrons short of a full octet.
2. Lewis acids are also called:
 - a) **Electrophiles.**
 - b) **Electron-deficient species.**
3. A **Lewis base** is a molecule or ion that has at least one pair of unshared electrons.
4. Lewis bases are also called:
 - a) **Nucleophiles.**
 - b) **Electron-rich species.**



III. Molecular Structure:

A. Bond Lengths:

1. **Bond lengths** between atoms of a given type *decrease* with the amount of multiple bonding.
2. Bond length *increases* with the size of the bonded atom.
3. Bond length between a given atom and atoms of a single row *decrease* with increasing electronegativity.

B. Bond Angles:

1. Groups bonded to a central atom are arranged so that they are as far apart as possible.
2. A central atom with four groups attached is tetrahedral, having angles of 109.5° .
3. A central atom with three groups attached is trigonal planar, having angles of 120° .
4. A central atom with two groups attached is linear, having angles of 180° .
5. A pair of unshared electrons is considered as a group.

C. Conformations:

1. **Conformations** of a molecule are obtained by rotation of a group about a bond.
2. Each unique conformation dictates a unique molecular geometry.

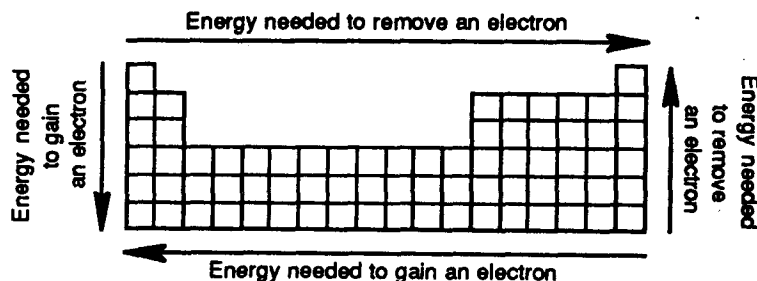
IV. The Periodic Table:

A. Rows:

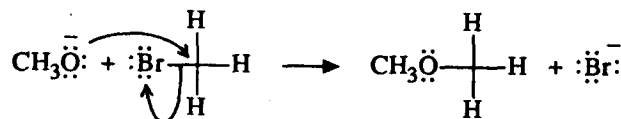
1. The number of electrons in the **valence shell** of a neutral Group A atom is equal to the group number.
2. Atoms gain or lose valence electrons to form stable ions that are isoelectronic with the noble gases (Group VIIIA elements).
3. The valence electrons in all atoms of a given row come from the same valence shell.
 - a) The energy required to remove an electron from a neutral atom *increases* to the right.
 - b) The energy required to gain an electron to a neutral atom *decreases* to the right.

B. Columns:

1. All atoms in a given column have the same number of valence electrons.
2. The distance between the nucleus and the valence electrons *increases* down a column.
 - a) The energy required to remove an electron from a neutral atom *decreases* down a column.
 - b) The energy required to gain an electron to a neutral atom *increases* up a column.

**V. Representations:****A. Curved-arrow Formalism:**

1. The movement of electrons is portrayed using curved arrows is called **curved-arrow formalism**.
 - a) The arrow always originates from the source of electrons.
 - b) The arrow always points to the electron destination.
2. The products are drawn by breaking and forming appropriate bonds.
3. Charges are assigned when necessary.

**B. Resonance Structures:**

1. **Resonance structures** are used to represent molecules and ions when a single Lewis structure is inadequate.
2. Resonance structures represent the movement of electrons *only*!
3. The conversion from one structure to another is represented by a single double-headed arrow.
4. A **resonance hybrid** is a weighted average of the different resonance structures.
5. Sometimes a resonance hybrid is depicted as a single structure in which:
 - a) The resonating bonds are depicted by dashed lines.
 - b) Partial charges are indicated by a lower-case Greek delta and the appropriate charge ($\delta+$ or $\delta-$)

