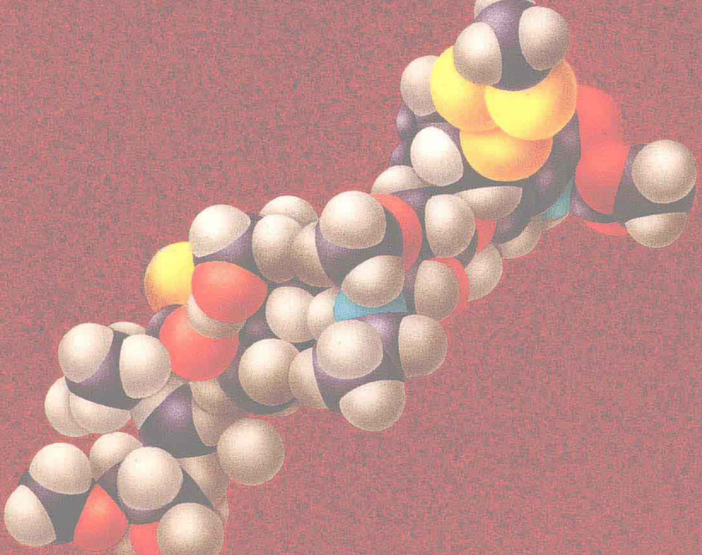
STUDY GUIDE AND
SOLUTIONS MANUAL FOR

ORGANIC CHEMISTRY

SECOND EDITION



NEIL E. SCHORE

Study Guide and Solutions Manual for Organic Chemistry

SECOND EDITION

Neil E. Schore
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Preface

From One Organic Chemistry Teacher to Another

"I study all the time, I understand what you're saying in the lecture, and I do all the problems. So how come I got a '12' on the exam?" Ouch! We've all heard this from our students, haven't we? (At least I *assume* I'm not the only one.) Why is it that perfectly reasonable students of perfectly reasonable intelligence sometimes wind up being hopelessly buried by this course? More to the point, what, if anything, can *we* do about it? Clearly, in a perfect world, where students have ample time to do everything they're supposed to do and know everything that they need to know from freshman chemistry, things would be better. Typically, however, that is not the case. Students are pressed to budget their time and divide it among their courses. Because they often can't spend sufficient time studying for each course during the term, they sometimes lag so far behind in their studying that, come exam time, they fall into the "Big Trap": they try to memorize everything. And then they get those "12"s and wonder what went wrong.

Well, we're the *teachers,* and we ought to know what's gone wrong and how to help the students do better. My experience has taught me that two critical factors almost always contribute to these predicaments: flawed understanding of basic concepts and lack of ability to apply the concepts to new, unfamiliar situations. The first involves an unsure grasp of mostly descriptive, informational material. Students must learn this fundamental material as surely as they learn the grammar and vocabulary of a foreign language. The basics can usually be mastered by serious study. Continuing emphasis on concepts and mechanisms, including the self-consistent, functional use of color in the textbook, and reemphasis in terms of relationships among topics in the "Introduction" and "Keys" sections of each chapter of this study guide are intended to make this process as manageable as possible for students.

The second factor is the killer for teachers: how to teach struggling students to (1) sort out the concepts and patterns relevant to a given problem and then (2) apply them in a logical way to the development of an answer. We all recognize that what we are trying to teach is not simply a piece of information, but a thought *process*. How does one go about teaching a thought process? The most successful way for me has been to lead students through a problem step-by-step, so they can experience the process, even if initially only from the outside looking in. They must be shown the choices that need to be made, why some are wrong and can be dismissed immediately, and how to evaluate the others. My goal in the preparation of the solutions to the end-of-chapter problems in the text was precisely this: to illustrate the thought process involved in getting from the problem to a reasonable answer. I've provided the greatest amount of detail in the earlier chapters, and I've *deliberately* omitted details in answers to some problems toward the end of the book. The learning process almost always requires *direct* experience on the students' part. It isn't enough for students to read an answer *even if it is fully understood!* Students must have opportunities to carry out the mental process for themselves. Therefore in many cases I've begun an answer with a hint, asking students to go back and attempt the problem again if they had difficulty the first time. Getting started is often the hard part, and this ploy at least gives serious students a second chance to make the connections required to proceed to a solution. It's a technique I use in helping students during office hours, and it seems to work.

I've also tried to be as rigorous and as complete as possible in the presentation of mechanisms, even to the extent of showing two-electron arrows in simple proton transfer processes. This might seem excessive to some, but remember, here we are dealing with students who may be in a position to derive clarifying insight from even the most insignificant of points. In the end, we must face the fact that our job is not really to "teach students organic chemistry." Our goal really has to be to teach students how to *learn* what organic chemistry is all about and how it *works*. Teaching students "how to learn" can be a difficult task. I hope the approach taken in this book is helpful in achieving that end.

Acknowledgments

The first edition of this study guide was prepared in camera-ready form by Ms. Marilee Urban, to whom I am eternally grateful. She deserved the bulk of the credit for getting it into print, even though "it" contained a good deal of confusion due in no small part to some of my hairbrained ideas regarding answering some of the questions. What did make sense in the first edition resulted from the diligent and time-consuming efforts of reviewers William Closson, Gene Hiegel, and Steven Zimmerman, and problem-solvers and solution-checkers Michael Gernon, Raji Iyer, Ramesh Krishnamurti, and Karl Seper. This second edition has in addition benefitted enormously from the advice and suggestions of many individuals at many stages. These include John Haber and Erica Seifert, as well as the reviewers of the Vollhardt/Schore textbook, many of whom had extremely valuable things to say about the end-of-chapter problems and my prior feeble attempts at presenting answers to them. To the extent that I **still** haven't gotten it right, I again take full responsibility: maybe the third time around will be the charm.

Without a doubt, the lion's share of credit for my getting anywhere in this project goes to my wife, Carrie, and kids Michael and Stefanie, for their patience and understanding. Hi, Mom and Dad!

Neil E. Schore
Davis, California

General Introduction *or* Whose "Brilliant" Idea Was It for Me to Take Organic Chemistry, Anyway?

Good question. What is the problem with organic chemistry that causes so many students to view the class with so much anxiety? I think there are at least two good reasons:

1. Very *bad* experiences in freshman chemistry. Even students *interested* in chemistry find significant stretches of ''Chem 1'' to be intolerably dull.
2. Comments from students who've just finished taking organic chemistry. For example: ''you have to memorize eight hundred million reactions, and then they don't even ask you the ones you've had in class on the tests.''

Let's take these one at a time. Freshman chemistry is a little like scrambled eggs with a lot of other ingredients mixed in: a little bit of theoretical chemistry (electronic structure, bonding), physical chemistry (gas laws, equilibria, kinetics), inorganic chemistry (periodic table, descriptive chemistry of the elements, coordination compounds), organic chemistry (hydrocarbons, other types of carbon compounds), and who knows what else. No wonder so many students finish the first year of chemistry without the slightest trace of an overview of what they've sat through, or the faintest hint of an idea of what's supposed to come next. The problem is that ''chemistry'' is a very big operation that covers a lot of territory. It starts with atoms, but can go in lots of directions, and each of these can get pretty complicated. For now, all you need to know is that only a portion of what you saw in freshman chemistry is necessary as background for organic chemistry. This will be the subject of the first chapter of your textbook.

As for the second reason people are afraid of organic chemistry, all that famous ''memorizing'' you have to do, like most stories heard over and over again, there is truth to it. You *will* have to memorize a lot of organic chemistry. However, you *won't* have to memorize eight hundred million reactions. If you try to do that, you will be lucky to pass the course *even if you succeed.* What you really have to memorize are some basic properties of atoms and molecules, a number of principles that describe why and how reactions take place, and a number of reaction *types* that later can be generalized to include the various reactions of organic compounds that you will see throughout the course. From this framework you will be shown how the various details of organic chemistry are derived from some basic principles or ''ground rules.'' You'll be expected to learn about, and *really understand* these ground rules, so that you can apply them in a logical way to completely new kinds of situations, and come up with sensible answers. It's a little like learning arithmetic. You all learned how to add when you were little. So if someone asked you to add $-1845\frac{2}{3}$ to $793\frac{1}{5}$, you would be able to figure out how to do it, even though it's pretty unlikely that you've added $-1845\frac{2}{3}$ to $793\frac{1}{5}$ ever before in your life. This is because you are familiar with some basic ground rules: what + and − signs mean, how to do fractions, the general methodology for adding (carrying numbers and all that). The difference is that you do arithmetic in elementary school and organic chemistry in college. The principles, the ground rules, and the methods of organic chemistry are going to go by quickly, and you're going to have to learn them well enough to make use of them . . . *quickly.*

That is where this study guide enters the picture. A textbook has *linear* makeup. It starts at the beginning with page 1, and goes on in a straight line until it gets to the end. Now that might be a decent way to present, say, history, where the book could follow a calendar of events as they occur over a period of time. However, it doesn't work quite as cleanly with chemistry, where the same basic principles operating in Chapter 2 are also cooking in Chapter 12 as well as Chapter 20. In a sense, organic chemistry is three-dimensional: there is a network of interrelationships between the various subtopics, *derived from these basic principles,* and hard to bring out clearly within the framework of a linear textbook. But it's a knowledge of these interrelationships that can make learning organic chemistry a much more reasonable job for a student to undertake. So, what you will find in each chapter of this study guide will be several features aimed at tying things together, so that you can see at every stage of the course the relationship between the new material, what has gone before, and what will be coming up. Each chapter in this guide will have at least the following four components:

1. A general introduction to the textbook chapter as a whole in the context of previously covered material.

2. An outline of the chapter, with brief comments on the nature and significance of each chapter section.
3. More detailed comments about those features of the chapters that are of greater significance in terms of the course as a whole.
4. Solutions to problems at the end of the chapter, with explanations.

As this book is a solutions manual, a comment on that aspect of it is also appropriate. The problems in the textbook range from ''drill'' problems, which require you to apply only a single new idea in a repetitive way to several simple cases, to ''think'' problems, where several ideas, new and old, have to be applied, often to cases which at first glance may look very different from the examples presented in the textbook chapter. This cross-section of problems is intended to illustrate the thought processes involved in analyzing this kind of subject matter, and to resemble the kinds of problems you might encounter in exams.

Try to do the problems!!! If you can't see how to do a problem at first glance, try to analyze its features: what is involved conceptually and what is its context, *before* looking here for the answer. Then, if you're still stuck, note that in some cases you will often find a short introductory comment in this manual before the actual answer to the problem. This is intended to show you where the problem fits into the chapter material and, perhaps, give you enough of a hint so that you might be able to go back and work it yourself. Then the answer will follow, plus an explanation. If you get a problem wrong, try to do two things: (1) understand the *process* for arriving at the answer, as illustrated in this guide, well enough so that you could answer a similar problem yourself without help, and (2) understand *why* the problem was asked in the first place—what points does it illustrate and what kinds of analogies, interpolations, or extrapolations of the basic subject matter does it involve. This kind of exercise will put you in a much better position to face the kinds of problems you are likely to encounter in exam situations.

Good luck!

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1

Structure and Bonding in Organic Molecules

The first chapter of the text covers the basic features associated with the bonding together of atoms to make molecules. Much of the material (at least through Section 1-8) is really a review of topics with which you may have some familiarity from freshman chemistry. In other words, it describes just those topics from freshman chemistry that are the most important to know in order to get off to a good start in organic chemistry: bonds, Lewis structures, resonance, atomic and molecular orbitals, and hybrid orbitals. Read the chapter, try the problems, read the comments below, and, if necessary, look to other supplementary sources for additional problems and examples. For instance, *Electron Movement: A Guide for Students of Organic Chemistry* by D. Weeks (Saunders, 1976) contains extensive coverage of Lewis structures and resonance.

Outline of the Chapter

1-1 Overview

1-2 Coulomb Forces

The simple *physical* basis of bonding between atoms. **Conceptually** important.

1-3 Ionic and Covalent Bonds

Review of principles involved.

1-4 Lewis Structures

Operationally, perhaps the most important section of the chapter. You **must** learn how to draw correct Lewis structures of molecules.

1-5 Resonance Structures
Applies to species for which no single Lewis picture adequately describes the true structure.

1-6 Atomic Orbitals
Review material.

1-7 Molecular Orbitals
Review material.

1-8 Hybrid Orbitals
Simplest way to understand the geometry of molecules in the context of the orbitals involved in bonding.

1-9 Structures and Formulas of Organic Molecules
General information section. Conventions for drawing formulas.

Keys to the Chapter

1-2 and 1-3. Coulomb Forces; Bonds

"Unlike charges attract" and "like charges repel." These consequences of elementary physics dealing with *electrostatics* and *Coulomb's law* are central to a basic understanding of chemistry. Not only do they determine whether, and how strongly, atoms will bond to each other (as described in this chapter), but they also influence an even more complicated process: whether two molecules are likely to react with each other. Time and time again we will return to simple electrostatics, in the context of the properties of the individual elements, to explain the reactions of organic chemistry. Most organic molecules contain *polarized covalent bonds.* In bonds of this type, one or more pairs of electrons are shared between two atoms, but because of an *electronegativity difference* between the atoms, the bonding electrons tend to be closer to the more electronegative atom, thereby creating a partial charge separation. In general, for A less electronegative than B, we have $A^{\delta+}{:}\,B^{\delta-}$. See the specific examples in Section 1-3. As you will see later on, most of the reactions in organic chemistry follow a general pattern. First, two nonbonded atoms with opposite charges or polarities are attracted to each other. Then, electrons move from the "electron-rich" to the "electron-poor" atom to form a new covalent bond between them. Because bonds are made up of electrons, it's very important to keep track of how many electrons are involved, and where they are located. *Lewis structures* are of **paramount** importance in this bookkeeping process.

1-4. Lewis Structures

Whether you've ever done Lewis structures before or not, follow the rules in Section 1-4 **very closely.** Become familiar with the number of electrons around common atoms and the common arrangements of these electrons in the bonds of molecules. This familiarity, brought about by doing **lots** of examples, is the best way to ensure that you will quickly and confidently be able to picture a Lewis structure for any of the types of species you will encounter later on. As you gain confidence through practice, you will be able to use shorthand notations, such as lines instead of dots for bonding electron pairs.

Organic chemistry involves reactions between organic compounds and other organic or inorganic species. These reactions can involve both bond-breaking and bond-forming processes, and the key to both is the *movement of electrons.* Lewis structures provide the bookkeeping system to help us keep track of electrons in reactions.

1-5. Resonance Structures

Two important conventions involving arrows are introduced in Section 1-5. The first is the use of *double headed arrows* between resonance structures. This is a special kind of notation because of the special role resonance forms play in organic chemistry. As shown in this section, many species have structures that cannot be represented by a single Lewis structure. They can only be described as intermediate in nature between two or more contributing forms, each of which **by itself** is an incomplete picture of the molecule's structure. We represent such a molecule by drawing the resonance structures separated by double headed arrows and enclosed in brackets. The true structure is called the *resonance hybrid.* The only difference between the resonance structures is a different location for the **electrons** from one to the next. The same geometrical arrangement of the atoms is maintained in all the resonance forms. Molecules that actually exist as resonance hybrids are often represented by only one Lewis structure. In cases like this you need to be aware of the fact that this is a shortcut used for convenience purposes only and that the real structure is still the resonance hybrid—the other resonance structures are implied even if they aren't written down.

The second convention in Section 1-5 is the use of *curved arrows* to show the movement of electron pairs. In this section the only application is in showing how the electron pairs shift in going from one Lewis structure of a resonance hybrid to another. Pictorial descriptions of electron movement using these arrows will be very useful tools to help you learn and understand organic chemistry.

1-6, 1-7, and 1-8. Orbitals

Atomic orbitals are a convenient way to represent the distribution of electrons in atoms. Note that the + and − signs associated with parts of these orbitals **do not** refer to electrical charges. They refer to mathematical signs of functions (*wave* functions) associated with the distribution of the electrons. Molecular orbitals are similar but are spread out over more than one atom. They provide an alternative to the Lewis electron-dot method for picturing bonds. The number of molecular orbitals involved in describing a bond is always exactly equal to the number of atomic orbitals contributed by the individual atoms. Overlap of atomic orbitals results in bonding, antibonding, and sometimes also nonbonding molecular orbitals. Bonding orbitals are always lower in energy (more stable) than the original constituent atomic levels, and antibonding orbitals are always higher in energy. Thus bonding electrons will be more stable than electrons in atomic orbitals and will give rise to strong bonds. Electrons in antibonding orbitals will reduce bonding.

Hybrid orbitals are derived by mixing atomic wave functions. They are used to explain the geometrical shapes of molecules. Hybridization provides several advantages for bonding. With the larger lobe of the hybrid orbital located in between the bonded atoms, more electron density is located where it can "do some good" by contributing to bonding. The participation of different numbers of *s* and *p* orbitals in the hybridization allows a wide range of bond angles, thereby permitting electron pairs to get as far away from each other as possible and minimizing unfavorable electrostatic repulsion.

Keep in mind some points on bookkeeping with hybridization. If an atom starts with one *s* orbital and three *p* orbitals, it will always end up with a total of four orbitals, no matter how they have hybridized for bonding purposes. Depending on the ratio of atomic orbitals used in the hybridization, we can describe the resulting hybrid orbitals as consisting of certain percentages of "*s* character" and "*p* character." For example, an *sp* orbital contains 50% *s* and 50% *p* character, whereas an sp^2 hybrid is $\frac{1}{3}$ *s* and $\frac{2}{3}$ *p* in nature. The total *s* and *p* character around an atom after hybridization always equals that which was present in the orbitals before hybridization:

1. *sp* hybridized atom: contains two *sp* orbitals (each one is $\frac{1}{2}$ *s* and $\frac{1}{2}$ *p* in character) and two ordinary *p* orbitals

$$2(\tfrac{1}{2}\,s + \tfrac{1}{2}\,p) + 2p = 1s + 3p$$

2. sp^2 hybridized atom: contains three sp^2 orbitals (each one is $\frac{1}{3}$ *s* and $\frac{2}{3}$ *p* in character) and one ordinary *p* orbital

$$3(\tfrac{1}{3}\,s + \tfrac{2}{3}\,p) + 1p = 1s + 3p$$

3. sp^3 hybridized atom: contains four sp^3 orbitals (each one is $\frac{1}{4}$ *s* and $\frac{3}{4}$ *p* in character)

$$4(\tfrac{1}{4}\,s + \tfrac{3}{4}\,p) = 1s + 3p$$

So in all cases exactly four orbitals are present and add up to the equivalent of one *s* and three *p*, even though each type of hybridization leads to a form of bonding and molecular shape very different from any of the others. As these examples show, the mathematical nature of hybridization is very flexible, to maximize favorable bonding attractions and minimize unfavorable electron–electron repulsions.

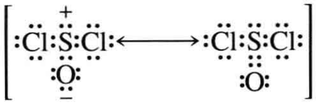
Prepare yourself to use the material in these sections: These are the basics, and everything else will build from them.

Solutions to Problems

1. (and 3—see below)

(a) $:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{F}}:$

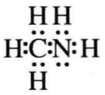
(b) $:\ddot{\underset{..}{Br}}:C:::N:$ Triple bond is needed to give octets for C and N atoms.

(c) 

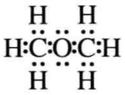
$\left[:\ddot{\underset{..}{Cl}}:\overset{+}{\ddot{S}}:\ddot{\underset{..}{Cl}}: \longleftrightarrow :\ddot{\underset{..}{Cl}}:\ddot{S}:\ddot{\underset{..}{Cl}}:\right]$

Major (octets)

Note that the availability of *d* orbitals allows S to be surrounded by a **fifth** electron pair.

(d) 

$H:\underset{H}{\overset{H}{C}}:\overset{H}{\underset{..}{N}}:H$

(e) 

$H:\underset{H}{\overset{H}{C}}:\ddot{\underset{..}{O}}:\underset{H}{\overset{H}{C}}:H$

(f) $H:\ddot{N}::\ddot{N}:H$ Double bond between nitrogens.

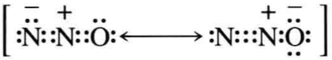
(g) 

$H:\overset{H}{C}::C::\ddot{O}:$

A molecule with two double bonds.

(h) 

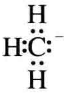
$\left[H:\ddot{N}::\overset{+}{N}::\overset{-}{\ddot{N}}: \longleftrightarrow H:\overset{-}{\ddot{\underset{..}{N}}}:\overset{+}{N}:::N:\right]$

(i) 

$\left[:\overset{-}{\ddot{N}}::\overset{+}{N}::\ddot{O}: \longleftrightarrow :N:::\overset{+}{N}:\overset{-}{\ddot{\underset{..}{O}}}:\right]$

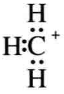
Major (O more
electronegative than N)

2. **(a)** $H:^-$ Hydride ion. Contrast H^+ (a proton) and H• (H atom).

(b) 

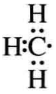
$H:\underset{H}{\overset{H}{C}}:^-$

A carb*anion.* C has an octet and a −1 charge.

(c) 

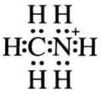
$H:\underset{H}{\overset{H}{C}}{}^+$

A carbo*cation.* C has only a sextet and a +1 charge.

(d) 

$H:\underset{H}{\overset{H}{C}}\cdot$

A carbon "radical." C is neutral, bonded to only three other atoms, and surrounded by 7 electrons.

(e) 

$H:\underset{H}{\overset{H}{C}}:\underset{H}{\overset{H}{N}}{}^+:H$

The methylammonium cation. The product of CH_3NH_2 + H^+. Compare NH_3 + H^+ → $NH_4{}^+$.