Experiments and Exercises in Organic Chemistry: A Challenge Oriented Approach

Preface

To the student:

Chemistry is the study of the composition, structure, properties and energetics of matter. Organic chemistry focuses on the study of compounds that contain carbon. The vast majority of compounds that have been characterized do contain carbon. Fredrich Wöhler deserves much of the credit for defining organic chemistry and developing the concept of isomers (see ***Experiment 4***). In 1835, Wöhler said:

> *Organic chemistry nowadays almost drives me mad. It gives me the impression of a primeval tropical forest, full of the most remarkable things, a monstrous and boundless thicket, a dreadful, endless jungle with no way of escape, into which one may well dread to enter for there seems no way out.*

During the last couple of centuries, great strides have been made towards unraveling the mysteries of organic chemistry. While still "full of the most remarkable things," organic chemistry has been developed into a comprehensible and fascinating science. Remember that 1835 was only 27 years after John Dalton revived and considerably expanded on Democritus' idea (ca 450 BC) that matter is made up of atoms. It was truly a remarkable achievement that with the limited concepts and techniques available, the early organic chemists were able to discover many reactions and determine the structure of many compounds. Our ability to study and probe atomic and molecular structures and chemical reactions has progressed rapidly due to the development of techniques, such as spectroscopy. Dalton and Wöhler would be truly amazed by the current state of organic chemistry. But don't be misled! Despite the fact that research in organic chemistry has enabled organic chemists to bring considerable order to the study of organic chemistry, the field is and always will be a fertile area for more research. Every discovery that is made enables the organic chemist to seek answers to even more intriguing questions.

Organic chemistry thrives on curiosity and is a great field for people who enjoy developing and using their creative abilities. As a result of conversations with other students, you are probably beginning this course with an attitude similar to that reflected by Wöhler's comment in 1835. Your first assignment then is to cast aside this attitude and replace it with a desire to explore the wondrous world of organic chemistry. To learn organic chemistry, you must be willing to put in considerable study time and have the desire to understand organic chemistry. Organic chemistry is not an easy subject but it is extremely important and potentially very rewarding. From the biochemical processes that enable you to read and interpret this print to the clothes you are wearing, the food you eat, the plastics in many items and the medicines given to improve health, we are enveloped in a world of organic chemistry.

To acquire the insight you will need in any field that uses organic chemistry, you will have to immerse yourself in the course and make yourself an active learner. Your instructor, classmates, organic chemistry textbook and laboratory book will help guide you through the course but you must assume the primary responsibility. You will learn by doing. Learning is strongly facilitated when you are able to relate a topic to a previous experience. The textbook problems **(do as many as you have time for and then do more)** and the laboratory help to provide experiences that facilitate learning.

The first and highest priority concern in the laboratory is safety. Some aspects of safety are discussed in a section that precedes the first experiment. Be sure you seriously read it and determine the reason for each statement. Most important, make sure you use **common sense and follow the instructions carefully. Do not deviate from the instructions without the instructor's permission.** Two of the primary safety concerns in a chemistry laboratory are the toxicity and flammability of organic chemicals . As stated earlier, you need to become an active learner in this course and this text will promote the appreciation of the importance of chemical toxicity by having you determine from Internet sites the relative toxicity of some of the chemicals you are using. In your previous chemistry courses, most of the experiments were conducted in aqueous solutions. Organic chemical reactions are commonly performed in flammable organic solvents. The best way to minimize fire danger is to totally avoid the use of flames in the organic chemistry lab. Unless the instructor gives you permission to use a Bunsen burner, always use an alternative heat source such as a heating mantle or a steam or oil bath. With safety considerations always in mind, remember that curiosity and creativity are great attributes. If you have an idea that you think might solve a problem or improve an experiment, discuss the idea with your instructor. It is possible that the instructor will encourage you to test your idea.

In order to help simplify the organic course material, your organic textbook will introduce generalizations or rules that will help you predict the structure of the products of some classes of organic reactions. The laboratory provides an ideal environment for learning and evaluating the "rules" of organic chemistry and for gaining experience with techniques for synthesizing, purifying and identifying organic chemicals. As a result of your studies in this course, you will be able to devise and carry out synthetic routes to desired products, classify reactions according to mechanism, use physical, chemical and spectroscopic properties to determine chemical structures and understand the role of organic chemistry. As you perform the experiments in the laboratory, this text will help you determine the applicability of each technique used and the relationship of the experiment to the classroom portion of the course. For example, each time a purification technique is used, you should ask several questions including:

What size sample is appropriate for this technique?
What phase must the sample be for this technique to be used?
What starting purity range should the sample be for this technique to be effective?
What kind of purity should be achievable with this technique?
What is a typical percent recovery using this technique?

It is extremely important that you ask these questions so that in new situations you will know which technique is the one most likely to achieve your goals.

Another method used in this book to encourage learning involves prelaboratory preparation. Each experiment will provide a list of activities that should be performed before you come to the laboratory. Proper preparation will significantly enhance learning and considerably shorten the time you need to finish the experiment. Your instructor might even require that you show him/her the completed prelaboratory preparation before you are allowed to begin the experiment.

There are many excellent organic laboratory texts available. This text has been in development during my 37 years of college teaching and 7 years since my retirement. Many qualities have been incorporated into the text that distinguish this text in some way from the many currently on the market. Almost all of the experiments contain some kind of challenge (such as determination of which of several possible products has been synthesized) that should help to make the experiments more fun and educational. Internet sites have been integrated into many of the experiments enabling a substantial decrease in the number of pages required and a corresponding minimization of price. References to the source of each experiment have been included whenever possible. Chemical costs and hazards have been minimized. Important links between lecture topics and lab experiences are provided along with an effort to encourage students to think about what they are doing. An exercise section has been included to fill in gaps where good experiments are not conveniently performed and to help students reinforce learning from the lecture part of the course. One of the special challenges is associated with my retirement. As a result, some of the experiments have not been tested by students in a classroom environment. A few have not been tested at all. At the end of the ***Table***

of Contents, there is a compilation of the development and testing status of each experiment. You should look at this as a special and positive situation. Because this book is a work in progress, updates will be made frequently. Each of you can contribute to this improvement process and attain a sense of ownership of the text. It is hoped that each of you will contribute suggestions that will lead to improved editions of the text.

You are about to begin a series of challenges that will help you learn organic chemistry. If you approach these challenges with a positive attitude, you will find that each time you synthesize, purify and/or identify a compound, you will feel a sense of accomplishment that will make your day. Most importantly, each time you use a procedure, ask yourself about the applicability of the procedure. There is a significant difference between people who have studied organic chemistry and people who have earned the title of organic chemist. This book will try to give you the insight or feel for the subject that bridges the gap from the apprentice to the master. And remember, the master realizes that the most important goal everyday is to continue to learn.

Do not be afraid of making mistakes. If you are not making mistakes, you are not doing anything. However, it is very important that you learn from your mistakes. Be sure to find out why you have missed problems. Chemistry keeps building and you don't want weaknesses in your foundation.

When a basketball player goes on a hot streak and seems to be able to hit every shot, broadcasters often say the player is "in the zone" or "feeling it". Achieving this kind of mood should be your goal in this course. When you are in the zone or feeling it, organic syntheses and structure determinations although still challenging, will be fun, satisfying and rewarding.

To the instructor:

About 40 years ago while teaching at SUNY@Stony Brook, I thought there was a need for an organic laboratory text based on an inquiry approach. A paper[1] about this time that the late Miles Pickering and I wrote entitled *The Odor of Optical Isomers* suggested that the experiment be presented to students with an inquiry approach. Miles later wrote two provocative articles[2] stating that organic lab books contained experiments that were essentially verification in nature and not the best approach for learning. Recently, several articles have again expressed similar concerns[3] although some still argue that recipes are educational as well.[4] While I did begin work on an organic lab book at Stony Brook, for several reasons, not the least of which was the publication of several good organic lab manuals, the project was indefinitely suspended. During that interim, I did author and/or co-author the *Handbook of Photochemistry*[5] and lab manuals for

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[1]Murov, S. L.; Pickering, M. *J. Chem. Educ.*, **1973**, *50*, 74.

[2]Pickering, M., *J. Chem. Educ.*, **1987**, *64*, 521-523, Pickering, M., *J. Chem. Educ.*, **1991**, *68*, 232- 2324.

[3]Mohrig, J. R., *J. Chem. Educ.*, **2004**, *81*, 1083-1086., Monteyne, K.; Cracolice, M. S.,. *Chem. Educ.*, **2004**, *81*, 1559, Horowitz, G., *J. Chem. Educ.*, **2007**, *84*, 346-353, Gaddis, B. A..; Schoffstall, A. M., *J. Chem. Educ.*, **2007**, *84*, 848-851, Mohrig, J. R.; Hammond, C. N.; Colby, D. A., *J. Chem. Educ.*, **2007**, *84*, 992-998, Domin, D. S., *J. Chem. Educ.*, **2009**, *86*, 274-277, Passarelli, M., *J. Chem. Educ.*, **2009**, *86*, 845., Chatterjee, S.; Williamson, V. M.; McCann, K.; Peck, M. L., *J. Chem. Educ.* **2009,** *86*, 1427, Bransford, J. D.; Brown, A. L.; Cocking, R. R., ed., http://www.nap.edu/openbook.php?record_id=6160

[4]Ault, A. *J. Chem. Educ.*, **2002**, *79*, 1177, Horowitz, G., *J. Chem. Educ.*, **2008**, *85*, 47.

[5]Murov, S. L.; Carmichael, I.; Hug, G., *Handbook of Photochemistry*, 2nd ed., Marcel Dekker, Inc., **1993**.

preparatory and general chemistry.[6] Now, several decades later, it seems once again to me that there is a need for an organic laboratory text **suited for today's students with significant differences from the lab texts now available.** To avoid the controversy concerning the meaning of "discovery" and/or "inquiry oriented," I have chosen to use the terminology, "challenge oriented." This should be especially appropriate because, as explained earlier, some of these experiments face the special challenge that testing will be performed by the users of this text.

Many of the best organic lab texts available are hard bound and almost as expensive as the huge organic textbooks commonly used for organic chemistry courses. If the students were to study a significant portion of the book, the cost would be well worth it but most students read only a small portion of the book during their two semester course. In addition, while a few of these books do include some experiments with a guided inquiry and/or problem solving approach, many still provide all the information on starting materials and products. The student is asked to carry out the procedure and verify that the instructions worked. Verification experiments do not provide students the kind of experience that is needed for real world learning. Additionally, although some books refer students to the Internet, this text integrates use of the Internet as a chemistry resource throughout enabling a considerable reduction in the number of pages. Today, most students have easier access to the Internet than books like the *Handbook of Chemistry and Physics.* This book takes advantage of this readily accessible resource.

Several goals have been established for the writing of this text.

1. Make the book efficient. An attempt has been made to include material that will be read and used. Experiments have been selected that work and have educational value. Material that is included in the organic chemistry textbook such as spectroscopic theory is not duplicated here. Tables of data on organic compounds that are used in the experiments are also not included as the Internet provides easy accessibility to the data. As students advance through the course using this book, they will gain valuable experience with the sources of useful information that are available online. More than enough experiments are included for a two semester course but instructors will probably use some handouts. For instructors who want more detailed discussions of techniques, technique only books are available.

2. To the extent possible while keeping safety concerns first, experiments have been selected and designed to provide a relevant, solvable challenge for the students. Most experiments require the students to solve some kind of problem or determine the identity of an unknown. Experiments that lead to aha moments or the identity of an unknown usually are more interesting than verification experiments to students and instructors. When possible, experiments that can be related to environmental or consumer issues have been included.

3. The cost and toxicity of chemicals has been seriously considered during the selection of the experiments. If your institution is anything like mine was, the chemical supply budget has not kept pace with inflation. Most experiments in this text use chemicals that have relatively low prices. Experiments that required high priced starting materials were excluded. In addition, every effort has been made to avoid experiments that require the use of highly toxic and/or very smelly chemicals. Students will be asked to look up the LD_{50} (oral rat) values of many of the key chemicals used and an exercise has been designed to give students a sense of the meaning of LD_{50} values.

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[6]Murov, S. L.; Stedjee, B., *Experiments and Exercises in Basic Chemistry,* 7th ed., Wiley, **2009**., Murov, S. L., *Experiments in General Chemistry,* 5th ed., Thomson, Brooks-Cole, **2007**.

4. In research articles, it is common practice to make every effort possible to include citations to all related and previously performed work. Articles in *The Journal of Chemical Education* also attempt to include pertinent citations. Unfortunately, this practice has not extended to laboratory texts. Most laboratory texts contain few or no references to research articles or previously published similar experiments. Because of this inadequacy, it is virtually impossible to give credit to the person(s) responsible for the original concepts and ideas that resulted in publication of an experiment. The original developer of an experiment deserves appropriate credit but unfortunately, for many experiments, this information is close to impossible to trace and for all practical purposes has been lost. In addition, instructors might want to check the original source of an experiment for accuracy and possible modifications or additions. An effort, albeit not complete, has been made in this book to site pertinent references especially those in *The Journal of Chemical Education*.

5. The integration of the Internet throughout the text accomplishes many goals. Since most students now have readily available access to the Internet, students are able to prepare for experiments in their residence and they gain valuable experience on one of the most important resources available today. As mentioned above, this also helps make the text shorter by not duplicating information available on the Internet in the text.

6. Questions are posed in each experiment to promote thinking by the student about the applicability of each method used and the relationship of the experiment to lecture topics. It is common for students to perform each experiment without trying to place the techniques and concepts into a grander scheme of things. For example, students when using a purification technique need to ask the kinds of questions presented earlier in the student portion of the ***Preface***.

What size sample is appropriate for this technique?
What phase must the sample be for this technique to be used?
What starting purity range should the sample be for this technique to be effective?
What kind of purity should be achievable with this technique?
What is a typical percent recovery using this technique?

It is very important for students to consider the lecture and laboratory portions of the course as an integrated entity. This text asks questions that hopefully will encourage students to think about the connections between experiments and lecture topics. Several experiments have been selected that investigate the "rules" of organic chemistry. Students often conclude that when a "rule" applies to a synthesis, only one product will form. The laboratory provides a real world experience with the rules. Students determine the ratio of possible products and the limitations of the rule. Laboratory experiments that evaluate the rules will give students a more realistic picture of the meaning of the rules.

7. An exercise section has been included after the experiments to fill in gaps in the students' organic chemistry experience. The first two exercises contains questions that review many of the essential concepts from general chemistry that students will need in organic chemistry. Other exercises use an inquiry approach to strengthen the student's insight into organic chemistry.

8. The issues of scale and green chemistry[7] are not simple. The use of microscale techniques affords many advantages. Costs of chemicals and disposal and risks are reduced. Many experiments can be completed in shorter amounts of time affording time to perform more experiments. On the other hand, students need to have sufficient material to perform identification procedures. Towards this end, the experiments in this book have been designed to use the smallest quantities possible that provide sufficient material for identification purposes. These amounts in today's semantics would probably be described as

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[7]Kirchhoff, M. M. *J. Chem. Educ.*, **2013**, *90*, 683-684.

small or mini-scale rather than microscale. The recent and justified goal of some educators of making laboratory experiments greener has certainly been noticed. Avoiding the use of chlorinated solvents is a goal worth pursuing. Towards this end, a challenge is issued to the users of this book to find greener methods of performing each experiment. Any useful ideas will be incorporated into future editions of these experiments. A few of the experiments included were designed to minimize environmental impact but considerably more work is needed in this area.

9. In general, the sequence of the experiments has been aligned with the sequence of the topics in most of the commonly used organic chemistry texts. However, the first ten experiments emphasize the basic techniques of organic chemistry. Some of these technique experiments involve reactions such as saponification or esterification that are not covered until the second semester of the course. The reactions involved in these experiments is secondary in importance to the technique that is being introduced. The fact that the students will not have a deep understanding of the reaction mechanism is not vital in these experiments. If desired, these experiments can be performed much later in the academic year. After ***Experiment 28***, the experiments appear in the approximate order that they were written rather than as a correlation with text concepts. Some can be performed early in the course (and used to replace others - as an example of reflux, ***32*** can be performed instead of ***5***) and others are best performed in the latter stages of the course.

10. A common feature to most of the goals discussed above is that this text makes an effort to provide students with more than information about organic chemistry. It tries to give the students a feel for organic chemistry. The English language really does not have an adequate word for this feel but perhaps **insight** comes the closest. It is the quality of insight that distinguishes the apprentice from the master. As presented earlier in the student directed portion of this ***Preface***, like basketball players, it is hoped that as a result of this course, the students will be "in the zone" or "feeling it". As teachers, we all need to do as much as we can to help students feel it. One important way of doing this is to make sure students recognize that their teachers continue to experience great joy from learning.

Acknowledgments

First and foremost, the students who tested these experiments at SUNY @ Stony Brook, Sangamon State Univ. (now the Univ. of Ill. at Springfield), Moorhead State Univ., Calif. State Univ. @ Bakersfield and Modesto Junior College deserve credit for working with often primitive versions of these experiments. Many of the students demonstrated special interest in improving experiments that still needed developmental work. My wife, Carolyn, and my children have always strongly supported my sometimes unusual excursions into science education. Finally, my grandchildren, Dylan Rosenow, Hope Solus, Carson Rosenow and Mylee Murov have provided the incentive I needed to finally produce a useable manuscript. Hopefully, use of this text will increase the percentage of students who have the vision necessary to successfully deal with the multitude of science related challenges currently confronting society.

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