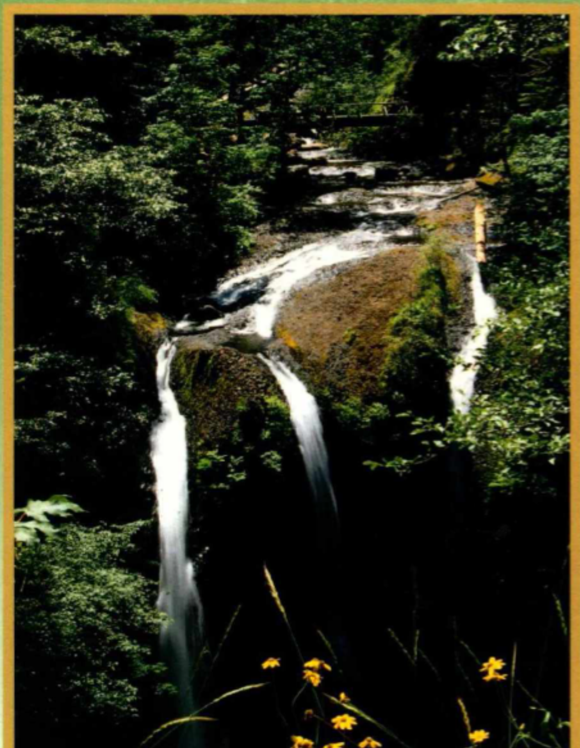
Green Organic Chemistry

Strategies, Tools, and Laboratory Experiments



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Preface to the First Edition

As we have developed the green organic chemistry program at the University of Oregon, it has become apparent to us that there is an urgent need and rapidly growing demand for green chemistry laboratory materials. As the field of green chemistry continues to undergo rapid growth and change, so too will this text. Future editions will incorporate new green chemical strategies and discussion materials, address new questions, and present new experiments designed to bring to life the evolving concepts and practice of modern organic chemistry.

The first section of this text is devoted to a description of green chemistry and the tools and strategies used in its implementation. This material is an essential complement to the experimental descriptions that follow. The experiments allow investigation of green organic chemical concepts in the laboratory setting. That said, the experiments are not essential to an analysis of the first, descriptive half of the text, and it is our hope that this text will prove useful to those interested in learning about the principles of green chemistry in general.

We have made the decision not to present the general "techniques" and "procedures" sections – melting point determination, recrystallization, spectroscopy, etc. – typically found in organic chemistry laboratory texts. We anticipate that this text will be used in conjunction with a text or manual containing descriptions of these procedures and techniques.[†] We have not written the experimental procedures with reference to any one particular such text, however, as we believe this will allow the greatest individual latitude in selection of a companion text suitable to your local setting. As we continue to work toward later editions, comments from you, the reader and user of this edition, about this decision will be valuable to us. Would you prefer this text to be a "stand-alone" text, or are you content to "package" it with a companion "techniques" text?

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† Examples of such texts include R. J. Fessenden, J. S. Fessenden, & P. Feist, *Organic Laboratory Techniques*, 3rd Ed.; Brooks/Cole: Pacific Grove, CA, 2001; J. R. Mohrig, C. N. Hammond, P. F. Schatz, & T. C. Morrill, *Techniques in Organic Chemistry*; W. H. Freeman & Co.: New York, 2003; J. W. Zubrick, *The Organic Chemistry Lab Survival Manual: A Student Guide to Techniques*, 5th Ed.; John Wiley & Sons: New York, 2000.

Nineteen experiments are included in this first edition. These experiments were designed to complement the content of the typical undergraduate organic chemistry sequence while illustrating the principles and strategies of green organic chemistry. We have presented the experiments in an order we have found useful, but they may be used in any desired sequence. Later editions of the text will include a wider range of experiments, including a number that are under active development. Given the nature of this first edition, here too is an opportunity for you to influence its further development. Please let us know of your personal experiences with the experiments, and feel free to suggest changes, as well as topics for experiments you would like to have available. In anticipation of one suggestion, we note here our intention to include in later editions microscale procedures in addition to the larger scale procedures reported in this edition.

KMD

JEH

February 11, 2003

Acknowledgments

The design and testing of the experiments presented in this text relied on the qualified and enthusiastic efforts of a group of talented co-workers to whom the authors are profoundly grateful: Dr. Scott Reed, Lauren Huffman, Marvin Warner, Dr. Robert Gilbertson, Gary Succaw, Lallie McKenzie, Kathryn Parent and Gerd Woehrle all made important contributions toward the experiments described in this text. We are deeply appreciative of the efforts of Dr. Leif Brown, who was the first to "run this experiment on a large scale," bringing this curriculum to our entire organic laboratory course and providing invaluable experimental troubleshooting in the process. We also thank Leif for many contributions to the experiment descriptions presented in this text. Dr. John Thompson at Lane Community College made a number of excellent suggestions for improving the labs as a result of his in-class testing of most of the experiments at LCC.

This project would not have been possible without the support of the chemistry department and the university administration. In particular, we thank Prof. David Tyler and Prof. David Johnson whose support in launching the program was invaluable. A number of our colleagues, including the many participants of our annual Green Chemistry in Education Workshops, have made important contributions. In particular, we thank Dr. Paul Anastas, Dr. Mary Kirchhoff, Dr. Julie Haack, Dr. Lauren Heine, Dr. Robert Hembre and Dr. Richard Wolf for their numerous contributions and enduring support of our efforts. We thank Dr. Haack for her continuing contributions to the development of green chemistry educational materials within the department and her support of this program as our Assistant Department Head. We also acknowledge the administrative support provided by Kristi Mikkelsen in the preparation of these materials and the organization of our annual workshops. Mary Dricken, Gary Nolan, and Sandi Smith (members of our chemistry department staff) all contributed to the remarkably smooth running of the laboratory program throughout its development, as well as the annual Green Chemistry in Education Workshop held at the University of Oregon each summer.

We are pleased to acknowledge gratefully the support of our efforts by the National Science Foundation, the Alice C. Tyler Perpetual Trust, the Green Chemistry Institute of the American Chemical Society, the Environmental Protection Agency and the American Chemical Society.

Finally, we express our appreciation to all the students (and their teaching assistants) of Chemistry 337 and Chemistry 338 at the University of Oregon, particularly those who either volunteered to be or put up with becoming guinea pigs in the testing and optimization of these new experiments, and last, but by no means least, the technical wizardry of Ryan Stasel, who late in the process recovered the electronic version of this text from a malfunctioning computer.

KMD

JEH

February 11, 2003

Preface

This text is the product of six years of work toward the development of a green organic chemistry laboratory program at the University of Oregon, culminating in the complete replacement of our organic chemistry laboratory sequence with a greener curriculum. When students learn organic laboratory chemistry at the University of Oregon, they learn green organic chemistry. While becoming versed in the essentials of organic chemical theory and practice representing an essential feature of the organic chemistry laboratory experience, they at the same time acquire the tools to assess the health and environmental impacts of chemical processes and the strategies to improve them. The conception, design, and implementation of our green organic chemistry laboratory program followed a rather complex path, and we feel that our experiences and thought processes, outlined in the following paragraphs, may be helpful to others contemplating the conversion to a greener curriculum.

Green Organic Chemistry in the Laboratory: Practical Solution & Golden Opportunity

Many of us have struggled with the problem of how to modify our organic laboratory curriculum to provide a modern organic chemical experience, reduce the amount of waste generated, and make the lab safer for our students. Now-traditional approaches to minimizing waste and improving safety in the organic laboratory involve use of microscale experimentation and provision of increased ventilation. We initially pursued this approach, renovating a laboratory, at considerable expense, to allow each student to perform his/her microscale work within a fume hood. Although these changes reduced the amount of waste and provided a safer working environment, we were frustrated by several major disadvantages. A significant practical problem was that the laboratory's capacity of eighteen students required us to schedule night and weekend laboratory sessions for some students. The fume hoods were expensive to install and to operate, and created a noisy workspace with restricted sight lines. More fundamentally, we felt that our exclusive reliance on microscale methods was not adequately preparing our students for work at the larger scale found in our research laboratories or in industry.

In the process of addressing these issues we asked the question, *"Can we use 'green' chemistry methods to teach organic laboratory skills and chemical concepts, using standard taper glassware, on the bench top?"* Our goal was to use the latest advances in green chemistry research to develop a new laboratory curriculum that would decrease our reliance on fume hoods, produce a less hazardous waste stream, and improve safety. The fact that green methods eliminate hazards rather than simply attempting to prevent exposure through (fallible) safety procedures made it ideal for implementing in the teaching laboratory setting. As we began to develop the idea, other benefits quickly became evident. Green chemical methods achieve hazard reduction at all reaction scales, permitting the introduction of larger-scale experimentation, using standard laboratory glassware. Green chemistry offers the opportunity to upgrade comprehensively the organic lab curriculum, replacing many classic but perhaps timeworn experiments. Green chemistry provides a unique context for more detailed discussions of chemical hazards and the effects of chemicals on human health and the environment.

We rapidly discovered there were few existing green experiments suitable for the organic chemistry teaching laboratory. This realization led us to search for existing experiments that could be modified to be greener and for new reports of green methods that could be adapted for use in the teaching laboratory. We established the following criteria for judging the suitability of potential new experiments.

- Reduces laboratory waste and hazards.
- Illustrates green chemical concepts.
- Teaches modern reaction chemistry and techniques, in parallel with lecture course.
- Provides a platform for discussion of environmental issues in the classroom.
- Can be accomplished by students during a typical organic laboratory period.
- Uses inexpensive, greener solvents and reagents.
- Is adaptable to both macroscale and microscale methods.

In cases where experiments were to be modified, we adopted a set of principles to guide the process of modifying the experiments.

- Eliminate (minimize) hazardous solvents whenever possible, both as reaction media and in solvent-dependent separations.
- Identify and use the most benign reagents possible, using mild, more selective reagents to replace traditional, overly reactive reagents.