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Organic Chemistry

A Small Scale Approach *to* Organic Laboratory Techniques

THIRD EDITION

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Gary M. Lampman
George S. Kriz
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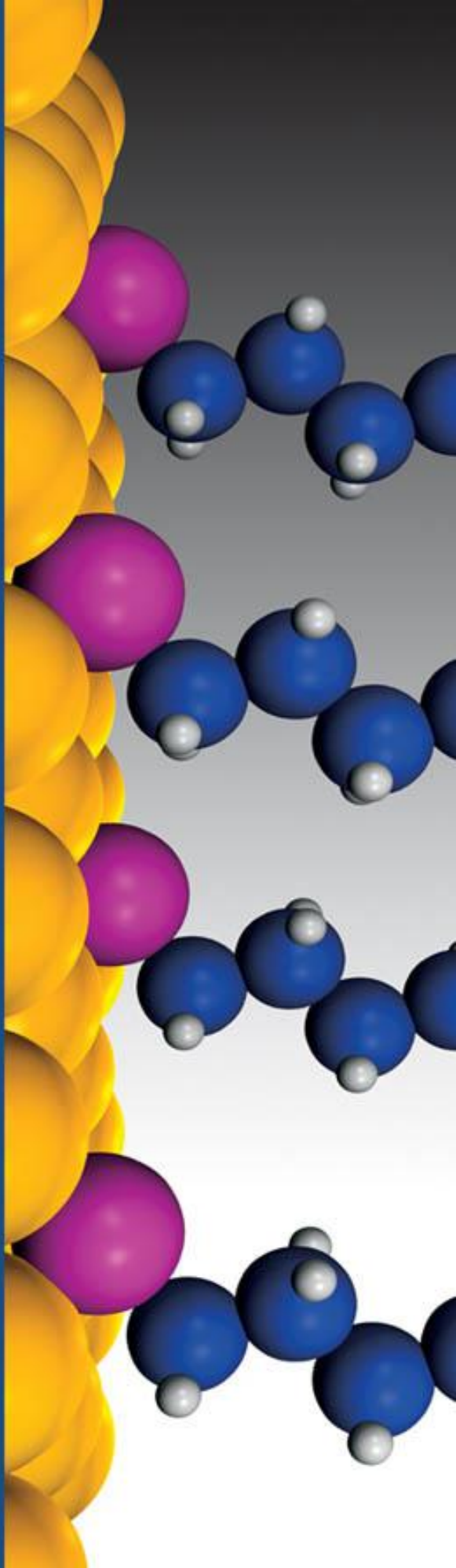

A SMALL-SCALE APPROACH TO

Organic Laboratory Techniques

Third Edition

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This book is dedicated to our organic chemistry laboratory students.

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Preface

STATEMENT OF MISSION AND PURPOSE IN REVISING THE TEXTBOOK

The purpose of this lab book is to teach students the techniques of organic chemistry. We desire to share our love of the organic chemistry lab and the joy it brings us with our students! In this edition, we have provided many new, up-to-date experiments that will demonstrate how organic chemistry is evolving. For example, new experiments involving nanotechnology and biofuels are included in this book. We have also selected several new experiments based on Nobel Prize awards, such as using organometallic catalysts for synthesis (Sonogashira coupling using a palladium catalyst and Ring-Opening-Metathesis polymerization using a Grubbs catalyst). Several new Green Chemistry experiments are also included, and the "green" aspects of experiments from our previous book have been improved. We think that you will be enthusiastic about this new edition. Many of the new experiments will not be found in other laboratory manuals, but we have been careful to retain all of the standard reactions and techniques, such as the Friedel-Crafts reaction, aldol condensation, Grignard synthesis, and basic experiments designed to teach crystallization, chromatography, and distillation.

SCALE IN THE ORGANIC LABORATORY

When we set out to write the first edition of *Introduction to Organic Laboratory Techniques: A Small-Scale Approach,* we initially envisioned it as a "fourth edition" of our successful "macroscale" organic laboratory textbook. During this period, we had gained experience with microscale techniques in the organic laboratory through the development of experiments for the microscale versions of our laboratory textbook. That experience taught us that students *can* learn to do careful work in the organic laboratory on a small scale. Since there are many advantages to working on a smaller scale, we recast our "macroscale" textbook as a **small-scale** approach to the laboratory. Working on a smaller scale greatly reduces cost since fewer chemicals are required and less waste is generated. There are also significant safety benefits due to the release of fewer hazardous fumes into the laboratory and a decreased chance of fires or explosions.

In the traditional macroscale approach, the chemical quantities used are on the order of 5–100 grams. In our version of the macroscale approach, called **small-scale**, the experiments use smaller amounts of chemicals (1–10 grams) and employ ₹19/22 standard tapered glassware. The microscale approach is described in another one of our textbooks, entitled *Introduction to Organic Laboratory Techniques: A Microscale Approach, Fourth Edition*. The experiments in the microscale book use very small amounts of chemicals (0.050–1.000 g) and ₹14/10 standard tapered glassware.

MAJOR FEATURES OF THE TEXTBOOK THAT WILL BENEFIT THE STUDENT

Organic chemistry significantly impacts our lives in the real world. Organic chemistry plays a major role in industry, medicine, and consumer products. Composite plastics are being increasingly used in cars and airplanes to decrease weight while increasing strength. Biodiesel is a hot topic today as we try to find ways to reduce our need for petroleum and replace it with materials that are renewable. Sustainability is the key word here. We need to replace the resources that we consume.

A number of experiments are linked together to create multistep syntheses. The advantage of this approach is that you will be doing something different from your neighbor in the laboratory. Wouldn't you like to be carrying out an experiment that is not the same as your neighbor's? Maybe you will be synthesizing a new compound that hasn't been reported in the chemical literature! You and your fellow students will not all be doing the same reaction on the same compounds: for example, some of you will be carrying out the chalcone reaction, others green epoxidation, and still others cyclopropanation of the resulting chalcones.

NEW TO THIS EDITION

Since the second edition of our small-scale textbook appeared in 2005, new developments have emerged in the teaching of organic chemistry in the laboratory. This third edition includes many new experiments that reflect these new developments. This edition also includes significant updating of the essays and chapters on techniques.

New experiments added for this edition include:

Experiment 1	Solubility: Part F Nanotechnology Demonstration
Experiment 25	Biodiesel
Experiment 26	Ethanol from Corn
Experiment 29	Reduction of Ketones Using Carrot Extract
Experiment 34	Aqueous-Based Organozinc Reactions
Experiment 35	Sonogashira Coupling of Iodoaromatic Compounds with Alkynes
Experiment 36	Grubbs-Catalyzed Metathesis of Eugenol with *cis*-1,4-Butenediol
Experiment 38	A Green Enantioselective Aldol Condensation Reaction
Experiment 40	Preparation of Triarylpyridines
Experiment 48	Synthesis of a Polymer Using Grubbs' Catalyst
Experiment 50	Diels-Alder Reaction with Anthracene-9-methanol
Experiment 58	Competing Nucleophiles in S_N1 and S_N2 Reactions: Investigations Using 2-Pentanol and 3-Pentanol
Experiment 64	Green Epoxidation of Chalcones
Experiment 65	Cyclopropanation of Chalcones

We have also included a new essay on biofuels. Substantial revisions were made to the *Petroleum and Fossil Fuels* essay, and other essays have been updated as well.

We have made a number of improvements in this edition that significantly enhance safety in the laboratory. We have also added several new experiments that incorporate the principles of Green Chemistry. The Green Chemistry experiments

decrease the need for hazardous waste disposal, leading to reduced contamination of the environment. Other experiments have been modified to reduce their use of hazardous solvents. In our view, it is most timely that students begin to think about how to conduct chemical experiments in a more environmentally benign manner. Many other experiments have been modified to improve their reliability and safety.

For the qualitative analysis experiment (Experiment 55), we have added a new optional test that can be used in place of the traditional chromic acid test. This new test is safer and does not require contact with hazardous chromium compounds. In keeping with the Green Chemistry approach, we have suggested an alternative way of approaching qualitative organic analysis. This approach makes extensive use of spectroscopy to solve the structure of organic unknowns. In this approach, some of the traditional tests have been retained, but the main emphasis is on using spectroscopy. In this way, we have also attempted to show students how to solve structures in a more modern way, similar to that used in a research laboratory. The added advantage to this approach is that waste is considerably reduced. The tables of unknowns for the qualitative analysis experiment (Experiment 55 and Appendix 1) have been greatly expanded.

New techniques have also been introduced in this edition. Two Green Chemistry experiments involve techniques such as solid phase extraction and the use of a microwave reaction system. Chiral gas chromatography has been included in the analysis of the products obtained in two experiments. A size-exclusion-chromatography column has been added to an HPLC unit to obtain molecular weights of polymers. A new method of obtaining boiling points using a temperature probe with a Vernier LabPro interface, laptop computer, and temperature probe has also been introduced.

Many of the chapters on techniques have been updated. New problems have been added to the chapters on infrared and NMR spectroscopy (Techniques 25, 26, and 27). Many of the old 60 MHz NMR spectra have been replaced by more modern 300 MHz spectra. As in previous editions, the techniques chapters include both microscale and macroscale methods.

CUSTOMIZED OPTIONS

Because we realize that the traditional, comprehensive laboratory textbook may not fit every classroom's needs or every student's budget, we offer the opportunity to create personalized course materials. This book can be purchased in customized formats that may exclude unneeded experiments, include your local materials, and, if desired, incorporate additional content from other Cengage Learning, Brooks/Cole products. For more information on custom possibilities, visit **www.signaturelabs.com** or contact your local Cengage Learning, Brooks/Cole representative. You can find contact information for your representative by visiting **www.cengagelearning.com** and using the "Find Your Rep" link at the top of the page.

SUPPORTING RESOURCES

Premium Companion Website with Pre-Lab Technique Video Exercises

The new, optional, premium companion website offers videos illustrating the steps required to *assemble an apparatus* or *carry out a technique* used in this book. These exercises can be viewed *prior* to going to the laboratory so students can

visualize the set-ups in addition to reading the technique description. Techniques with videos available are indicated with an asterisk in the Required Reading list at the start of each experiment and by a margin note at the beginning of the technique. The lab videos feature questions that can be assigned to students prior to attending lab, to ensure that they are prepared. An access card for the website may be bundled with a new book, or students can purchase Instant Access at **www.cengagebrain.com** with ISBN 0495911003.

Instructor's Manual

We would like to call your attention to the Instructor's Manual that accompanies our textbook and which is available as a digital download to qualified instructors. The manual contains complete instructions for the preparation of reagents and equipment for each experiment, as well as answers to each of the questions in this textbook. In some cases, additional optional experiments are included. Other comments that should prove helpful to the instructor include the estimated time to complete each experiment—and notes regarding special equipment or reagent handling.

We strongly recommend that instructors obtain a copy of this manual by visiting **www.cengage.com/chemistry/pavia** and following the instructions at the Faculty Companion site. You may also contact your local Cengage Learning, Brooks/Cole representative for assistance. Contact information for your representative is available at **www.cengagelearning.com** through the "Find Your Rep" link at the top of the page.

Digital Files of Text Art

New for this edition, select text art will be available for download of digital files from the Faculty Companion website for this textbook by visiting www.cengage.com/chemistry/pavia. These files can be used to prepare PowerPoint sets, overhead transparencies, and other lab documents.

ACKNOWLEDGMENTS

We owe our sincere thanks to the many colleagues who have used our textbooks and who have offered their suggestions for changes and improvements to our laboratory procedures or discussions. Although we cannot mention everyone who has made important contributions, we must make special mention of Albert Burns (North Seattle Community College), Charles Wandler (Western Washington University), Emily Borda (Western Washington University), and Frank Deering (North Seattle Community College), Gregory O'Neil (Western Washington University), James Vyvyan (Western Washington University), Jeff Covey (North Seattle Community College), Kalyn Owens (North Seattle CommunityCollege), Nadine Fattaleh (Clark College), Timothy Clark (Western Washington University), Tracy Furutani (North Seattle Community College).

In preparing this new edition, we have also attempted to incorporate the many improvements and suggestions that have been forwarded to us by the many instructors who have been using our materials over the past several years.

We thank all who contributed, with special thanks to our Executive Editor, Lisa Lockwood; Senior Development Editor, Peter McGahey; Assistant Editor, Elizabeth Woods; Senior Content Project Manager, Matthew Ballantyne; Media Editor,

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How To Use This Book

OVERALL STRUCTURE OF THE BOOK

This textbook is divided into two major sections (see Table of Contents). The first section, which includes Part One through Part Five, contains all of the experiments in this book. The second major section includes only Part Six and contains all of the important techniques that you will use in performing the experiments in this book. Interspersed among the experiments in Part One through Part Three are a series of essays. The essays provide a context for many of the experiments and often relate the experiments to real-world applications. When your instructor assigns an experiment, he or she will often assign an essay and/or several techniques chapters along with the experiment. Before you come to lab, you should read through these. In addition, it is likely that you will need to prepare some sections in your laboratory notebook (see Technique 3) before you come to the lab.

STRUCTURE OF THE EXPERIMENTS

In this section, we discuss how each experiment is organized in the textbook. To follow this discussion, you may want to refer to a specific experiment, such as Experiment 11.

Multiple-Parts Experiments

Some experiments, such as Experiment 11, are divided into two or more individual parts that are designated by the experiment number and the letters A, B, etc. In some experiments, for example Experiment 11, each part is a separate, but related experiment, and you will most likely perform only one part. In Experiment 11, you would do Experiment 11A (Isolation of Caffeine from Tea Leaves) or Experiment 11B (Isolation of Caffeine from a Tea Bag). In other experiments, for example Experiment 32, the various parts can be linked together to form a multi-step synthesis. In a few experiments, for example Experiment 20, the last part describes how you should analyze your final product.

Featured Topics and Techniques Lists

Directly under the title of each experiment (see Experiment 11), a list of topics appears. These topics may explain what kind of experiment it is, such as isolation of a natural product or Green Chemistry. The topics may also include major techniques that are required to perform the experiment, such as crystallization or extraction.

Required Reading

In the introduction to each experiment, there will be a section labeled Required Reading. Within this section, some of the required readings are labeled **Review** and some are labeled **New**. You should always read the chapters listed in the **New** section. Sometimes it will also be helpful to do the readings in the **Review** section.

Special Instructions

You should always read this section since it may include instructions that are essential to the success of the experiment.

Suggested Waste Disposal

This very important section gives instructions on how to dispose of the waste generated in the experiment. Often your instructor will provide you with additional instructions on how to handle the waste.

Notes to Instructor

It will usually not be necessary to read this section. This section provides special instructions for the instructor that will help to make the experiment successful.

Procedure

This section provides detailed instructions on how to carry out the experiments. Within the procedure, there will be many references to the techniques chapters, which you may need to consult in order to perform an experiment.

Report

In some experiments, specific suggestions for what should be included in the laboratory report will be given. Your instructor may refer to these instructions or may have other instructions that you should follow.

Questions

At the end of most experiments will be a list of questions related to the experiment. It is likely that your instructor will assign at least some of these questions, along with the laboratory report.

Contents

Introduction

Welcome to Organic Chemistry!

Organic chemistry can be fun, and we hope to prove it to you. The work in this laboratory course will teach you a lot. The personal satisfaction that comes with performing a sophisticated experiment skillfully and successfully will be great.

To get the most out of this laboratory course, you should do several things. First, you must review all relevant safety material. Second, you should understand the organization of this laboratory textbook and how to use it effectively. The textbook is your guide to learning. Third, you must try to understand both the purpose and the principles behind each experiment you do. Finally, you must try to organize your time effectively before each laboratory period.

LABORATORY SAFETY

Before undertaking any laboratory work, it is essential that you familiarize yourself with the appropriate safety procedures and that you understand what precautions you should take. We strongly urge you to read Technique 1, "Laboratory Safety", before starting any laboratory experiments. It is your responsibility to know how to perform the experiments safely and to understand and evaluate the risks that are associated with laboratory experiments. Knowing what to do and what not to do in the laboratory is of paramount importance, as the laboratory has many potential hazards associated with it.

ORGANIZATION OF THE TEXTBOOK

Consider briefly how this textbook is organized. Following this introduction, the textbook is divided into six parts. Part One consists of 16 experiments that introduce you to most of the important basic laboratory techniques in organic chemistry. Part Two contains two experiments that introduce you to the modern, computer-based techniques of molecular modeling and computational chemistry. Part Three consists of 36 experiments that may be assigned as part of your laboratory course. Your instructor will choose a set of for you to perform experiments.

Part Four is devoted to the identification of organic compounds and contains one experiment that provides experience in the analytical aspects of organic chemistry. Interspersed within these first four parts of the textbook are numerous essays that provide background information related to the experiments and that place them into a larger, overall context, showing how the experiments and compounds can be applied to areas of everyday concern and interest. Part Five contains 13 project-based experiments that require you to develop important critical-thinking skills. Many of these experiments have a result that is not easily predicted. To arrive at an appropriate conclusion, you may have to use many of the thought processes that are important in research. Part Six is composed of a series of detailed instructions and explanations dealing with the techniques of organic chemistry.

The techniques are extensively developed and used, and you will become familiar with them in the context of the experiments. The techniques chapters include infrared spectroscopy, nuclear magnetic resonance, ^{13}C nuclear magnetic resonance, and mass spectrometry. Many of the experiments included in Parts One through Five utilize these spectroscopic techniques, and your instructor may

choose to add them to other experiments. Within each experiment, you will find the section "Required Reading," which indicates the techniques you should study to do that experiment. Extensive cross-referencing to the techniques chapters in Part Six is included in the experiments. Many experiments also contain a section called "Special Instructions," which provides special safety precautions and specific instructions to you, the student. Finally, most experiments contain a section entitled "Suggested Waste Disposal," which provides instruction on the correct means of disposing reagents and materials used during the experiment.

ADVANCE PREPARATION

It is essential to plan carefully for each laboratory period by reading the experiment ahead of time, along with any of the assigned technique chapters. Rather than following the instructions blindly, you should try to understand the purpose of each step in a procedure. Then you will be able to interpret your results while you are performing an experiment and hopefully troubleshoot an experiment if you obtain unexpected results. We cannot emphasize strongly enough that you should come to the lab *prepared*.

If there are steps in a procedure or aspects of techniques that you do not understand, you should not hesitate to ask questions. You will learn more, however, if you first try to figure things out on your own. Don't rely on others to do your thinking for you.

You should read Technique 2, "The Laboratory Notebook, Calculations, and Laboratory Records," right away. Although your instructor will undoubtedly have a preferred format for keeping records, much of the material here will help you learn to think constructively about laboratory experiments in advance. It would also save time if, as soon as possible, you read the first nine techniques chapters in Part Six. These techniques are basic to all experiments in this textbook. The laboratory class will begin with experiments almost immediately, and a thorough familiarity with this particular material will save you much valuable laboratory time.

BUDGETING TIME

As just mentioned in "Advance Preparation," you should read several techniques chapters of this book even before your first laboratory class meeting. You should also read the assigned experiment carefully before every class meeting. Having read the experiment will allow you to schedule your time wisely. Often, you will be doing more than one experiment at a time. Experiments such as the fermentation of sugar or the chiral reduction of ethyl acetoacetate require a few minutes of advance preparation several days ahead of the actual experiment. At other times, you will have to catch up on some unfinished details of a previous experiment. For instance, usually it is not possible to accurately determine the yield or melting point of a product immediately after it is first obtained. Products must be free of solvent to give an accurate weight or melting point range; they have to be "dried." Usually, this drying is done by leaving the product in an open container on your desk or in your locker. Then, when you have a pause in your schedule during the subsequent experiment, you can determine these missing data from a dry sample. Through careful planning, you can set aside the time required to perform these miscellaneous experimental details.

PURPOSE

The main purpose of an organic laboratory course is to teach you the techniques necessary to deal with organic chemicals. You will also learn the techniques needed for separating and purifying organic compounds. If the appropriate experiments are included in your course, you may also learn how to identify unknown compounds. The experiments themselves are only the vehicles for learning these techniques. The techniques chapters in Part Six are the heart of this textbook, and you should learn these techniques thoroughly. Your instructor may provide laboratory lectures and demonstrations explaining the techniques, but the burden is on you to master them by familiarizing yourself with the chapters in Part Six.

Besides good laboratory technique and the methods of carrying out basic laboratory procedures, other things you will learn from this laboratory course include

1. How to record data carefully
2. How to record relevant observations
3. How to use your time effectively
4. How to assess the efficiency of your experimental method
5. How to plan for the isolation and purification of the substance you prepare
6. How to work safely
7. How to solve problems and think like a chemist

In choosing experiments, we have tried whenever possible to make them relevant and, more important, interesting. To that end, we have tried to make them a learning experience of a different kind. Most experiments are prefaced by a background essay to provide context, as well as some new information. We hope to show you that organic chemistry pervades your life due to its many common uses (drugs, foods, plastics, perfumes, and so on). Furthermore, you should leave your course well trained in organic laboratory techniques. We are enthusiastic about our subject and hope you will receive it with the same spirit.

This textbook discusses the important laboratory techniques of organic chemistry and illustrates many important reactions and concepts. In the traditional approach to teaching this subject (called **macroscale**), the quantities of chemicals used are on the order of 5–100 grams. The approach used in this textbook, the **small-scale** approach, differs from the traditional laboratory in that nearly all of the experiments use smaller amounts of chemicals (1–10 grams). However, the glassware and methods used in small-scale experiments are identical to the glassware and methods used in macroscale experiments.

The advantages of the small-scale approach include improved safety in the laboratory, reduced risk of fire and explosion, and reduced exposure to hazardous vapors. This approach also decreases the need for hazardous waste disposal, leading to reduced contamination of the environment.

Another approach, the **microscale** approach, differs from the traditional laboratory in that the experiments use very small amounts of chemicals (0.050–1.000 grams). Some microscale glassware is very different from macroscale glassware, and a few techniques are unique to the microscale laboratory. Because of the widespread use of microscale methods, some reference to microscale techniques will be made in the techniques chapters. A few experiments in this textbook feature microscale methods. These experiments have been designed to use ordinary glassware; they do not require specialized microscale equipment.