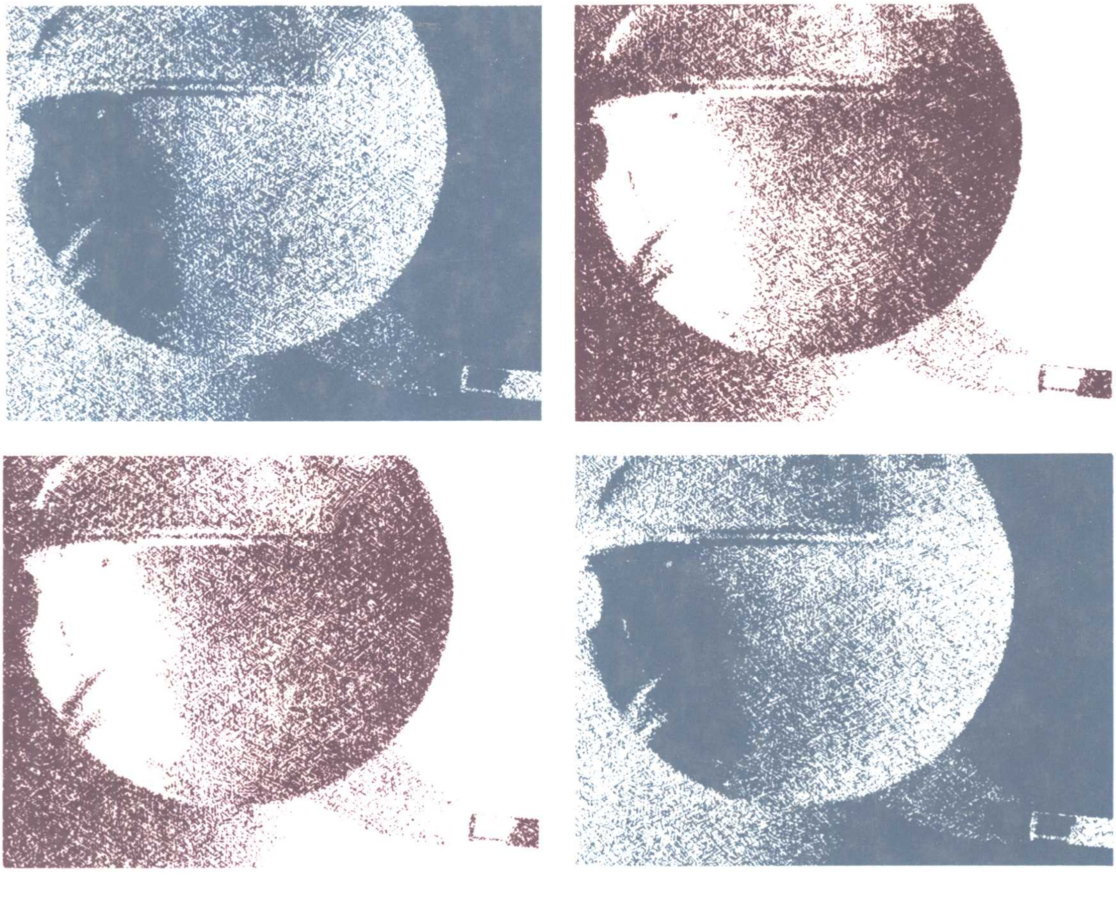
OPERATIONAL ORGANIC CHEMISTRY

A Laboratory Course

Second Edition



JOHN W. LEHMAN

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SECOND EDITION

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PRENTICE HALL, Englewood Cliffs, New Jersey 07632

To My Parents

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Preface to the Second Edition

Operational Organic Chemistry has been thoroughly reviewed and extensively rewritten for the second edition. The experimental sections have been reorganized; Part I now contains eleven experiments that cover all the major laboratory operations, and Part II contains thirty-nine experiments that are correlated with topics from a typical organic chemistry lecture course. Such correlations can be made for Part I experiments as well, but it is suggested that most of them (particularly the first five) be done early to teach the basic operations. Nine experiments are completely new: a simple introductory experiment that teaches acid-base chemistry and stoichiometry (Experiment 1); two experiments that explore different kinds of isomerism with the help of molecular models (12 and 16); a synthesis of a urea-inclusion complex (14); an aromatic bromination without Br_2 (29); a synthetic experiment that also introduces linear free-energy relationships (34); a structure determination involving an uncommon reduction reaction (36); a synthetic/mechanistic experiment involving a molecular rearrangement (38); and a literature search that culminates in an organic synthesis (50). Eleven experiments (8, 11, 17, 18, 19, 26, 27, 28, 31, 33, and 47) have been extensively revised to include completely new procedures or yield different products. For example, the Williamson synthesis of phenetole that appeared in the first edition has been changed to a synthesis of phenacetin with a simplified procedure (26), and the aromatic nitration experiment (28) now uses nitronium fluoborate and includes a competitive rate study. The Procedure sections (and usually the Methodology sections as well) of the remaining experiments have been rewritten to reduce the amounts of chemicals, add more safety information, provide additional experience with spectral analysis, or in some cases make the experiments work better. Thirty new Minilabs have been added, and most of them are now described briefly in their associated experiments.

Most students liked the humor in the Situation sections in the first edition, but not all instructors were amused. In order that the Situations would not imply a casual attitude toward the task of teaching or learning organic chemistry in the laboratory, they were rewritten so that they coincide more closely with the given experimental objectives. The Experimental Variations that were included with each experiment in the first edition have been revised to include detailed procedures when appropriate, and these are presented under the new heading Collateral Projects. References to related experiments described elsewhere have been moved to the *Instructor's Manual.* Some of the Topics for Report have been moved to the Report sections that now follow the Procedure sections, and others will be found in the Exercises sections, which have been augmented by many new exercises.

The emphasis on laboratory safety in the first edition has been reinforced by the more frequent use of hazard warnings and handling precautions within the experimental procedures. Several carcinogenic or particularly hazardous chemicals have been eliminated from experiments in this edition. Carbon tetrachloride has been replaced by Freon TF (1,1,2-trichlorotrifluoroethane), an essentially nontoxic solvent that can be purchased in quantity at a modest price (see the *Instructor's Manual* for suppliers). Chromium(VI) oxide has been replaced by aqueous sodium hypochlorite in the oxidation of isoborneol (Experiment 8), and two other experiments that used chromium(VI) reagents have been deleted. Thiamine hydrochloride has replaced sodium cyanide as the catalyst for the benzoin condensation (49). Chloroform is required for only one major experiment (19), and ethylene bromide, dioxane, and peroxybenzoic acid are not used at all.

In response to suggestions from many users of the first edition, infrared and nuclear magnetic resonance spectroscopy are employed to a much greater extent in this edition. IR or PMR spectra of starting materials are given in many experiments, and information about spectral interpretation has been added to the Methodology sections. Spectra of many products are included in the *Instructor's Manual;* they can be reproduced and distributed if it is impractical for students to record their own spectra. Part III, Qualitative Analysis, has been expanded to provide additional information about the interpretation of IR and PMR spectra. The operations dealing with IR and NMR spectrometry ⟨OP-33 and OP-34⟩ have been expanded to include descriptions of Fourier transform IR, carbon-13 NMR, and chemical-shift reagents. Experiment 48 now includes the interpretation of a mass spectrum, and the corresponding operation ⟨OP-36⟩ has been augmented accordingly. Most of the other descriptions of operations have required only minor revisions, but a section on HPLC has been added to the column chromatography operation ⟨OP-16⟩, and the gas chromatography operation ⟨OP-32⟩ has been expanded to cover open-tubular columns and McReynolds constants.

The Appendixes dealing with laboratory notebooks and checklists have been extensively revised in response to preferences expressed by users of the first edition. Appendix IV on stoichiometric calculations has been rewritten to reflect the widespread use of dimensional analysis techniques in general chemistry. The Bibliography has been updated to include many new sources published since 1980, and the description of bibliographic sources in Appendix VII has been revised accordingly. Experiment 50 contains an extensive section on searching the chemical literature, with detailed information about *Chemical Abstracts* and *Beilstein.*

Throughout the text, certain cross-references are given in angle brackets; these items can be found in the following parts of the book:

⟨OP-00⟩: Part V, Operations, pages 597-775

⟨Bib-X00⟩: Bibliography, pages A-37-A-49

⟨Test C-0⟩: Part III, Classification Tests section, pages 551-565

⟨Procedure D-0⟩: Part III, Derivatives section, pages 565-580

Instructors and laboratory coordinators should be aware that the *Instructor's Manual,* which is available free of charge from Allyn and Bacon, Inc., is an essential adjunct to any laboratory course that uses *Operational Organic Chemistry.*

Acknowledgments

I wish to acknowledge the valuable contributions of Glenda Knigge and Nasser Kamazani, who lab-tested many new procedures; Bonnie Hoyer, who helped develop some procedures using Freon TF; Anne Marie Torcoletti and Linda Clancy, who tested procedures and catalysts for Experiment 33; Professor William Haag, who assisted me with the revision of Experiment 47; and Professor Gerald Weatherby, who provided a number of helpful suggestions. I am indebted to the many users of the first edition of *Operational Organic Chemistry* who completed a questionnaire; their responses and comments have been particularly helpful in the preparation of the second. Thanks are due to the administration of Lake Superior State University for approving a leave that provided the time to complete the manuscript and to the chemistry department of the University of Michigan for granting me visiting faculty appointments. I also wish to thank James M. Smith and Kathy Smith of Allyn and Bacon and Jane Hoover of Lifland et al., Bookmakers, who assisted me during the manuscript preparation and later stages of publication. Most of the spectra in this book and the *Instructor's Manual* are reproduced from the spectral libraries of the Aldrich Chemical Company, whose helpfulness and generosity are gratefully acknowledged.

J.W.L.

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Introduction

Purpose and Organization of the Book

Operational Organic Chemistry is about organic chemistry as it is practiced in the laboratory. It is intended to be more than just a compilation of procedures that, if followed step by step, eventually result in the accumulation of data or the preparation of organic substances. It is a *textbook* of experimental chemistry that will help you learn how to perform the fundamental operations of organic chemistry in the laboratory and how to apply them intelligently in new situations. A cook must learn such basic techniques as peeling, slicing, and grating before he or she can prepare an adequate meal; you will have to learn such operations as extraction, distillation, and recrystallization before you can prepare an organic compound such as aspirin or isoamyl acetate. A *good* cook does not follow a recipe mechanically but possesses sufficient understanding of the methodology of cooking to improvise. If you unthinkingly follow a "recipe" for aspirin, you are not going to learn much about aspirin in the process, nor will you understand the reasons for what you are doing or the chemistry involved in the synthesis. You may have gone through the motions of making aspirin, but you will have no idea how to apply what you have done to a different preparation. Some students approach a chemistry experiment as if it were a one-of-a-kind phenomenon — they follow the directions, write up a report, and promptly forget about it. But no experiment in this book is unique; each consists of a set of interrelated operations performed in a logical sequence, and the lessons learned in one experiment will be applied to other experiments.

This book is divided into five parts, preceded by the Laboratory Safety section. Part I contains eleven experiments whose purpose is to help you learn the basic operations by applying them to a preparation or to the solution of a specific problem. For example, you will measure a melting point not only to learn *how* to measure a melting point, but also to establish the identity of a substance you have isolated or synthesized. Many of the operations will be reinforced by repeated application in the experiments in Part I so that you can master them. Once you are familiar with the operations, you will use them in the experiments in Part II, which are correlated with topics from the lecture course. The best way to learn most theoretical concepts is to apply them in the laboratory; in this way, their relationship to the "real world" of organic chemistry can be better understood and appreciated. The thirty-nine experiments in Part II will give you practical experience in dealing with the concepts of organic chemistry and will increase your proficiency in the laboratory. Part III is a comprehensive, self-contained introduction to organic qualitative analysis that will teach you how to identify organic compounds using chemical and spectral methods. Some experiments in Parts I and II contain references in the forms ⟨Test C – 19⟩ and ⟨Procedure D – 4⟩. These refer to the chemical tests and preparations of derivatives described in Part III on pages 551 – 580. Part IV describes some challenging, open-ended research projects that you should undertake only if you are an advanced or highly motivated student. Part V contains the descriptions of all the operations that are referred to by number in the experiments in the form ⟨OP – 5⟩. Appendixes I through V contain illustrations of laboratory equipment and information about laboratory notebooks, reports, experimental plans, and calculations. Appendix VI contains tables of properties for qualitative analysis. Appendix VII describes many of the sources mentioned in the Bibliography entries and serves as a guide to the literature of chemistry; in conjunction with Experiment 50, it will help you to carry out a comprehensive literature search. References to entries listed in the Bibliography are made throughout the text in the form ⟨Bib – F7⟩, where the letter refers to a category and the number to a location within that category; for example, F7 is the seventh book listed under category F (Spectroscopy).

Organization of the Experiments

Immediately following the title of each experiment is a list of topics that classify the experiment and correlate its contents with textbook material. For the synthetic experiments, this list generally includes the kind of compound reacting, the kind of compound being synthesized, the reaction type, and significant intermediates.

Each experiment also includes material under some or all of the following headings.

Operations. Most or all of the operations used in an experiment are listed at the beginning of the experiment. These Operations lists include general separation or analytical methods (such as gas chromatography and NMR spectrometry) as well as basic laboratory techniques (such as vacuum filtration). Each operation is identified by an operation number, such as OP – 12 for vacuum filtration, and the description of an operation can be located quickly using the special headings at the top of the odd-numbered pages in Part V. In the Operations lists, the numbers printed in boldfaced type indicate operations being used for the first time; you should read these descriptions thoroughly before you come to the laboratory. Once you have used an operation, you should not have to reread the entire description the next time you use it, but you should at least read the Summary and review the Operational Procedure to refresh your memory. Eventually you should have to refer to the operation descriptions only if you encounter experimental difficulties or are applying an operation in a new situation.

Objectives. Each experiment is designed to fulfill a number of objectives, which usually include both experimental objectives that will be met by successful completion of the experiment (such as preparing a specified compound or identifying an unknown) and learning objectives relating to information, methods, and theoretical concepts that will be learned or reinforced as you carry out the experiment.

Situation. Many scientists study more or less familiar objects that can be readily observed, like stars, minerals, or ring-tailed wombats, but chemists deal with fundamental particles that cannot be seen or fully understood. It is easier to empathize with a wombat than with a molecule of *N*,*N*-diethyl-*meta*-toluamide ("Deet" for short; see Experiment 37)—even though the Deet is a more practical companion for a trek through the woods. Thus, nonchemists seldom understand just what motivates chemists to seek out and solve research problems that pertain to the invisible world of atoms and molecules. Each experiment is introduced by a Situation section intended to give you an appreciation of organic chemistry as a problem-solving endeavor rather than a collection of dry facts. Most Situations portray research problems of the kind that are encountered by professional chemists; some are more fanciful and need not be taken too seriously. In all cases, their purpose is to help you approach each experiment as a stimulating challenge to be met rather than an ordeal to be endured.

Background. Chemistry is an *experimental* science—the concepts of chemistry are based on observations of chemical phenomena, and no theory can stand for long without a solid foundation of experimental facts. A major purpose of any laboratory course is to put into practice the theoretical concepts dealt with in lectures. If you do not see the relationship between an experiment and the associated lecture material, the main point of the experiment will be lost. The Background section in each experiment is intended to serve as a link between the experimental work and the related concepts that are presented in the lecture course. This section may also relate historical sidelights or interesting facts that show the relevance of the experiment to the real world.

Methodology. A laboratory course gives you an opportunity to learn by experience, but you will not learn much of value unless you appreciate the significance of the experience at the time. If you follow a procedure mechanically without understanding the purpose of each step, you will be unprepared to deal with unexpected complications when they arise, to modify the procedure when necessary, or to take a shortcut when the situation warrants it. The Methodology section of an experiment describes and explains the experimental approach and may provide additional information that can help you interpret your results or cope with experimental situations as they arise.

Prelab Assignments. You should always read through the entire assigned experiment *before* you come to the laboratory, paying particular attention to the Methodology and Procedure sections. The Prelab Assignments section of an experiment lists additional tasks to be completed before the lab period, such as reading operations, performing calculations, or writing an experimental plan. Ordinarily you will not be allowed to begin an experiment until your prelab write-up has been approved by the instructor.

Reactions and Properties. The Reactions and Properties section gives balanced equations for the relevant reactions and tabulates the physical properties of reactants, products, and certain other chemicals. The Properties table provides the data needed for most of the prelab calculations.

Procedure. Many of the experimental procedures in Part I are spelled out in considerable detail so as to inform or remind you of necessary steps that you might otherwise overlook. In most Part II experiments, the procedures are considerably less detailed. By the time you get to Part II, you will be expected to know how to perform most operations proficiently without the aid of frequent reminders. You should therefore regard the Procedure section more as a guide to the laboratory work than as a set of step-by-step instructions.

Safety Precautions. The characteristics of some hazardous chemicals and precautions for their use are described under a separate heading that appears in the Procedure sections of experiments in which such chemicals are used. See the Laboratory Safety section (pages 8 – 15) for general information about hazardous chemicals.

Report. The Report section of an experiment describes specific calculations, analytical data, or other information that should be incorporated into your laboratory report. Your instructor will describe the format you should follow and indicate any additional material that should be included in lab reports. In many cases it will be necessary to read the Background and Methodology sections thoroughly in order to complete your report or the assigned exercises.

Collateral Projects. The Collateral Projects section describes additional projects that are related to the basic experiment. You are encouraged to complete as many of the projects as you have time for, but you must obtain your instructor's permission before starting any unassigned project.

Minilabs. A short, self-contained Minilab is included with most of the experiments. Although each Minilab is associated with an experiment that is related in subject matter, you do not have to carry out a Minilab in conjunction with its experiment. Do not start any unassigned Minilab without first receiving permission from your instructor.

Exercises. Your instructor will assign some of the Exercises to be completed and submitted with your laboratory report.

Library Topics. The assignments in the Library Topics section are intended to help you become more familiar with the chemical literature, which is described in Appendix VII. Your instructor may make specific assignments or allow you to choose your own. Information on most topics can be found in sources in the Bibliography, particularly under category L.

Laboratory Organization

Because of wide variations in individual working rates, it is usually not possible to schedule experiments so that everyone can be finished in the allotted time; if all laboratories were geared to the slowest student, the objectives of the course could not be accomplished in the limited time available. As a result, some students will invariably get behind during a lab period and find it necessary to put in extra hours outside their scheduled laboratory section in order to complete the course. The students who fall into this group do not necessarily lack ability—some of the brightest students may also be among the slowest—but they are usually not well organized and thus fail to make the best use of their time. The following suggestions should help you work more efficiently in the laboratory:

1. *Be prepared to start the current experiment the moment you reach your work area.* Don't waste the precious minutes at the start of a laboratory period doing calculations, reading the experiment, washing glassware, or carrying out other activities that should have been performed at the end of the previous period or during the intervening time. The first half hour of any lab period is the most important—if you can use it to collect your reagents, set up the apparatus, and get the initial operation (reflux, distillation, etc.) under way, you should be able to complete the experiment in the designated time period.

2. *Organize your time effectively.* Set up a regular schedule that allows you to read the experiment and the operation descriptions a day or two before the laboratory period—an hour before the lab is much too late! Plan ahead so that you know approximately what you will be doing at each stage of the experiment. A written experimental plan, prepared as described in Appendix V, is invaluable for this purpose.

3. *Organize your work area.* Before performing any operation, all of the equipment and supplies you will need to use during the operation should be set out neatly on your bench top in approximately the order in which they will be used. Small objects like spatulas and any item that might be contaminated by contact with the bench top should be placed on a paper towel, laboratory tissue, or mat. After each item is used, it should be removed to an out-of-the-way location (for example, dirty glassware to a washing trough in the sink) where it can be cleaned and then returned to its proper location when time permits. It is important to keep your locker well organized, with each item placed in a specific location when not in use, so that you can immediately find the equipment you need. This will also enable you to notice when a piece of equipment has been misplaced or stolen, so it can be hunted down or reported to the instructor without delay.

Laboratory Etiquette

Although a little courtesy does help maintain peace and harmony in any work situation, this section is not about "good manners" as such. It is a set of common-sense rules that must be observed if the laboratory is to be a place where students can work together safely and efficiently.

1. Return all chemicals and supplies to the proper location after use. You will understand the reason for this rule if you ever experience the aggravation of hunting high and low for a reagent, only to find it at another student's station in a far corner of the lab. Chemicals that are being weighed out may be left at the balance if there are students waiting to use them; otherwise, they should be returned to the reagent shelves. Containers should be taken to the reagents to be filled; reagent bottles should not be taken to your lab station.

2. Measure out only what you need. Liquids and solutions should be measured into graduated containers so that you will take no more than you expect to use for a given operation. Solids can usually be weighed directly from their containers or measured from a special solids dispenser.

3. Prevent contamination of reagents. Do not use pipets or droppers to remove liquids from reagent bottles, and do not return unused reagent to a stock bottle. Be sure to close all bottles tightly after use — particularly those containing anhydrous chemicals and drying agents.

4. When you must use a burner in the lab, tell your neighbors, unless they are already using burners. This will enable them to cover any containers of flammable solvents and to limit or modify their use of such solvents during your operation. In certain circumstances, for example, when ether extractions are being performed, you should use a different heat source, move your operation to a safe location (for instance, under a fume hood) or find something else to do while flammable solvents are in use.

5. Leave all community property where you found it. Some items, such as ringstands, steam baths, lab kits, clamps, and condenser tubing, may not be supplied in student lockers. Such items are often part of the standard equipment found at each laboratory station, or they are obtained from the stockroom at the beginning of the laboratory period. Since such items may be needed by students in other lab sections, they should always be returned to the proper storage space at the end of the period.

6. Clean up for the next person. There are few experiences more annoying than finding that the lab kit you just checked out is full of dirty glassware, or that your lab station is cluttered with paper towels, broken glass, and