MODERN EXPERIMENTAL ORGANIC CHEMISTRY

THIRD EDITION

Royston M. Roberts □ John C. Gilbert
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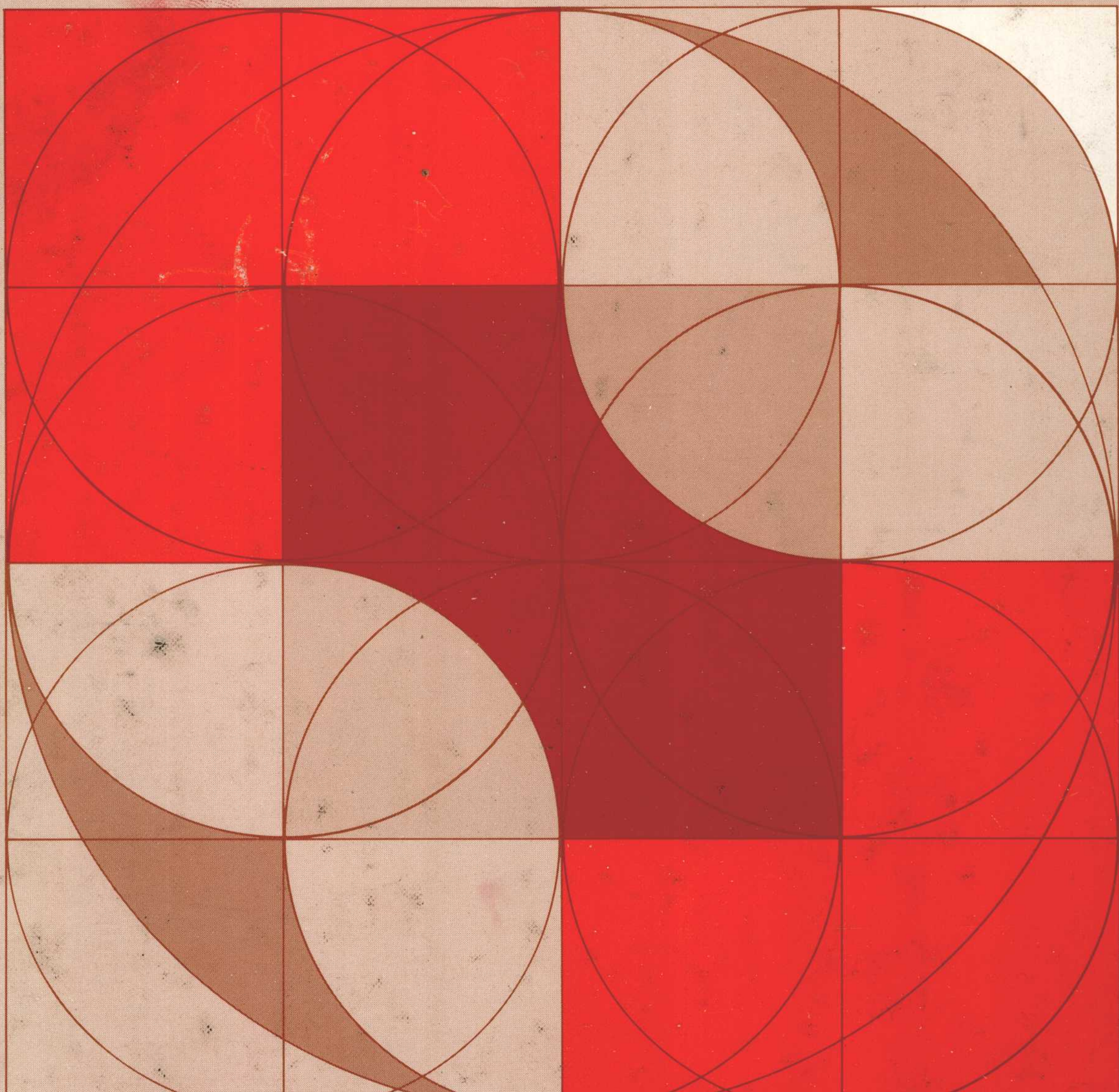

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PREFACE

The third edition of this book continues our original goal of providing students with an essentially self-contained laboratory *textbook* that requires little or no supplementation for complete understanding of the experiments. Thus laboratory procedures are preceded by a thorough discussion of the theoretical as well as the practical aspects of the experiment. Moreover, the incorporation of modern spectroscopy into an elementary organic textbook—an innovative feature of the first edition—has been expanded.

This revision may be briefly characterized as follows: (1) all experiments that have been proved satisfactory and valuable by thousands of students using the first two editions have been retained, (2) any experiments found to be less satisfactory or useful have either been removed or improved, (3) new textual material and experiments have been added, (4) all material and experiments have been updated, and (5) *safety in the laboratory* has been strongly emphasized.

Certain sections have been deleted or modified in the current edition. The chapter on alkynes, which involved a procedure requiring mercuric sulfate, has been eliminated because of concern over the toxicity of mercury. The preparation of triphenylmethyl radical has also been removed because of the difficulty with reproducibility by inexperienced students. The section on studies of molecular models has been deleted because a number of persons expressed the view that such studies are not appropriate laboratory work (although this section was enthusiastically suggested by some users of the first edition!). The experiments on alkylations of benzene have been replaced with an alkylation of *p*-xylene because of the growing concern over the toxicity and possible carcinogenicity of benzene. In fact *the use of benzene has been eliminated throughout the book,* except in one instance where it is utilized as a cosolvent in the thin-layer chromatographic analysis of derivatized amino acids. Some of the classical tests for carbohydrates have been removed from Chapter 22. The isolation of tropylium iodide (Chapter 18) has been made more dependable by a simple modification of the experimental procedure.

New material has been inserted throughout the third edition. There is a new section on *uv absorption spectroscopy* in Chapter 4, and uv spectra and exercises now appear in appropriate places throughout the book. A *malonic ester synthesis* has been added in Chapter 14; the enolate anion of dimethyl malonate is alkylated with 1,3-dibromopropane to form dimethyl cyclobutane-1,1-dicarboxylate, which can be converted to the corresponding diacid and thence to cyclobutane carboxylic acid.

Chapter 11 illustrates the interesting new technique of *phase transfer catalysis* in the preparation and reaction of dichlorocarbene. The increasing importance of photochemical techniques is exemplified by the *photochemical reduction-dimerization* of 4-methylbenzophenone to produce 4,4′-dimethylbenzopinacol; this has been added in Chapter 20. The latter compound is used in a *pinacol-pinacolone rearrangement* experiment, allowing a determination of migratory aptitudes of aryl groups.

A new chapter on *polymers* (Chapter 21) includes a new procedure for the addition polymerization of styrene that permits the use of a safer catalyst than benzoyl peroxide, the one specified by most other laboratory manuals and by previous editions of this book. Condensation polymerization is illustrated by the *"Nylon Rope Trick,"* a spectacular example of polymerization at the interface of two liquid layers. The preparation of a *rigid polyurethane foam* is also described in Chapter 21, illustrating an important new industrial application of polymer chemistry. In response to a number of suggestions from those who have used the previous editions, the chapter on qualitative organic analysis has been expanded to include a *general scheme for the separation of mixtures* of unknown compounds. Moreover, the nitrous acid test for amines has been replaced with modified Simons and Ramini tests to avoid the production of potentially carcinogenic nitrosamines. A new appendix describes *laboratory techniques for heating and stirring.*

The entire text has been updated, specifically the chapters on spectroscopy, organometallic chemistry, and the use of organic chemistry literature.

A significant development in recent years has been the growing awareness of the toxic and carcinogenic nature of many organic compounds. In preparing this revised edition, we felt a strong sense of responsibility to inform students of the potential danger inherent in handling certain substances. In the earlier editions we emphasized the usual precautions to be taken in the handling of flammable, corrosive, and noxious organic chemicals. Now, in view of recent warnings about the toxic and carcinogenic properties of compounds formerly thought to be rather innocuous (such as benzene, acetonitrile, nitrosamines, and carbon tetrachloride), we felt more stringent precautions should be taken in laboratory courses to protect students from contact with these substances.

We have considered every chemical used as substrate, reagent, or solvent in the experiments, and we have avoided use of the potentially dangerous ones as far as is practical. For example, other solvents have been substituted for benzene except in one experiment. In every experiment involving a possibly toxic substance, we have called for its handling in a protected system or in a fume hood. To dramatize safety precautions of all kinds, we have added a Do It Safely section at the beginning of most Experimental Procedures. We believe that in this edition we have provided a text for the safest possible course that will still offer a satisfactory introduction to experimental organic chemistry.

We would like to call attention to the *Instructor's Manual,* which is available without charge from the publisher. This manual contains lists of recommended desk equipment, shelf reagents and solvents, lists of required chemicals and equipment—by chapter and alphabetically, notes on the Experimental Procedures—including time requirements, answers to selected exercises, and suggestions for optional experiments taken from recent issues of the *Journal of Chemical Education.*

We are pleased to acknowledge helpful comments from many colleagues who have used the previous editions of this book, and we earnestly solicit comments on this edition. Special thanks are due to Aubrey Skinner and Robert G. Landolt for their assistance in updating the literature chapter and to Kevin Cann, Sophon Roengsumran, John Ginascol, and Jim Walter for development and testing of some of the new procedures.

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CONTENTS

INTRODUCTION

The laboratory part of an introductory course in organic chemistry is complementary to the lecture part; this is where you learn firsthand that the compounds and reactions described in lectures are not merely abstract notations. In addition, many of the theoretical concepts discussed in the lectures are amenable to experimentation at even an introductory level, and you will find that collecting and interpreting your own data will add reality to the theoretical framework of the subject.

Probably the most important purpose of the laboratory, however, is the introduction it provides to the experimental techniques of the practicing organic chemist. Learning to handle organic chemicals and manipulate apparatus is obviously a necessary part of a chemist's education. Less obvious, but equally important, is the learning of the scientific approach to laboratory work, which results in what is called good experimental technique. Some suggestions to aid in developing good technique are given in the following paragraphs.

Never begin any experiment unless you understand the overall purpose of the experiment and the reasons for each operation involved. This requires *studying* (not just reading) an experiment *before coming to the laboratory.* For this reason laboratory experiments are always assigned several days in advance, except under unusual circumstances. You will find that not only will your performance in laboratory be better if you are well-prepared but also you will benefit much more from the experiments, in knowledge as well as in grades.

Neatness is an important part of good technique. Carelessness in handling chemicals may not only lead to poor results but is often unsafe. Similarly, careless assembly of apparatus is not only aesthetically displeasing but is also dangerous.

The procedures given in this book are meant to be followed closely. There is usually a reason why each operation is to be carried out exactly as described, although the reason may not at first be obvious to the beginning student. In the earlier chapters of the book the operations required in the experimental procedures are described rather specifically, but in later chapters, after experimental techniques have become more familiar to you, the directions are less specific. In this way we hope to avoid your feeling that you are following "cookbook" directions. As you gain more practice in the techniques of the organic laboratory, you may even formulate alternative procedures for performing a reaction, purifying a product, and so on. However, for the sake of safety it will be wise for you to check any original plans with your instructor. In more advanced courses you may expect to use your chemical initiative more freely.

In some of the experimental procedures, stars (★) have been inserted to indicate points at which the experiment may be interrupted without affecting the results unfavorably. This has been done to help instructors and students plan to make the best use of laboratory time. For example, some experiments may be started toward the end of a laboratory period, carried through to a starred point (★), and then discontinued until the next laboratory period, the reaction mixture being safely stored in the desk in the interim. In cases where it is already obvious from the text that the experiment may or should be interrupted, stars are not inserted.

One of the most valuable characteristics that you can develop as an experimentalist is being *observant* during all stages of an experiment. Was there a fleeting color change when a drop of reagent was added to the solution? Was a precipitate formed? Is the reaction exothermic? Such observations may seem insignificant at the time but may later prove to be vital to the correct interpretation of an experimental result. All such observations should be *recorded* in a notebook.

A permanent record of all laboratory work should be kept in a *bound notebook,* approximately 8 × 10 in., rather than in a loose-leaf or spiral notebook. Pages of a bound book are less likely to tear out accidentally and be lost. Always write in ink. It will be easier to keep the notes neat and legible if the pages are lined horizontally. (Although notebooks with vertical as well as horizontal lines are sometimes recommended for laboratory notes, particularly in physical chemistry, they are less desirable for organic chemistry laboratory notes. In the special cases where graphs are necessary, they may be pasted in.) Use the first page as a title page, and reserve two additional pages to be filled in as a table of contents. The pages should be numbered throughout the notebook.

Your instructor will probably have specific directions regarding the format of your notebook and of any reports you may be asked to submit. In the case of the notebook these may include a preliminary "write-up," in which you give the title of the experiment, reference(s), complete equations for the main and side reactions, and calculations of the theoretical yield in synthetic experiments. You may be allowed some flexibility in style, but proper recording of experimental results does not allow great literary license. Appendix 2 contains suggested formats for your notebook for both preparative and investigative types of experiment.

The overriding requirements of good experimental description are accuracy and completeness of observation and recording. The results should usually be summarized and conclusions should be drawn from each experiment. If the results are obviously not those expected, an explanation should be given.

SAFETY IN THE LABORATORY

Public and professional concerns over the potential health-related dangers of chemicals have grown in recent years. The chemical laboratory is indeed a potentially dangerous place; it contains flammable liquids, fragile glassware, and corrosive and poisonous chemicals. Nevertheless, if proper precautions are taken and safe procedure is followed, it is no more dangerous than an ordinary kitchen or bathroom. To an experienced laboratory worker, "proper precaution and safe procedure" is synonymous with knowledge and awareness of the properties of the substances handled and of the limitations that should be placed upon the use of various types of equipment, as well as an element of common sense. However, an inexperienced student cannot be expected to possess extensive knowledge of what constitutes safe laboratory operation. This must be learned and developed in the same way as are the theoretical aspects of organic chemistry in the lecture part of this course.

We have therefore included a series of sections entitled "Do It Safely," which are featured throughout the book. These sections accompany most of the experiments, and they are somewhat more detailed for those experiments likely to be performed in the first semester of organic laboratory. In many instances the dangerous aspects of specific chemicals are discussed. The purpose of these sections is to inform you of some precautions always taken by an experienced worker in the laboratory. We hope you read and accept this feature of the book with the same attitude with which it is written, that is, with a *positive* attitude toward developing safe technique and the knowledge that will lead to what might be called "common sense in the laboratory." Some important *general* safety considerations are discussed below. You should read them carefully now and review them prior to each laboratory period until they become "second nature" to you.

DO IT SAFELY

1. When you first receive laboratory equipment, examine the glassware closely for small cracks, chips, or other imperfections that might weaken it. It is particularly important to check round-bottomed flasks and condensers (see Equipment Commonly Used in the Organic Laboratory, pictured inside the back cover) carefully. Cracks in a round-bottomed flask may cause it to break during use, spilling quantities of potentially dangerous and flammable chemicals. Cracks at the ring seals of condensers where the inner tube and the water jacket are joined may allow water to drain into a flask containing reagents, which may react violently with water. Replace any such imperfect glassware immediately. Take the time to properly store your equipment in your locker or drawer. Carelessly stored glassware may become cracked as a result of opening and closing drawers. *Develop the habit of examining your glassware before each use.*

2. Nearly all organic substances are **flammable.** It is best to avoid the use of flames whenever possible. There may be times, however, when the use of laboratory burners is necessary, as in the distillation of particularly high-boiling liquids. Refer to Appendix 5.

When flames are used, you should take care to observe the following precautions:

a. A burner should be used to heat a flammable liquid only when it is contained in a flask protected by a condenser (see Figures 2.2 and 7.1). *Never* heat a flammable liquid in an *open* container with a burner; if possible, use a steam bath or an electrical heating device instead. In Table 2.1 the flammability of many commonly used solvents is indicated; if a solvent is not listed there, however, you should not assume that a substance is nonflammable. Consult your instructor.

b. Avoid pouring flammable liquids from one container to another within several feet of a flame. Do not pour waste flammables into the center trough of your work bench; they may be carried near a flame farther down the bench.

3. Most of the chemicals that you will encounter in the laboratory are *at least* mildly toxic, and many may be corrosive or caustic. The reasons for the following guidelines should be apparent.

a. Never *taste* anything in the laboratory unless your instructor specifically tells you to do so.

b. **Always wear safety glasses or goggles when in the laboratory** to avoid possibly irreversible eye damage from splashing chemicals in case of an accident. Remember that even when you are not actually working with chemicals, another student may have an accident in which you may become involved. *Contact lenses are particularly dangerous in a laboratory environment and should not be worn.*

c. Avoid the inhalation of vapors of the solvents and other substances that you use or encounter. Use a fume hood insofar as possible when pouring and handling volatile substances and for carrying out reactions in which noxious gases are released. If this is not feasible, affix appropriate gas traps (described among the Experimental Procedures) to your apparatus.

d. Use appropriate equipment and glassware to handle and transfer chemicals from one container to another. Generally avoid allowing chemicals to come into contact with your skin. It is prudent to keep a pair of ordinary kitchen rubber gloves in your drawer and to use them when you are measuring and transferring particularly harmful liquids and solutions. Most chemicals can be removed from the surface of the skin by washing thoroughly with soap and warm water. This should be done promptly following any contamination. Avoid using organic solvents such as acetone or ethanol to remove chemicals from your skin; such solvents may actually hasten the absorption of the chemical through the skin.

4. Familiarize yourself with the layout of your laboratory. Note particularly the location of fire extinguishers, fire blankets, safety showers, and eye-wash fountains. Your instructor will explain the operation and purpose for each of these safety devices. Read the section entitled "First Aid in Case of Accident," which is provided inside the front cover of the book.

GLASSWARE: PRECAUTIONS AND CLEANING

The cardinal rule in handling laboratory glassware is *never apply undue pressure or strain to any piece of glassware.*

This rule applies to insertion of thermometers or glass tubes into rubber stoppers, rubber tubes, or corks. "If you have to force it, don't do it!" Make the hole larger or use a smaller piece of glass. Lubricate the rubber or cork with a little water or glycerol. Always grasp the glass part very close to the rubber or cork part when pushing the glass into it.

These directions will become less necessary as more and more laboratories are making the transition to all ground-glass-jointed apparatus. However, the cardinal rule stated above applies to this glassware as well; take care that strain does not develop because of carelessly positioned components. Strained glassware will break at times when heated, or simply upon standing.

If ground-glass-jointed glassware is available, it is important that the joints be properly lubricated so that they do not "freeze" and become difficult, if not impossible, to separate. Proper lubrication can be accomplished by putting a thin layer of grease on opposite sides of the male joint, mating the two joints, and then rotating them together to cover the surfaces of the joints with a thin coating of grease. The quantity of lubricant used is important since too much grease may cause ultimate contamination of the reaction whereas too little will permit the joints to freeze.

Glassware is most easily cleaned *immediately* after use. Most chemical residues can be removed by washing the glassware with detergent and water or with common organic solvents such as toluene or acetone. (*Caution:* Do *not* use acetone to clean apparatus that contains residual amounts of bromine since a powerful lachrymator, bromoacetone, may thus be formed.)

More stubborn residues may require the use of powerful chemical cleaning solutions such as chromic acid (concentrated sulfuric acid and chromic anhydride) or potassium hydroxide in ethanol. Gentle warming of the organic solvent or cleaning solution on a steam bath will generally hasten the cleaning process. Before you resort to the use of any cleaning agents other than detergent and water, consult your instructor for permission and directions concerning their safe handling.

Brown stains of manganese dioxide on glassware may sometimes be encountered; these can generally be removed by rinsing the apparatus with a 30% aqueous solution of sodium bisulfite.

It is good practice to wipe off any lubricant from ground-glass-jointed glassware with a towel or tissue wetted with a solvent such as acetone or hexane before washing with detergent and water. Otherwise the lubricant will stick to the brush used to scrub the glassware and be carried by the brush onto all surfaces it touches.

DISPOSAL OF CHEMICALS

Your laboratory should be supplied with containers for the proper disposal of waste chemicals. Liquid and solid organic wastes should be placed in appropriately labeled containers. In this way environmental pollution is minimized, and the buildup of solids and flammable liquids in drain traps and pipes is avoided. Aqueous solutions may be discarded in the sink using running water. Do not discard aqueous waste into the organic liquid waste container because the acidic, basic, or other types of solutes possibly present in such solutions may initiate chemical reactions among the organic wastes in the container.

Solid inorganic wastes such as desiccants (see Appendix 1) should be discarded in an appropriate container. This procedure will provide for a cleaner and safer laboratory and will protect the janatorial staff from inadvertently being exposed to powdery and perhaps dangerous chemicals.

Many laboratories have a special place to discard broken glassware. Ask your instructor if this is the case in your laboratory.