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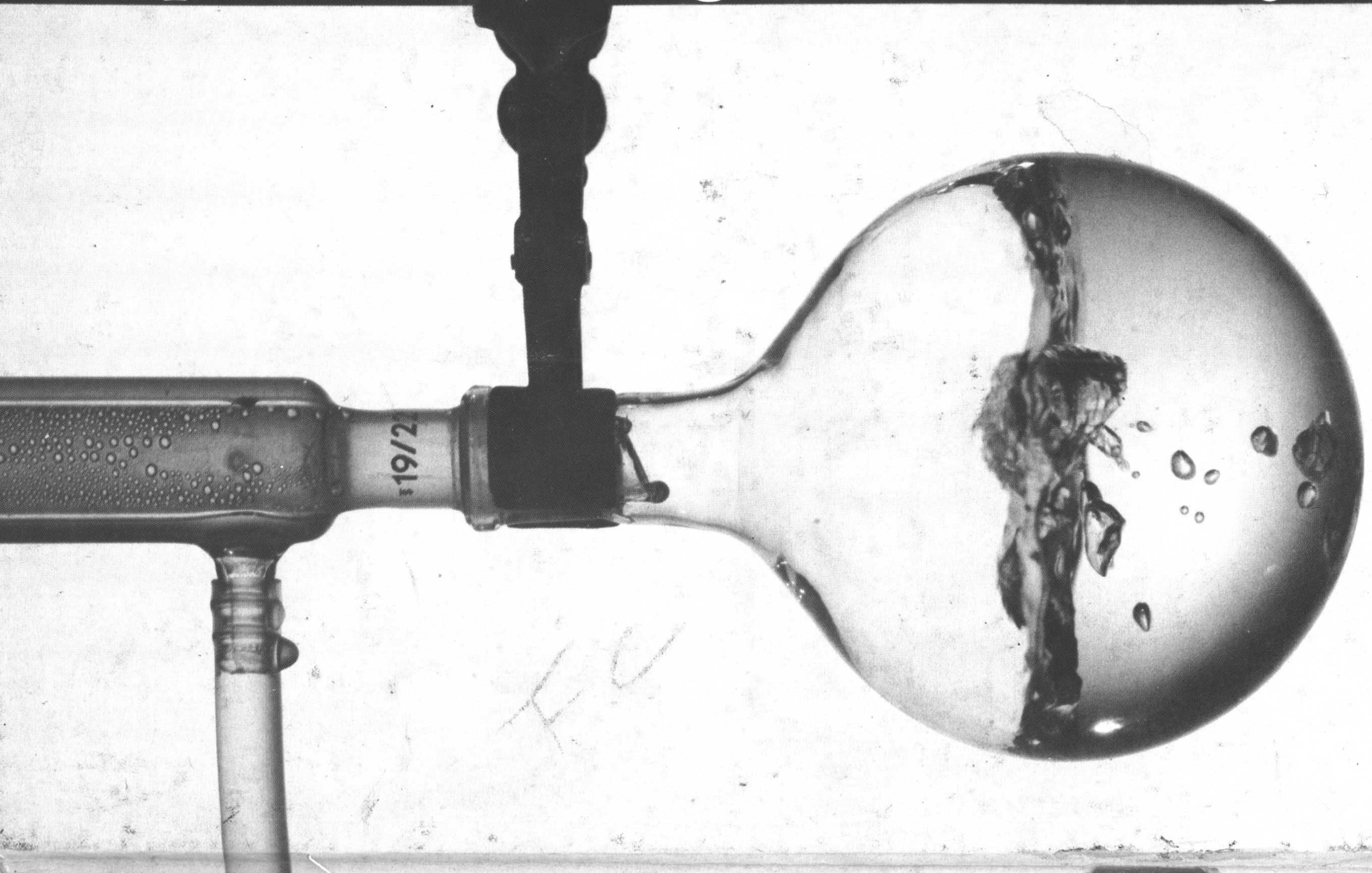

EXPERIMENTAL ORGANIC CHEMISTRY

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Preface

We have written *Experimental Organic Chemistry* to complement the teaching of organic chemistry with an effective laboratory program that introduces students to the modern methods, techniques, and experimentation of organic chemistry. We believe that the combination of workable experiments with detailed experimental background and operational information will enhance students' interest in the laboratory and enable them to perform effectively and confidently. To fulfill this goal we have designed new, but thoroughly tested, experiments that can be performed within the natural constraints of health and safety standards, time and instrument availability, and laboratory economy. Laboratory operations are thoroughly described so that students can be expected to begin their experiments knowing what they are to observe and how to direct their experiment to a successful conclusion.

Experimental Organic Chemistry consists of three sections: the introduction to basic techniques and chemical transformations (Experiments 1–20), qualitative organic analyses (Experiments 21–26), and experiments in multistep syntheses, reaction mechanisms, and modern synthetic methods (Experiments 27–40). Basic laboratory techniques are introduced during realistic laboratory operations in Experiments 1–20 and serve as the foundation for subsequent experiments. Experiments 21–26 are sequential but may be employed at any time in the laboratory program after the introduction of basic techniques. Individual experiments in the section of Experiments 27–40 are not interdependent and can be rearranged to fit the needs of organic chemistry laboratory courses at a variety of schools.

In designing experiments for this laboratory textbook we have been attentive to the sequence of topics that are normally presented in the lecture portion of the organic chemistry course. Following experiments that explain basic laboratory techniques (Experiments 1-7), we proceed to introduce students to most of the important transformations of organic compounds. Reactions with aliphatic compounds are employed until Experiment 14 to correspond with the early emphasis on aliphatic systems in the lecture course. Although we have not included an early experiment on free radical halogenation reactions for reasons of health and safety, this textbook emphasizes substitution, elimination, addition, and oxidation transformations in correspondence with most modern lecture texts.

The vast majority of experiments found in *Experimental Organic Chemistry* will not be found in other laboratory textbooks. Our experiments have been selected from those that complement the lecture program so that students can be effectively introduced to the modern practices of organic chemistry with experiments that are attentive to laboratory safety and laboratory economy. Experiments 8–12, for example, use the reaction series substitution-elimination-addition to introduce students to the basic reactions of aliphatic organic compounds including instructions for the drying of organic liquids, choices of solvents for chemical reactions, and product analyses by gas-liquid partition chromatography and infrared spectroscopy. In addition, we have selected preparative experiments that can be expected to yield the desired products when performed by students in the introductory laboratory program. As an illustration, we have designed a new synthesis of benzocaine for this textbook (Experiment 28) because of students' frustrations with their inability to isolate this compound using standard procedures found in other laboratory textbooks.

One of the unique features of this book is its extensive use of sequential experiments whereby the product of one experiment is the reactant in the next experiment. Because each of the sequential experiments employs commercially available reactants or alternate experiments, student failure to produce the desired product in one experiment does not limit continuation of the sequence. Sequential experiments describe an ultimate design that cannot be identified in singular experiments and afford lower costs for laboratory operation.

We believe that an introduction to modern instrumental analyses including those performed through infrared or nuclear magnetic resonance spectroscopy and gas chromatography should be an integral component of the organic chemistry laboratory. We have therefore designed this laboratory textbook to expose students to instrumental analyses even when access to the necessary instrumentation is limited. Chemical instrumentation is introduced to provide students with some technical understanding of how specific instruments are operated and how to interpret the results obtained. However, each instrument-oriented experiment is designed to display actual experimental results without requiring actual student operation of the instrument. For example, Experiment 10 describes a chromatogram in the detail expected for correct gas chromatographic analysis; students may analyze this chromatogram or, when such instrumentation is available, follow the Experimental Procedure for an analysis of the experimentally obtained mixture. More than 60 spectra are included to promote student familiarity with spectral analyses of organic compounds.

Laboratory techniques are introduced in sufficient detail so that students can properly employ them to achieve the desired experimental result. In addition, these techniques are introduced at places in the text where they are expected to be used. For example, the introductions to distillation at reduced pressure (Experiment 14) and sublimation (Experiment 16) are given in experiments in which these laboratory operations are employed. Prelab and postlab questions test student understanding of experimental methods and techniques.

Important laboratory operations are reinforced and amplified in subsequent experiments.

Both traditional and modern methods for the structural identification of organic compounds are employed. In each experiment where an organic compound is isolated or synthesized, students are directed to identify the product by commonly used procedures. Experiments 13 and 21–26 provide detailed methods and procedures for the identification of unknown compounds. This section of experiments rapidly introduces students to the physical properties and chemical transformations of the major functional groups encountered in organic compounds. Appendix A lists the physical properties of more than 1400 organic compounds and provides melting points for their most useful derivatives. The selection of these compounds is based on their commercial availability and cost.

We have attempted to minimize the use of hazardous chemicals and procedures in the laboratory without minimizing student exposure to important techniques and procedures. The experiments selected meet reasonable health and safety standards. Cautionary statements regarding the handling of chemicals and the operation of laboratory procedures are provided along with instructions for the disposal of waste chemicals.

Laboratory economy is emphasized in two ways: by the use of sequential experiments and the employment of relatively inexpensive reagents. In addition, we have kept to a minimum the number of different reagents and solvents that must be employed in the laboratory program. Stock solutions prepared for the organic chemistry laboratory are standardized to minimize the number of different solutions that must be available in the laboratory. Finally, solvent recovery is promoted.

We have been accustomed to using thoroughly tested workable experiments in our laboratory program and the experiments we have developed for this textbook are no exception. Several have been used in our program for more than four years, and all the experiments have been class tested by Hope College students during two successive years. Their performance in this laboratory program has surpassed our expectations, and their helpful comments have led us to expect similar effectiveness and confidence from students in the future.

Our efforts in designing these laboratory experiments and in writing this laboratory textbook have been assisted by numerous individuals. We are grateful to Richard Paske who tested many of these experiments prior to their use in the organic chemistry laboratory. The organic chemistry classes who used the preliminary editions of this textbook receive our special thanks. Their enthusiasm and encouragement made this project worthwhile.

Furthermore, we are indebted to the people who reviewed the manuscript at different stages of its development: Steven Baldwin (Duke University), Edward L. Biersmith (Northeast Louisiana University), Kenneth G. Hancock (University of California, Davis), John R. Holum (Augsburg College), Evan Kyba (University of Texas, Austin), P. W. Le Quesne (Northeastern University), Anthony LoTempio (Broome Community College), John Meisenheimer

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The efforts of Wiley personnel, particularly our editor Gary Carlson, receive our sincere thanks.

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Introduction

The laboratory portion of the organic chemistry course lays the foundation upon which the basic principles of this experimental science can be understood. Organic chemistry has developed from experimental observations made in the laboratory. These observations have been summarized, tested, and correlated with related experimental information to form the basis of chemical theories and principles. By following the procedures in this manual and *observing the chemical changes and operations* involved, you will participate in the development of organic chemistry and better understand the basic principles of this experimental science.

Organic compounds have characteristic physical properties. They are gases, liquids, or solids. Some are classified as acids or bases. Certain organic compounds are soluble in water, but most are insoluble in this most common solvent. Because of the wide spectrum of their physical properties, organic compounds require a variety of techniques both for their isolation and purification and for their chemical transformations. Your success in this laboratory is dependent on your awareness of the physical properties of the compounds with which you are working, particularly their melting and boiling points, solubilities, densities, colors, and odors. *Laboratory techniques* for organic chemistry that include extraction, crystallization, distillation, reflux, and chromatography are based on the physical properties of organic compounds and are integral components of this laboratory program.

You will be required to identify the compounds you isolate or prepare. There are currently several million known organic compounds. The exact identification of any one of these compounds requires specific information concerning its source and its chemical and physical properties. In this laboratory course you will be introduced to the methodology for the *characterization* of organic compounds and for their *structural identification* by spectral means.

Your ability to observe chemical changes and your understanding of the changes that occur will be tested in the organic chemistry laboratory. Consequently, *you must thoroughly read the laboratory experiment and fully understand the laboratory procedure before you enter the laboratory.* Your success and safety in the laboratory is dependent on your awareness of the procedures you intend to employ and on the materials you plan to use.

Safety in the Laboratory

Standard safety practices are an essential part of all laboratory operations. The chemicals you employ in this laboratory are usually flammable, some are irritating, and many possess known or as yet undetermined toxic characteristics. Although the experiments you perform in this laboratory manual have been designed for safe operation, you should be prepared for any eventuality. Accidents in the organic chemistry laboratory can be avoided if you enter the laboratory properly prepared for the experiment, if you use good sense in reacting to unexpected situations, and if you rigidly follow basic safety rules that are enforced to ensure your personal safety.

RULES FOR YOUR PERSONAL SAFETY

1. **Wear safety glasses or other eye protection in the laboratory at all times.** Normally eyeglasses with safety lenses can be used, but goggles or safety glasses with side-shields are the better protection. Contact lenses do not protect your eyes. In fact, wearing contact lenses in the laboratory may result in eye irritation due to fumes in the air, since the eye cannot rapidly cleanse itself when the contact lens is in place.
2. **Never work alone in the laboratory.** The presence of another person in your laboratory in the event of a serious accident may save your life. You may work in the laboratory only during authorized times.
3. **Acts of carelessness, including those done in jest, endanger the safety of laboratory participants and are strictly prohibited.** Be aware of what others around you are doing; your safety also depends on their care in performing laboratory operations.
4. **Eating, drinking, or smoking in the laboratory is prohibited.** Laboratory chemicals that may have toxic properties dissolve in foods kept in the laboratory. Smoking represents a serious fire hazard.
5. **Keep your work area neat and uncluttered. Cleanup chemical and water spills at once. Unplug electrical equipment and turn off water and gas outlets when not in use.** If a chemical spill occurs and you are unfamiliar with the safe cleanup procedure for that chemical, immediately contact your laboratory instructor for assistance.
6. **Learn the location and proper use of fire extinguishers, fire blankets, safety showers, and eyewashes.**
7. **Avoid skin contact with chemicals.** If you spill a chemical on your skin, immediately wash the affected area with soap and water. Do not touch your face after handling chemicals; wash your hands after coming into contact with chemicals and chemical containers; and always wash your hands before leaving the laboratory. Rubber gloves should be worn when handling skin irritants.
8. **Do not heat an assembly of laboratory apparatus that is closed to the**

atmosphere and do not close an assembly of laboratory apparatus in which a gas is being evolved. Pressure buildup can cause serious damage. Always check your laboratory apparatus before you begin an experiment to ensure that the system is properly vented.

9. **Do not use flames in an unventilated laboratory area and never produce a flame near containers of flammable compounds.** Although you may be required to use a Bunsen burner to heat organic liquids for distillation in several laboratory experiments, the use of a flame for heating is to be avoided unless absolutely necessary.
10. **Maintain a familiarity with the general physical properties, fire hazards, and toxicities of chemicals that are stored in the laboratory.** Be prepared to react immediately to accidents to yourself or to your neighbor. Always inform your laboratory instructor immediately of any accidents, unexpected occurrences in the laboratory, or physical irritation due to exposure to chemicals.

The most common injuries incurred in the laboratory include cuts from broken glassware, burns from hot glassware or metal, and chemical burns on the skin or in the eyes. *To avoid cuts from broken glass tubing or thermometers, you should lubricate the tubing or thermometer with a drop of glycerine or water before insertion into a rubber or cork stopper and protect your hands with a cloth towel.* In the event of personal injury from cuts or burns, your instructor should be notified immediately and the following procedures should be adopted:

Cuts. If the cut is not serious, wash the affected area with water and dilute soap solution. If bleeding is serious, direct pressure with a clean, preferably sterile, dressing should be applied, and a physician should be contacted.

Heat Burns. Minor burns, where the tissue is not charred, can be treated by flushing with cold water. Serious burns should be treated by a physician.

Chemical Burns. Chemicals on the skin or in the eyes should be flushed with large amounts of flowing water from an eyewash. A physician should be contacted immediately in the event of eye damage.

Strong acids and bases damage skin tissue and may cause severe chemical burns if not immediately washed from the skin with copious amounts of water. These chemicals should always be handled with extreme care, and suitable procedures for their use that include (a) pouring the reagent from the laboratory container into a beaker or flask for subsequent volumetric or weight measurement and (b) always pouring acid into water, never the reverse, should always be employed.

Lachrymators are chemical substances that produce eye irritation and generally cause the production of tears. These chemicals, which are also referred to as "tear gases" when used in aerosol sprays, must be used only in well-ventilated areas and, preferably, in a fume hood. Although a short exposure to small amounts of lachrymator does not generally cause eye damage, a burning sen-