Basic Experimental ORGANIC CHEMISTRY

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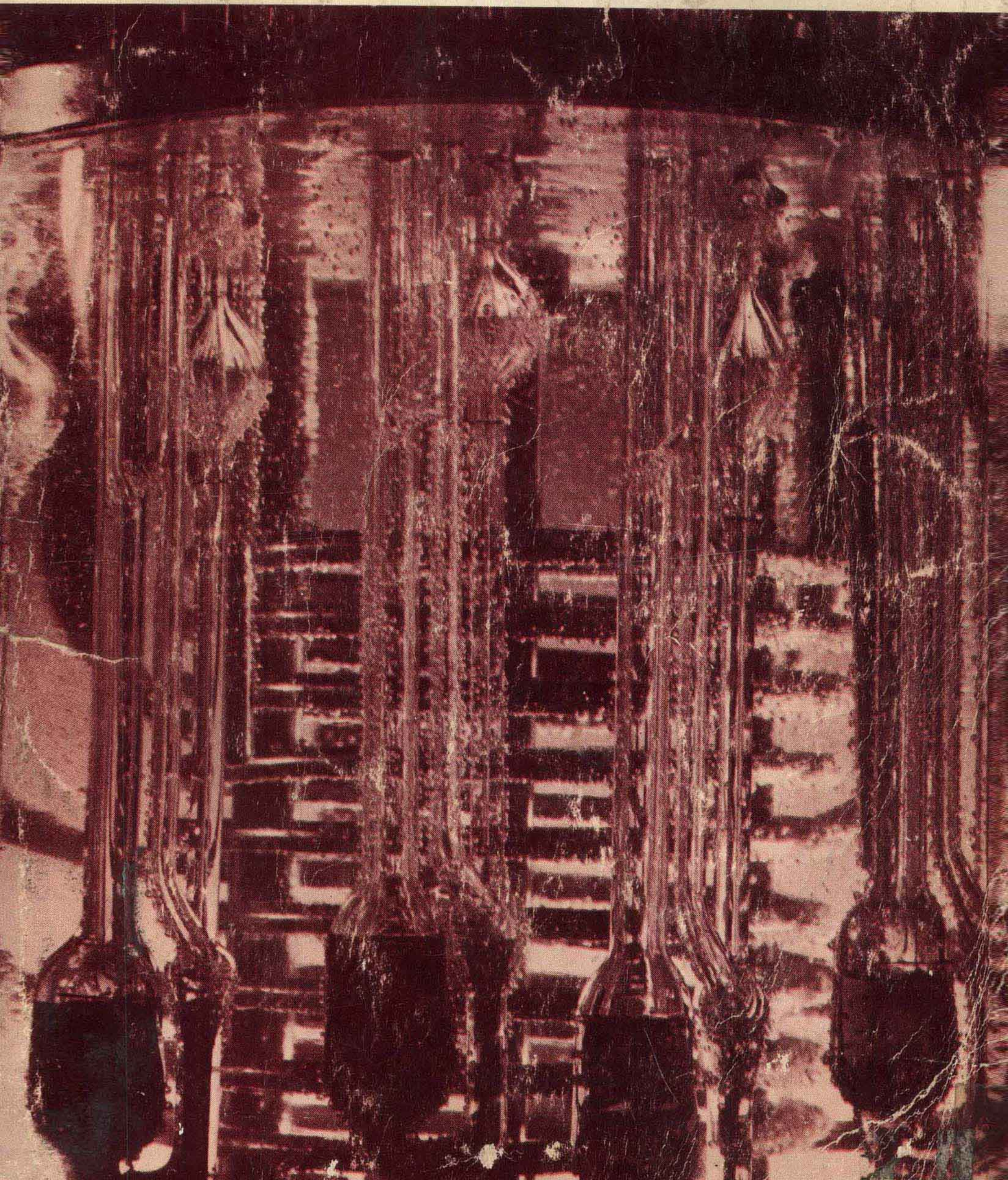

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Preface

The experiments described in this book have been developed in connection with the teaching of general organic chemistry at the University of California at Berkeley. The number of experiments is considerably in excess of those normally performed in a two-semester course involving about sixty 3-hr laboratory periods; therefore some choice of experiments is offered. Naturally, experiments may be selected for use in a one-semester course. The contents of this book have also been published as Part I of the two-part *Laboratory Text in Organic Chemistry;* therefore, some references to Part II occur. Part II of the two-part book, entitled *Advanced Techniques and Synthesis*, is designed for use in an advanced course in organic preparations, and to serve as an introduction to the techniques used in research in organic chemistry. The original figure numbers (68–71) have been retained for the illustrations in Appendix I of economical designs of ground-jointed equipment.

The authors feel that the prime function of laboratory work in general organic chemistry is the teaching of the techniques, skills, and philosophies involved in the synthesis, purification, and identification of organic compounds. Illustration of lecture material is delegated to a secondary position, and is introduced only as a part of experiments designed primarily to contribute toward the accomplishment of the principal objective stated above. For these reasons, a majority of the experiments are concerned with a study of important techniques or a study of synthetic methods. "Test-tube experiments" are confined, for the most part, to brief tests made on compounds synthesized by the students, except for the introduction to separation and characterization of organic compounds offered in Chapter 29. Further, synthesis on a "semimicro" scale has been carefully avoided, for the authors feel that this type of work teaches the student very little about handling quantities of materials. Sufficient training in manipulation of small amounts should be acquired during the work in separation and identification of organic compounds (Chap. 29).

Inclusion of a scheme for separation and identification of organic compounds is a major innovation in this book. Incorporation of this type of work in the introductory course has proved quite satisfactory. Indeed, it has been found especially useful in the one-semester course, for it is of direct interest to premedical and other biology-oriented students who take the brief course. A total of ten or twelve 3-hr laboratory periods, at the end of the course, is recommended for the work on identification.

Some of the experiments in this book are similar to those found in other laboratory manuals, but a major portion of the experiments have been developed or considerably modified in this laboratory. So far as is consistent with cost of materials, the lowest molecular weight compounds have been avoided, for the properties and methods of synthesis of these compounds are usually not typical of the series as a whole. A unique feature is the inclusion of several heterocyclic preparations adaptable to the elementary course. This seems especially appropriate, in view of the increased importance of heterocyclic chemistry.

Major emphasis has been placed on development of detailed directions that are accurate and reliable, for it is felt that this is necessary for proper instruction at the elementary level. Experiments that "don't work" destroy the student's interest and undermine his confidence in the worth of the course. Most of the experiments have been performed by the authors, and all have been performed by many hundreds of students, under close observation by the authors. It is believed that the procedures have been modified until all the hazards and pitfalls have been either eliminated or properly recognized and described. It is also believed that there have been ferreted out most of the clever devices by which students can follow the directions without getting the same results as would be obtained by an experienced chemist.

The procedures described in this book are limited to those appropriately performed with simple equipment. The wording of the directions is such that the experiments may be performed satisfactorily in laboratories where steam outlets are not available on the student benches, and where sufficient hood space is available only for brief mixing or transferring operations. Certain simple and inexpensive items of equipment which are used are very convenient but not commonly described in elementary laboratory manuals. For convenience, these items are illustrated in the text, and the stock equipment used for the student lockers is described in the Appendix. As a part of this locker equipment for the elementary course, there are described certain pieces of glassware, equipped with ground joints, which cost no more than twenty-five dollars per locker (about fifteen dollars more than the alternate equipment it replaces). This relatively modest investment allows performance of most of the manipulations without boring of corks or stoppers; however, an alternate list of equipment without ground joints is also presented.

Advanced manipulations that require expensive equipment, such as mechanical stirring, distillation at reduced pressure, and fractional distillation through an efficient column are not included in these experimental procedures. A deliberate effort has been made to avoid types of preparations that cannot be performed adequately in an elementary course. For example, no Grignard reaction appears, for a student who performs this experiment on a small scale without mechanical stirring is likely to acquire a serious misconception of how a research worker carries out such reactions in high yield. Such manipulations as are required for proper execution of the Grignard and related reactions are described in Part II of the two-part book. Similarly, only a simple type of Friedel-Crafts reaction is described in this book, whereas more complicated types are described in Part II. Such a distribution avoids the necessity for a student's "unlearning" a part of the material learned in his elementary course.

In the Introduction, there are recommended certain procedures for the operation of an elementary laboratory course in organic chemistry. These recommendations are offered as a suggestion or a point of departure, and not without an awareness that a teacher of this course is likely to develop his own methods, based on his personal experience and local conditions. Some of the methods described are somewhat original, however, and may be of interest to other instructors and to students. These have evolved from experience in the handling of relatively large classes, with the help of one graduate teaching assistant for each 20 to 25 students in the class.

The authors gratefully acknowledge the substantial assistance received in preparation of this book from their many colleagues who have taught the elementary course at Berkeley. We are indebted to the many students in Chemistry 129 and Chemistry 185 who did most of the experimental work involved in the development of new experiments. The original illustrations, many of which have survived revision, as well as the new illustrations in the revised edition, were prepared by Dr. William L. Stanley, of the U.S. Department of Agriculture Laboratory, Albany, California. We are also indebted to Professor Herbert O. House, of the Massachusetts Institute of Technology, for his careful and helpful review of the manuscript.

J. C.
H. R.

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Basic Experimental Techniques and Procedures

1

Introduction

THE EXPERIMENTS IN PART I of this laboratory text are designed to accompany the lecture material in an elementary course in organic chemistry; however, illustration of lecture material is only a minor function of these experiments. The purpose is more concerned with expansion and extension of lecture material, and, above all, with teaching the techniques, skills, and philosophies involved in carrying out experimental work in organic chemistry. These objectives should be borne well in mind as the experiments are performed.

Since thoughtless performance of the experiments rapidly degenerates into routine following of a prescription, as from a cookbook, with the chemicals receiving more exercise than the student, it is an advantage to reserve the beginning of each week's laboratory period for quiz or discussion. Periodic, short quizzes are effective devices for stressing the important principles involved in the experiments. The discussions are of value for emphasizing and clarifying these same principles, demonstrating any new techniques or apparatus, and pointing out physical hazards, if any, involved in the particular experiments. Study of the experiment prior to performance is further encouraged by the requirement that a major portion of the notebook write-up be completed and approved before the starting material for the experiment may be secured. This latter matter is discussed in detail below, under "Notebooks and Reports."

Experiments are graded on the basis of the quality and quantity of the product, the technique, and the notebook write-up; hence, due attention should be directed to all of these aspects of the work. Final reports on the completed experiments are due at specific times noted on a schedule issued at the start of each semester. Points are deducted, of course, if the reports are late. The laboratory portion of the total grade for the course is the summation of the scores on the experiments, the short quizzes, and a laboratory examination given during the last period of the semester.

The first four experiments consist of nonpreparative exercises designed to acquaint the student with the apparatus and techniques used in carrying out the subsequent preparations, and, especially, in isolating and purifying the products. Except for the final chapter in Part I, the remaining experiments are almost entirely of a preparative type, the making of organic compounds. In each chapter, there is followed a uniform pattern which involves discussion of (a) the main reactions, (b) the side reactions, and (c) the purification procedure used for isolating the product. This approach has as its objective familiarizing the student with the principles involved so that he will be less prone to follow the directions without any conception of the significance of the operations; furthermore, it furnishes a background for the explanations of the ratios of reagents specified and the choice of synthetic method. The final chapter in Part I is devoted to an introduction to the study of methods of separating and characterizing organic compounds. These topics are of sufficient importance that an advanced course is frequently devoted entirely to their study; however, an introduction to the methods used is in order in the elementary course.

NOTEBOOKS AND REPORTS

For reporting experiments, a bound notebook of approximately eight and one half by eleven inches is used. When an experiment is completed, and the notebook write-up is completed, the notebook is presented to the laboratory instructor, who checks it and may ask questions concerning the experiment. The form in which the notebook report is made will depend on whether the experiment is *preparative* or *nonpreparative.*

Nonpreparative experiments. In this type of experiment, no pre-write-up is required; that is, no entries are made in the book before the experiment is performed. As the experiment is performed, a record of observations made, including any specified tables, is entered in the notebook. In case any tests involving chemical reactions are performed, balanced equations for these reactions must always be included in the write-up. When the experiment is reported, the instructor checks and initials the notebook.

Preparative experiments. These experiments are reported in a formal manner as described below, and *all entries up to and including the* *calculation of theoretical yield* must be in the notebook before the experiment is begun. The experiments are written up in several sections, and, of these sections, those numbered I–III appear on the *left-hand page,* and those numbered IV–VII appear on the *right-hand page.* Thus, the essential data pertaining to a given preparation are on a double page in the notebook.

Left-hand page:

I. Main reactions
II. Side reactions
III. Other methods of preparation

Right-hand page:

IV. Table of reactants and products (illustrated under ethyl iodide, Chap. 6)
V. Yield data
  Theoretical yield
  Actual yield
  Percentage yield
VI. Observed properties of product (melting point, boiling point, color, crystal form, and so on)
VII. Description of short experiments or tests (including equations for any reactions)

After the notebook has been written up as far as calculation of theoretical yield, it is presented to the laboratory instructor, who checks and initials it. The approved notebook must then be presented at the storeroom in order to obtain one of the starting materials for the experiment. After the preparation has been completed, the write-up is completed, and the experiment is reported to the laboratory instructor, who initials it. At this time, the material prepared is also given to the instructor, in a labeled bottle (widemouthed bottle for solids, narrow-mouthed, glass-stoppered bottle for liquids). On the label is printed the name of the substance, its melting point or boiling point, the actual and percentage yields, and the student's name. An illustration of a properly prepared label follows.

ETHYL IODIDE B.P. 69–72° YIELD 27.6 g (75.2%) FRANCISCO GOMEZ

SAFETY PRECAUTIONS

Although many things are involved in good technique in the organic laboratory, certain things are fundamentally important and should always be borne in mind. These are listed below in two categories: *important points* and *very important points.* Violation of the important points is likely to lead to poor technical results and possibly to minor injury, whereas violation of the very important points may lead to permanent or fatal injury. In order to encourage the student to respect these points, the instructors keep a record of each student's violations, and this record is considered in determining the student's final grade for the course.

Very important points. 1. Never heat inflammable solvents, even in small amounts, with *or near* a flame unless the solvent is in a flask under reflux or attached to a condenser for distillation. Do not pour inflammable solvents from one vessel to another when a flame is near (within three feet).

2. When ether (diethyl ether) is being distilled, heat on a water bath and use as a receiver an ice-cooled distilling flask attached to the condenser with a sound cork.

3. Never use carbon disulfide except with specific authorization and instructions.

4. Never heat a closed system of any kind.

5. It is not regarded as discreet to heat or mix *anything* close to the face. Keep the face as far back as possible during *all* heating or mixing operations. A *special alert* should be maintained against violation of this very important point, for it is instinctive to hold a vessel directly in front of the face when pouring into it, especially if a volume is being measured.

6. Never work in the laboratory except during a regular period when an instructor is present. Any exceptions to this must be specifically authorized in writing by the *instructor in charge of the course.*

7. *Everyone* in the laboratory, including teachers, must wear some type of eye glasses at all times, and this applies equally to those who are, and those who are not, doing actual experimental work at a given moment. Ordinary glasses are regarded as sufficient for routine wear, since they will nearly always prevent damage to the eyes that might result unexpectedly in elementary laboratory work. In case experiments involving known hazards, especially hazard of explosion, are being undertaken, either a complete face shield or goggles equipped with safety glasses and side shields should be worn.

Important points. 1. Keep your working space neat at all times and clean when you leave for the day. Neatness is good technique, and technique is one of the things on which a student is graded.

2. Avoid unstable assemblies of apparatus, such as props consisting of books, pencils, matchboxes, and the like. Assemblies with a high center of gravity (as when a reagent is added through the top of a condenser) should be assembled and operated with extreme caution.

3. In boring corks, use the cork borer as a cutting instrument, not as a gouging instrument. Do not bore against a piece of wood, such as the top or sides of the desk.

4. In forcing glass tubing through a cork or stopper, do not use any part of the anatomy as a backstop for the tubing because it might break. When pushing the cork, hold the tubing very close to the cork. Whenever possible, *pull* the cork on. Never push a cork on the sidearm of a distilling flask while holding the flask; hold the *sidearm* close to the cork.

When forcing a rubber hose on a glass tube, always moisten the tube with glycerol or smear it very lightly with silicone grease. This makes the hose slip on easily.

5. A flexible metal spatula is usually recommended for breaking up caked solids in bottles. Do not use a glass stirring rod, for it is likely to break and cause injury. Do not use a tool sufficiently heavy and rigid to easily break the bottle, for this also may result in injury.

6. An Erlenmeyer flask is commonly used for crystallization. Never crystallize from a beaker unless specifically directed to do so.

7. Do not place volatile solvents in a beaker, even for short periods of time.

8. Taste nothing in the laboratory unless specifically directed to do so.

9. Never assemble apparatus over a sink or deliver distillate into a sink.

10. Do not evacuate a flat-bottomed flask unless it is a heavy-walled suction flask. Erlenmeyer flasks are especially likely to collapse.

11. Materials that give off noxious fumes should be handled in a forced-draft hood. Such materials include phosphorus trichloride, bromine, chlorosulfonic acid, benzenesulfonyl chloride, fuming nitric acid, acetyl chloride, and others.

12. Use care in disposing of hazardous chemicals, whether residual lots or unused lots. This applies especially to substances reacting violently with water, such as sodium metal, acetyl chloride, and chlorosulfonic acid. Poisonous, water-soluble substances, such as potassium cyanide, should be put directly into a drain and washed down thoroughly. Concentrated sulfuric acid should be added to water, not vice versa.

If the above points are ignored, it is wise to read the following paragraphs with particular care.

IN CASE OF ACCIDENT

The most common minor accident is that of cutting the hand with glass tubing. Such a cut is ordinarily treated by applying an antiseptic and bandaging. However, this kind of cut may need special attention. If the rate of blood flow indicates that an artery or vein has been cut, a tourniquet should be put on the arm at once and a physician consulted. If the forearm or hand has been seriously cut, and control of one or more fingers has been lost, a tendon has probably been cut and a physician should be consulted at once. It is best to have a physician examine any deep cut for glass, but this is especially indicated if the cut is sensitive to pressure, or if the piece of glass was shattered.

In case of *fire*, the student's first concern should be to remove himself from danger. In no case should a hasty effort be made to extinguish the fire before it is noticed by an instructor. This is a good way to get the clothing on fire. Only after one's own safety is assured should the matter of extinguishing the fire be considered. Since all laboratories should be adequately equipped for fighting fire, the only hazard is to the people in the vicinity of the fire. If the clothing does catch fire, it is imperative that the person not run, but that he lie on the floor and smother the flames. Among other things, this keeps the flames away from the head. When a person's clothes are on fire, he usually needs help from his neighbors or the instructors in smothering the flames with a fire blanket, a coat, or anything that can be seized instantly. Because a few seconds' delay can result in very serious injury, every person in the laboratory should plan in advance what he will do in case of such an emergency to himself or his neighbor.

If corrosive or hot reagents get into the eyes, the most important thing is to flood the eyes *immediately* with water. As soon as the outsides of the eyes are well washed, the eyes should be forced open and irrigated with plenty of water. This should be continued for at least two or three minutes. Then a bland oil should be put into the eyes, and a physician consulted as quickly as possible. Delay at this point is especially hazardous. Each student should locate the water outlet nearest his desk which is suitable for eye washing and fix its position so well in mind that he can find it with his eyes shut.

The general treatment for corrosive reagents on the skin is immediate, thorough scrubbing with soap and water, followed by massage with glycerine. For most chemical burns, it is very poor policy to apply a burn ointment. Such preparations usually contain grease, and this helps the reagent to penetrate the tissue.

2

The Melting Point

THE PHYSICAL PROPERTIES of a substance, such as color, odor, crystalline form, melting point, and boiling point, are useful characteristics for recognizing and identifying organic compounds. For solid substances, by far the most important characteristic is the melting point. It may be determined rapidly and accurately, using simple apparatus and small samples of material, and it furnishes reliable information as to the compound's identity and purity. This combination of ease and significance makes a melting-point determination exceedingly useful for recognizing a known compound and characterizing a new one.

The manner in which a melting point indicates a compound's purity and identity is an important consideration which should be well understood by a student of organic chemistry. The *melting point of a substance is defined* as the temperature at which liquid and solid may exist in equilibrium with each other. In other words, at this temperature the escaping tendency of molecules from the solid phase is just equal to the escaping tendency from the liquid phase. When the solid and liquid are in contact, molecules are constantly passing from solid to liquid phase and vice versa, but there is no net change in the amount of each phase unless heat is added to or taken from the system. When molecules pass from the solid state to the liquid state, heat is absorbed (heat of fusion); therefore, if heat is put into the system some of the solid melts, and if enough heat is added all the solid will melt. Conversely, if heat is removed from the system some of the liquid crystallizes, or freezes, and if enough heat is removed all the liquid will freeze. Thus, the melting point and freezing point are the same temperature. Finally, it should be pointed out that, as heat is slowly removed from the system, the tem-