laboratory text for

organic chemistry

A SOURCE BOOK OF CHEMICAL AND PHYSICAL TECHNIQUES

daniel j. pasto/carl r. johnson

Preface

This text has evolved from a previous book, *Organic Structure Determination* (OSD), by the same authors. *OSD*, first published in 1969, has continued to be widely used. In its first few years, the most significant utilization of *OSD* was as a text and lab manual for modern variations of a traditional course in organic qualitative analysis. Over the years, many schools have phased out separate courses in this subject and integrated the material, in part, into various other courses, especially beginning organic laboratory courses and lecture courses on spectroscopic methods in organic chemistry. In the last several years, a number of schools have used *OSD* as a core text for the organic laboratory. Although the authors did not specifically design the book for this purpose, it appeared to serve very well. Now with multiple purposes in mind we have revised *OSD*. We believe that we have provided a textbook of exceptional versatility, a textbook that will serve the student in a variety of classes beginning with the introductory organic laboratory and continuing through the first year of graduate school and thereafter as a reference book.

In the present text, Part I provides a detailed discussion on background material and specific instructions on techniques used in running chemical reactions, isolation and separation of products, and characterization of organic compounds. Part II provides a thorough introduction to the major spectroscopic methods used by the organic chemist. Part III integrates spectroscopic and chemical methods used in organic qualitative analysis. Tables of physical properties and derivatives of many common organic compounds are included, as is a chapter on searching the chemical literature.

This book has been written with the following applications in mind:

1. *An undergraduate organic laboratory textbook.* The key ingredients that are missing are the actual experiments. There are none of the traditional melting point, distillation, extraction, simple synthetic transformations, etc., experiments that are available in the scores of laboratory manuals on the market! Why not? Almost without exception, when a traditional laboratory manual is adopted, a significant percentage of the experiments performed are from "handouts." There are two main reasons for this. First, each school's facilities and equipment pose special limitations and/or unique advantages. Second, each teacher or group of teachers have their own favorite experiments. The use of relatively few experiments in a given manual and the duplication of descriptive chemistry found in any modern organic text makes the usual laboratory manual a rather poor investment for the student.

With the present text plus an organic textbook, the students have the necessary information on background and techniques to do any experiment that they are likely to be assigned. For each experiment, the students will require a handout giving specific instructions in as much detail as is appropriate along with references to theories and techniques provided in this text and their organic text.

2. *A textbook for a senior or first-year graduate course in organic applications of spectroscopy.* Part II discusses uv, ir, proton and carbon-13 magnetic resonance spectroscopy, and mass spectrometry at a level appropriate for a survey course. Numerous spectra and tables of spectral data are provided. Part III correlates the various spectral methods plus chemical tests for the identification of organic compounds. This book and a spectral problem workbook would be ideal for a survey course in organic spectroscopy.

3. *A textbook for a modern qualitative organic analysis course.* This text integrates spectroscopic methods with chemical methods for the identification of organic compounds. Nineteen tables of data on physical properties and derivatives are included.

4. *A reference book for the practicing organic chemist.*

To all who have helped with the preparation and production of this book we express our deep gratitude. We thank those users of *OSD* who provided perceptive criticisms and suggestions. We are indebted to Professor Maurice Shamma of Pennsylvania State University, Professor Leon Stock of The University of Chicago, and Professor Christopher S. Foote of the University of California, at Los Angeles, who reviewed this text. Don Schifferl of the University of Notre Dame kindly recorded various FT-NMR spectra. Our thanks go to the Prentice-Hall staff, particularly Linda Mihatov, who ably guided the book through production.

The authors would be pleased to receive corrections, comments, and suggestions from our users for improvement of later editions.

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OSHA TENTATIVE LIST OF CARCINOGENS

The Occupational Safety and Health Administration (OSHA) has issued a list of chemicals for which there is some evidence of carcinogenicity. *Special care should be taken to minimize exposure to these substances.* The list that follows contains compounds selected from the complete OSHA tentative Category I carcinogen list (*Chemistry and Engineering News*, July 31, 1978, p. 20) on the basis of their common occurrence in organic laboratories. Of particular importance is the appearance of the solvents *benzene, carbon tetrachloride, chloroform*, and *dioxane* on the list. In many procedures toluene can be substituted for benzene and dichloromethane can be used in place of chloroform or carbon tetrachloride. Tetrahydrofuran or 1,2-dimethoxymethane can often replace dioxane.

Compounds Selected from the OSHA Tentative Carcinogen List

Acetamide
Asbestos
Aziridine
Benzene
Benzidine
4-Biphenylamine
Bis(2-chloroethyl) sulfide
Bis(chloromethyl) ether
Carbon tetrachloride
Chloroform
Chromic oxide
Coumarin
Diazomethane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dimethyl sulfate
p-Dioxane
Ethyl carbamate
Ethyl diazoacetate
Ethyl methanesulfonate

1,2,3,4,5-Hexachlorocyclohexane
Hydrazine and its salts
Lead(2+) acetate
Methyl methanesulfonate
N-Methyl-*N*-nitrosourea
4-Methyl-2-oxetanone
1-Naphthylamine
2-Naphthylamine
4-Nitrobiphenyl
1,2-Oxathiolane 2,2-dioxide
2-Oxetanone
Phenylhydrazine and its salts
Polychlorinated biphenyl
Thioacetamide
Thiourea
o-Toluidine
Trichloroethylene
Vinyl chloride

General classes of compounds for which the carcinogenic risk is apparently high include:

—Alkylating reagents
—Arsenic and its compounds
—Azo compounds
—Beryllium and its compounds
—Cadmium and its compounds
—Chromium and its compounds
—Estrogenic and androgenic steroids
—Hydrazine derivatives
—Lead(II) compounds
—Nickel and its compounds
—Nitrogen mustards (β-halo amines)
—*N*-Nitroso compounds
—Polychlorinated substances
—Polycyclic aromatic amines
—Polycyclic aromatic hydrocarbons
—Sulfur mustards (β-halo sulfides)

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Laboratory Text for Organic Chemistry

a source book of chemical and physical techniques

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ORGANIC LABORATORY TECHNIQUES

part I

1 Introduction to the Organic Laboratory

1.1 SUCCESS IN THE ORGANIC LABORATORY

The first step to success in an organic laboratory course is to be prepared *before* you enter the laboratory! Carefully study each experiment before you come to the lab. Outline in a schematic way in your laboratory notebook (Sec. 1.4) the reactions and/or operations you are expected to carry out. Include in your outline a sketch or brief description of any special apparatus that will need to be assembled. When you enter the lab, you should be prepared to begin your experimentation both rapidly and efficiently. The organic chemistry laboratory is perhaps the most expensive space on a square-foot basis that you will occupy during your academic studies. Laboratory time is valuable and limited. The laboratory is neither the time nor the place to be wondering about what to do or to be reading an experiment for the first time!

The second step to success is to be aware of *what* you are doing and *why* at all times. There is nothing more frustrating to the laboratory supervisor nor more humiliating to the student than to have conversations such as the following occur:

SUPERVISOR: What reaction are you running now?

STUDENT: Uh—I don't remember—just a second, let me look in my laboratory instructions.

Such students are not likely to become accomplished chemists, surgeons, or cooks.

Neatness and organization are important. Keep your laboratory area and locker neat and organized. Keep your glassware clean (Sec. 1.6) and ready to use.

Use odd moments—while a reaction mixture is refluxing or a solution filtering, etc.—to clean up your glassware. It is especially important that you allow enough time at the end of each session to clean your equipment so that you may begin experimentation promptly in the next session.

Record your operations and observations in your laboratory book as you go along. Observe good safety practices at all times (Sec. 1.2).

1.2 LABORATORY SAFETY

As in most things we do, there is a certain risk associated with working in an organic laboratory. This risk may be immediate—toxic effects of chemicals, fire, explosions, burns by highly acidic or caustic materials, cuts by broken glassware—or insidious—exposure to chemicals that may cause allergic reactions or may be carcinogenic. Since there is no substitute for hands-on experience in the organic laboratory, risks must be minimized by strict adherence to safety practices.

The first thing a chemist should do when beginning work in a new laboratory is to learn the locations and methods of use of the emergency facilities:

exits	fire blankets
eye wash facilities	gas masks
fire extinguishers	first aid supplies
safety showers	

Of equal importance is knowing how to secure help fast when it is needed.

1.2.1 Eye Protection

1. Wear recommended safety glasses or goggles at all times in the laboratory. If you normally wear prescription lenses, consult with your instructor as to their suitability. (Contact lenses are *not* eye protection devices; in fact, in an accident they may increase the degree of injury to the eye. It is recommended that contact lenses not be worn in the laboratory or that full eye protection be used in conjunction with them at all times.)
2. Never look directly into the mouth of a flask containing a reaction mixture, and never point a test tube or reaction flask at yourself or your neighbor.
3. Avoid measuring acids, caustics, or other hazardous materials at eye level. Place a graduated cylinder on the bench and add liquids a little at a time.

1.2.2 Fire

1. Use flames only when absolutely necessary. Before lighting a flame, make sure there are no highly flammable materials in the vicinity. Promptly extinguish any flame not being used.

2. Learn the location and use of fire extinguishers. For wood, paper, or textile fires, almost any kind of extinguisher is suitable. For grease or oil fires, avoid the use of water extinguishers—they simply spread the burning material. For fires involving electrical equipment, use carbon dioxide or dry chemical extinguishers. For fires involving active metals or metal hydrides, use dry chemical extinguishers or sand.

   To put out a fire, first cool the area immediately surrounding the fire with the extinguishers to prevent the spread of the flames; then extinguish the *base* of the blaze. Remember to aim the extinguisher at the base of the fire and not up into the flames.
3. When clothing is afire, the victim should not run any distance. This merely fans the flames. Smother the fire by wrapping the victim in a fire blanket. Use a coat or roll the victim on the floor if a fire blanket is not readily available, or douse the flames under the emergency shower.

1.2.3 Handling of Chemicals

1. Be cautious at all times when handling chemicals, especially those about which you know little.
2. Work in the hood as much as possible. Keep chemical vapors, particularly of solvents, to a minimum in the laboratory. Handle all chemicals that produce corrosive, toxic, or obnoxious vapors in an efficient hood.
3. Avoid direct contact with organic chemicals. Use plastic or rubber gloves when handling hazardous materials.
4. A lab coat or apron can protect you as well as your clothing.
5. Handle compressed gas cylinders with care. Always move them with a cart and strap them in place.
6. Never pour large quantities of volatile solvents into the sink.
7. Use special precautions with sealed glass vials of hazardous materials. Never subject a sealed glass container to severe thermal shock, e.g., do not place a commercial vial of methylamine, etc., into a Dry Ice bath.
8. Never use your mouth to pipette dangerous liquids. Always use a rubber safety bulb for pipetting.
9. When working with any potentially dangerous reaction, use adequate safety devices—safety shields, gloves, goggles, etc.
10. Do not smoke, eat, or drink in the laboratory.

1.3 FIRST AID

Although severe injuries seldom occur in the chemistry laboratory, it is wise for all chemists to be familiar with such important first-aid techniques as stoppage of severe bleeding, artificial respiration, and shock prevention. Why not consult a first-aid manual today?

1.3.1 Treatment of Chemical Injuries to Eyes

The most important part of the treatment of a chemical injury to the eye is that done by the victim himself in the first few seconds. Get to the eye wash fountain or any source of water immediately, and wash the injured eye thoroughly with water for at least 15 min. Thorough and long washing is particularly important in the case of alkaline materials. A physician should be consulted at once.

1.3.2 Burns from Fire and Chemicals

Chemical burns of all types should be immediately and thoroughly washed with water. Ethanol may prove more effective in removing certain organic substances from the skin.

For simple thermal burns, ice cold water is a most effective first aid measure. If cold water or a simple ice pack is applied until the pain subsides, healing is usually more rapid.

For extensive burns, place the cleanest available cloth material over the burned area to exclude air. Have the victim lie down and call a physician and/or ambulance immediately. Keep the head lower than the rest of the body, if possible, to prevent shock. Do not apply ointments to severe burns.

1.3.3 Cuts and Wounds

The most common minor laboratory accident involves cuts on the hand. Such cuts can usually be treated by applying an antiseptic and a bandage. If the cut is deep and possibly contains imbedded glass, a physician should be consulted.

For severe wounds—don't waste time! Use pressure directly over the wound to stop bleeding. Use a clean cloth over the wound and press with your hand or both hands. If you do not have a pad or bandage, close the wound with your hand or fingers. Raise the bleeding part higher than the rest of the body unless broken bones are involved. Never use a tourniquet except for a severely mangled arm or leg. Keep the victim lying down to prevent shock. Secure professional help immediately.

1.4 NOTEBOOKS AND REPORTS

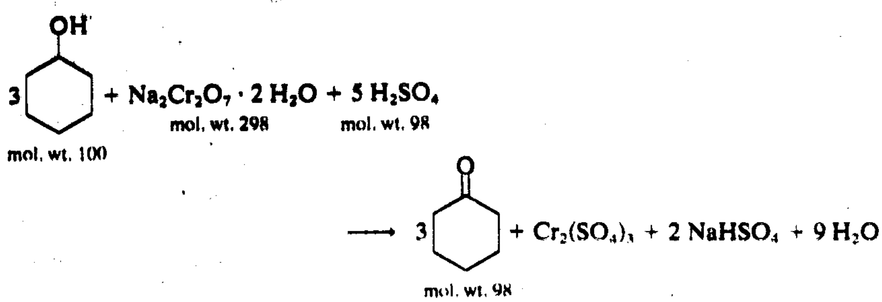
A bound notebook with numbered pages should be obtained for use as a laboratory notebook. In keeping a laboratory notebook, whether for class or research purposes, there is one cardinal rule: When one makes an observation, it should be written down immediately. Neatness and order, though important, are secondary. Chemists should never get into the habit of recording experimental observations on loose sheets of paper to be transcribed later into a bound notebook. Loose pages tend to get lost, and one's immediate impressions are often tempered with time. One poor recall can be very costly in terms of time, materials, and reputation. The laboratory notebook should be kept at your side in the laboratory at all times. Observations should be recorded when they are made, and plenty of space should be allowed in your notebook for comments, additions of later information, and computations. Adequate references for the procedures used and data cited should be included.

Students should get into the habit of coding all samples, spectra, analyses, etc. with their initials and notebook page numbers. For example, the code RAF-2-147-D appearing on an infrared spectrum weeks, months, or years after the spectrum was originally run indicates that the spectrum is that of compound D described on page 147 of laboratory notebook 2 of chemist RAF. This system will allow the chemist or anyone else to look up the history and source of the compound immediately. Label all samples that you are to turn in or that you intend to store until later. *Never leave unlabeled chemicals in your locker.*

Your laboratory supervisor will probably have specific instructions concerning the format of your notebook; the format used, in part, will depend on the nature and purpose of the experiment. For example, in an experiment involving the synthesis of a particular compound, the format illustrated on the following page is useful.

1.5 CALCULATION OF YIELD

For practical reasons related to costs, reaction rates, positions of equilibria, side reactions, etc., organic reactions are most frequently run with reactants in non-stoichiometric quantities. One reactant is chosen to be the *limiting reagent* which ultimately restricts the theoretical amount of product that can be formed. For example, the oxidation of cyclohexanol to cyclohexanone with sodium dichromate in aqueous sulfuric acid proceeds according to the following *balanced* equation:



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