introduction to

ORGANIC LABORATORY TECHNIQUES

a contemporary approach

Second edition

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ORGANIC LABORATORY TECHNIQUES

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PREFACE TO THE SECOND EDITION

We have been pleased by the favorable response that the first edition of this textbook has received. Realizing the features that made the first edition successful, we have attempted to maintain these strengths in our revisions. Nevertheless, we felt that some improvements were necessary, and these improvements should enhance this second edition.

We have devoted considerable effort toward improving the safety of the experiments. The introductory chapter, *Laboratory Safety,* has been extensively rewritten to place greater emphasis on safe laboratory practice. Additional material on the hazards associated with common organic solvents has been included. The flammability, toxicity, and potential carcinogenicity of these solvents have been discussed. Wherever possible, carcinogenic substances have been eliminated from the experimental procedures. In those few cases where such potential carcinogens could not be eliminated, additional instruction about the safe handling of these materials has been added. For instance, while we have retained the use of carbon tetrachloride and deuterochloroform as solvents for spectroscopy in some experiments, an increased emphasis on safety has been included. Other than for spectroscopy, chloroform is used for only one experiment (Experiment 29). The use of benzene has been eliminated completely.

Because of sharp increases in the prices of many chemicals, we have felt it advisable to reduce the quantities of chemicals that many of the experiments require. As an example, the quantities of chemicals required for the following experiments have been reduced, as compared with the first edition of this textbook.

Experiment 2, *Acetanilide*
Experiment 3, *Phenacetin*
Experiment 10, *Isopentyl Acetate*
Experiment 25, *Nucleophilic Substitution Reactions: Competing Nucleophiles*
Experiment 31, *Triphenylmethanol and Benzoic Acid*
Experiment 44, *p-Aminobenzoic Acid*
Experiment 47, *Tetraphenylcyclopentadienone*

Many experiments have been improved in order to make them even more successful. Experiments that have been extensively modified include:

Experiment 6, *Caffeine from Tea*
Experiment 7, *Caffeine from Coffee*

Experiment 9, *Ethanol from Sucrose*
Experiment 25, *Nucleophilic Substitution Reactions: Competing Nucleophiles*
Experiment 36, *Dyes, Fabrics and Dyeing*
Experiment 37, *Chromatography of Some Dye Mixtures*
Experiment 38, *Lycopene and β-Carotene*
Experiment 45, *Benzocaine*
Experiment 53, *Identification of Unknowns*

We have added a number of new experiments in an effort to include modern organic reactions or new techniques. The new experiments include:

Experiment 14, *Methyl Stearate from Methyl Oleate* (hydrogenation)
Experiment 20, *Thin-Layer Chromatography for Monitoring the Oxidation of Borneol to Camphor*
Experiment 27, *Chromic Acid Oxidation of Alcohols* (kinetics)
Experiment 29, *Phase Transfer Catalysis: Addition of Dichlorocarbene to Cyclohexene*
Experiment 30, *Markovnikov and anti-Markovnikov Hydration of Styrene* (hydroboration/oxidation and oxymercuration)
Experiment 32, *Nitration of Methyl Benzoate*
Experiment 34, *Friedel-Crafts Acylation*
Experiment 48, *Enamine Reaction: 2-Acetylcyclohexanone and* $\Delta^{1,9}$*-2-Octalone*
Experiment 49, *Benzyne Formation and the Diels-Alder Reaction: Preparation of 1,2,3,4-Tetraphenylnaphthalene*

Along with the new experiments, we have also added an essay, *Detection of Alcohol: the Breathalyzer*. We have updated the essays that appeared in the first edition, as well. Page references to the appropriate sections of the Techniques chapters have also been added. A new Technique chapter, Technique 18, *Guide to the Chemical Literature,* has been added.

We feel that the strengths of the first edition have been maintained in our revision. The essential features, including the interesting experiments that cover both organic and biochemical aspects of organic chemistry, the covering essays, and the complete discussions of the laboratory techniques, have been maintained. The changes that have been made should enhance our textbook, strengthening it in the areas of laboratory safety, amounts of chemicals required, and illustrations of current organic chemical reactions and techniques.

In the course of our revisions, many persons made valuable contributions to our efforts. We should like to acknowledge the assistance that these people provided. Special mention must be made of the contributions of Professor Willard A. Brown, of Western Washington University, who provided invaluable instruction in the use of his word processing computer program; Professors John A. Miller, of Western Washington University and Rex Widener, of St. Martin's College, who provided helpful suggestions regarding some of the laboratory experiments; and Professors Ralph Dougherty, of Florida State University, Thomas Fisher, of Mississippi State University, Larry Miller, of the University of Minnesota, Alfred Ordman, of Beloit College, and Wesley Pearson, of St. Olaf College, for their extensive reviews of the first edition. We

should like to thank the Bellingham division of Georgia-Pacific Corporation for performing an ethanol analysis. We must also express our gratitude for the suggestions and comments submitted by the many instructors who have used the first edition and who replied to our questionnaire or who contributed other materials and suggestions.

Many students participated in the development and testing of the new or revised experiments. We wish to thank Angela Blaisdell, James Hungerford, Neva Jean Jones-Pavia, David Keegan, John Michnick, Marc Norsen, Arthur Pinkers, Mark Rees, Vasilios Tsimtsirakis, David Veltkamp, and Virginia Wolff. Special thanks must also be given to the students who were enrolled in our laboratory classes during the period when we were testing our revised procedures. Their patience and helpfulness were most valuable.

Again, we must make special mention of the contribution of Mr. Robert D. LaRiviere, who created the new illustrations in this edition. We feel that his excellent drawings have made our book much more attractive and useful.

Finally, we must thank our wives (the same ones we had when we wrote the first edition!), Neva-Jean, Marian, and Dian for bearing with us again as we struggled through the large task of refining our ideas into a finished manuscript. We are most grateful for their support, understanding, and patience.

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FOREWORD TO THE STUDENT AND WORDS OF ADVICE

Welcome to organic chemistry! Organic chemistry can be fun, and we hope to prove it to you. That word *fun* may be misleading; it doesn't mean "less work." On the contrary, the work in this laboratory course will teach you a lot, and you will have to hustle to keep abreast of it all. For you to get the most out of the laboratory course, you should strive to do several things. First, you need to understand the organization of this laboratory manual and how to use the manual effectively. It is your guide to learning. Second, you must try to understand both the purpose and the principles behind each experiment you do. Third, you must try to organize your time effectively **before** each laboratory period.

ORGANIZATION OF THE TEXTBOOK

Let us consider briefly how this textbook is organized. There are four introductory sections, of which this Foreword is the first; a section on laboratory safety is second; advance preparation and laboratory records make up the third; and laboratory glassware is the fourth. Beyond these introductory sections, the textbook is divided into two parts. Part One consists of about 60 experiments, which may be assigned as part of your laboratory course. Interspersed within Part One are various covering essays that provide background information related to the experiments. Part Two comprises a series of detailed instructions and explanations dealing with the techniques of organic chemistry. While the experiments themselves may not seem to deal explicitly with instruction in the ordinary techniques of organic chemistry, those techniques are extensively developed and used. You become familiar with them in the context of the experiments. Within each experiment, you will find a section, entitled "Special Instructions," that indicates which techniques should be studied to do that experiment. That section also lists special safety precautions and specific instructions to the student. The Appendix to this textbook contains sections dealing with infrared spectroscopy and nuclear magnetic resonance spectroscopy. While only a few experiments specifically using these spectroscopic techniques are included in Part One, the techniques can easily be incorporated in the experiments by your instructor.

ADVANCE PREPARATION

Earlier you were told that you would have to hustle to keep abreast of the material you might expect to learn in your organic chemistry laboratory course. This means that you should not treat these experiments as a novice cook would

treat a Fanny Farmer cookbook. You should come to the laboratory with a plan for the use of your time and some understanding of what you are about to do. A really good cook does not follow the recipe line by line with a finger, nor does a good mechanic fix your car with the instruction manual in one hand and a wrench in the other. In addition, it is unlikely that you will learn much if you try to follow the instructions blindly, without understanding them. It can't be emphasized strongly enough that you should come to the lab **prepared.**

If there are items or techniques you don't understand, you should not hesitate to ask questions. Since other students are not always reliable sources, you should ask an instructor or a laboratory assistant. You will also learn more if you figure things out on your own. Don't rely on others to do your thinking for you.

You should read the section entitled "Advance Preparation and Laboratory Records" right away. Although your instructor will undoubtedly have a preferred format, much of the material here will help you in learning to think constructively about laboratory experiments in advance. You will also have to learn to keep complete records **for your own use,** no matter what the results may be. It would also save time if as soon as possible, you read at least the first four technique sections in Part Two. These techniques are basic to all the experiments in this textbook. The laboratory class will begin with experiments almost immediately, and a thorough familiarity with this particular material will save you much valuable laboratory time. You should also read the section on safety. Knowing what to do and what not to do in the laboratory is of paramount importance, since the laboratory has many potential hazards associated with it.

BUDGETING TIME

As mentioned in the Advance Preparation section, you should have read several chapters of this book even before your first laboratory class meeting. You should also read the assigned experiment carefully before every class meeting. Having read the experiment, you should schedule your time wisely. Often you will be doing more than one experiment at a time. Experiments like the fermentation of sugar require a few minutes of advance preparation **one week** ahead of the actual experiment. At other times you will have to catch up on some unfinished details of a previous experiment. For instance, usually it is not possible to determine accurately a yield or a melting point of a product immediately after you first get the product. Products must be free of solvent to give an accurate weight or melting-point range; they have to be "dried." This drying is done usually by leaving the product in an open container in your desk. Then when you have a pause in your schedule during the subsequent experiment, you can determine these missing data using a sample that is dry.

THE PURPOSE

The main purpose of an organic chemistry laboratory is to teach you the techniques necessary for a person dealing with organic chemicals. You will learn how to handle equipment that is basic to every research laboratory. You will also learn the techniques needed for separating and purifying organic compounds. If the appropriate experiments are included in your course, you may also learn how to identify unknown compounds. The experiments themselves

are only the vehicle for learning these techniques. The technique chapters in Part Two are the heart of this textbook, and you should learn them thoroughly. Your instructor may provide laboratory lectures and demonstrations explaining the techniques, but the burden is on you to master them fully by familiarizing yourself with the material in the technique chapters. Your instructor simply will not be able to explain or demonstrate everything.

In choosing experiments, we have tried whenever possible to make them relevant and, more important, interesting. To that end, we have tried to make them a learning experience of a different kind. Most experiments are prefaced by a background essay to place things in context and provide you with some new information. We hope to show you that organic chemistry pervades your lives, (drugs, foods, plastics, perfumes, and so on). We may not have succeeded totally with this book, but we have made a good beginning. We hope that organic chemistry itself is the dominant aspect of the text and that the level of expected performance has not been downgraded one iota. You should leave your course well trained in organic laboratory techniques. We are enthusiastic about our subject and hope you will receive it with the same spirit.

DONALD L. PAVIA
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LABORATORY SAFETY

In any laboratory course, familiarity with the fundamentals of laboratory safety is critical. Any chemistry laboratory, particularly an organic chemistry laboratory, can be a dangerous place in which to work. Understanding potential hazards will serve well in minimizing that danger for you. Remember that if you have a serious accident, it will not be reversible. You won't get a second chance!

EYE SAFETY

ALWAYS WEAR APPROVED
SAFETY GLASSES OR GOGGLES

First and foremost, ALWAYS WEAR APPROVED SAFETY GLASSES OR GOGGLES. This sort of eye protection must be worn whenever you are in the laboratory. Even if you are not actually carrying out an experiment, a person near you might have an accident that could endanger your eyes, so eye protection is essential. Even dishwashing may be hazardous. Cases are known in which a person has been cleaning glassware only to have an undetected piece of reactive material explode, sending fragments into the person's eyes. To avoid this sort of accident, it is necessary to wear your safety glasses at all times.

LEARN LOCATION OF
EYEWASH FACILITIES

If there are eyewash fountains in your laboratory, you should determine which one is nearest to you. In case any chemical enters your eyes, go immediately to the eyewash fountain and flush your eyes and face with large amounts of water. If an eyewash fountain is not available, the laboratory will usually have at least one sink fitted with a piece of flexible hose. When the water is turned on, this hose can be aimed upward and directly into the face, thus working much like an eyewash fountain. Care should be taken not to set the water flow rate too high, or damage to the eyes can result.

FIRES

USE CARE WITH OPEN FLAMES
IN THE LABORATORY

NO SMOKING

Equally important is the need to stress caution about fire. Because an organic chemistry laboratory course deals with flammable organic solvents at all times, the danger of fire is always present. Because of this danger, DO NOT SMOKE IN THE LABORATORY. Furthermore, exercise supreme caution when you light matches or use any open flame. Always check to see whether your neighbors on either side, across the bench, and behind you are using flammable solvents. If so, either delay your use of a flame or move to a safe location, such as a fume hood, to use your open flame. Many flammable organic substances are the source of dense vapors that can travel for some distance down a bench. These vapors present a fire danger, and you should be careful, since the source of those vapors may be far away from you. Do not use the bench sinks to dispose of flammable solvents. If your bench has a trough running along it, only **water** (no flammable solvents!) should be poured into it. The trough is designed to carry the water from the condenser hoses and aspirators—not flammable materials.

LEARN LOCATION OF FIRE EXTINGUISHERS,
FIRE SHOWERS, AND FIRE BLANKETS

For your own protection in case of a fire, you should learn immediately where the nearest fire extinguisher, fire shower, and fire blanket are. You should learn how these safety devices are operated, particularly the fire extinguisher. Your instructor can demonstrate how to operate the extinguisher.

If you have a fire, the best advice is to **get away from it** and let the instructor or laboratory assistant take care of it. DON'T PANIC! Time spent in thought before action is never wasted. If it is a small fire in a flask it usually can be extinguished quickly by placing an asbestos pad or a watch glass over the mouth of the flask. It is good practice to have an asbestos pad or a watch glass handy whenever you are using a flame. If this method does not take care of the fire and if help from an experienced person is not readily available, then extinguish the fire yourself with a fire extinguisher.

Should your clothing catch on fire, DO NOT RUN. Walk *purposefully* toward the nearest fire blanket or fire shower station. Running will fan the flames and intensify them. Wrapping yourself in the fire blanket will smother the flames quickly.