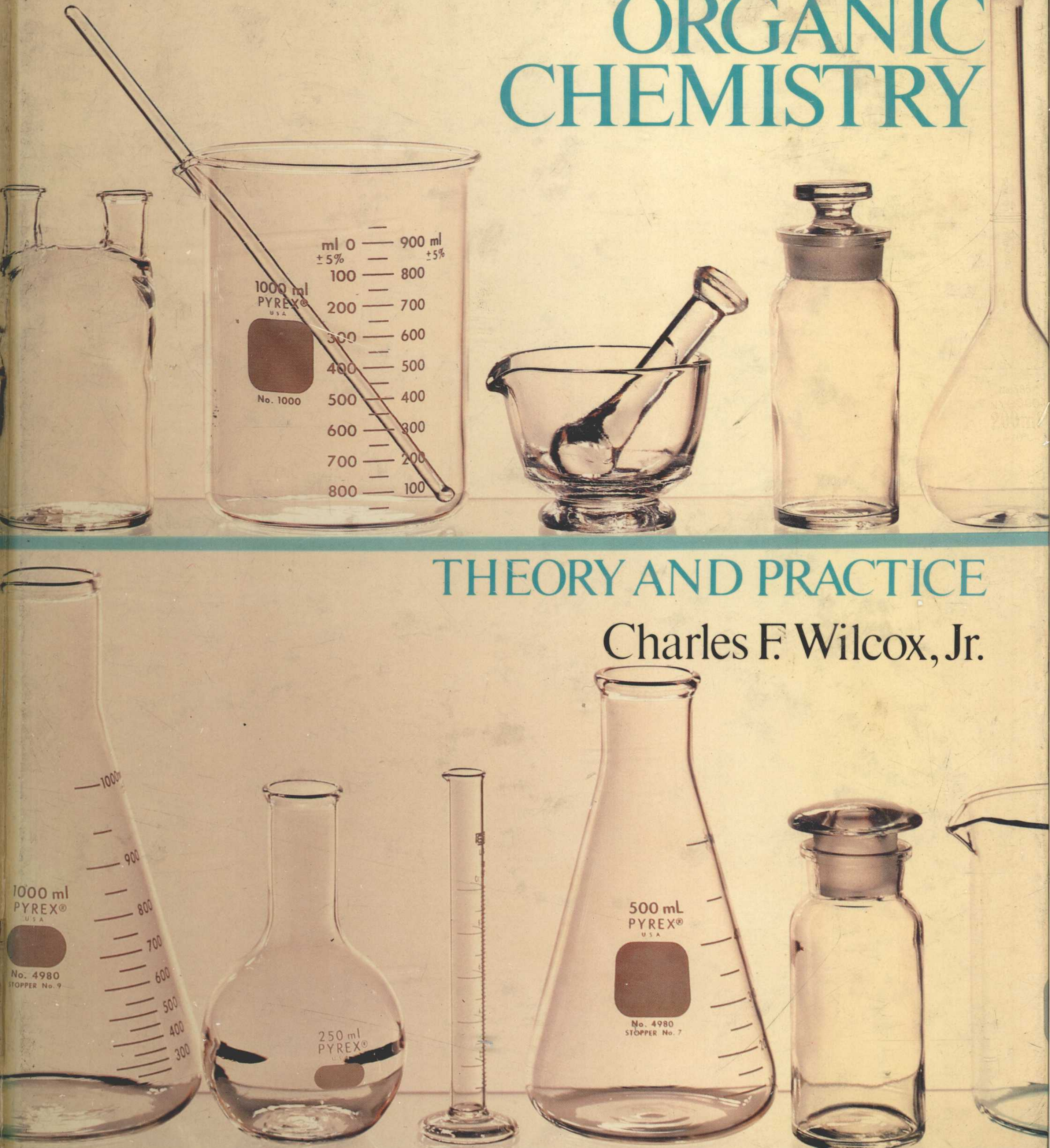
EXPERIMENTAL ORGANIC CHEMISTRY



THEORY AND PRACTICE

Charles F. Wilcox, Jr.

EXPERIMENTAL ORGANIC CHEMISTRY

Theory and Practice

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Cornell University

MACMILLAN PUBLISHING COMPANY
NEW YORK
Collier Macmillan Publishers
London

Experimental Organic Chemistry
is dedicated to the memory of
JOHN R. JOHNSON
scholar and teacher.

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Printed in the United States of America

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A portion of this book is reprinted from *Laboratory Experiments* in Organic Chemistry, Seventh Edition, by Roger Adams, John R. Johnson, and Charles F. Wilcox, Jr., copyright © 1979 by Macmillan Publishing Co., Inc.

Macmillan Publishing Company
866 Third Avenue, New York, New York 10022

Collier Macmillan Canada, Inc.

Library of Congress Cataloging in Publication Data

Wilcox, Charles F., Date:
Experimental organic chemistry.
Includes index.
QD261.W498 1984 547'.0028 83-11253
ISBM 0-02-427600-6

Printing: 2 3 4 5 6 7 8 Year: 4 5 6 7 8 9 0 1 2

ISBN 0-02-427600-6

Preface

For more than 50 years, through seven editions, the text *Laboratory Experiments in Organic Chemistry* by Adams, Johnson, and (for the last three editions) Wilcox has been widely used. As the teaching of organic laboratory work evolved, the original brief manual was expanded to incorporate new needs. Now, with Roger Adams and Jack Johnson deceased, it was felt that the time had come to make a fresh start. The present text is that effort. Readers familiar with the seventh edition will recognize much of it in the new text, but closer examination will also reveal significant deletions, changes, and additions.

A new title, *Experimental Organic Chemistry: Theory and Practice*, was chosen to express the author's conviction that in learning how to do experimental organic chemistry students can and should understand the theoretical basis for both the reactions they study and the separation methods used to purify the products. It is self-evident that if students are to carry out experiments above a blind, mechanical level they need to understand the underlying chemistry. In the same vein, it is argued that a thorough grasp of the fundamentals of separation methods is essential because more effort is usually spent in isolating products than in running reactions. Another essential aspect of organic chemistry is the identification of materials and the evaluation of their purity.

With these several needs in mind, the book has been divided into three parts. Part I describes the more common separation methods and the theories underlying them. In this author's view, a powerful unifying theme that correlates the various separation methods is the concept of vapor pressure and how it is affected by molecular interactions. For this reason distillation is presented first. The basic ideas presented in the chapter on simple and fractional distillation are developed and extended in the following chapters.

Part II presents the identification of organic compounds by both classical chemical-test methods and modern spectrometric techniques. The section on classical methods does not attempt to present anything like a full identification scheme, but restricts itself to the common functional groups. At Cornell, our introductory organic laboratory course uses a blend of both approaches. The chemical methods, especially when done on the small scale described here, reinforce good laboratory technique. They also encourage clear chemical thinking. Spectrometry has become an integral part of research, and students should be exposed to it in a first course in order to develop an early understanding of its power and limitations. Although at Cornell the material of this chapter is introduced only after some preparative experiments taken from Part III have been performed, its placement in Part II simplifies the organization.

Part III provides a number of preparative experiments. The primary objective in their selection has been to provide syntheses and transformations that illustrate general reactions or mechanistic principles and furnish products in satisfactory yields. In a few cases a preparation has been included because the product is particularly interesting. Preference has been given to the use of relatively inexpensive reagents and a scale has been chosen that is practical in the hands of beginning students but minimizes cost and waste disposal. The author is keenly aware of the heightened sense of chemical toxicity and the challenges it raises. An effort has been made to eliminate, or at least sharply reduce, exposure to potentially toxic substances. With regret, therefore, several otherwise attractive preparations have been deleted. Where the risks were significant, but felt not to be severe enough to require deletion, appropriate warnings have been included.

A list of apparatus suitable for the laboratory work and of the chemicals needed for each experiment is given in the *Instructor's Manual.*

The author acknowledges gratefully his indebtedness to many colleagues and instructors throughout the country for suggestions and friendly criticism, including Macmillan's reviewers—W. J. Burke, Dennis McMinn, and Bradford P. Mundy. Particular thanks go to Drs. J. B. Ellern and Forrest Sheffy. Thanks also go to the many students who have suffered through the problems of early versions of the experiments and have contributed so much to their resolution.

C. F. W., Jr.

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times in the laboratory. Prescription glasses are not a substitute for safety glasses and must be supplemented with a pair of plastic goggles that fit over them. Goggles provide even more protection than safety glasses, and some laboratories specifically require the wearing of goggles.

Contact lenses, too, should *never* be worn in the laboratory without safety glasses or goggles. Contact lenses cannot be removed rapidly enough to prevent damage from reagents splashed in the eyes, and they offer no protection against shrapnel.

Fire Hazards. One of the chief dangers of organic laboratory work is the fire hazard associated with the manipulation of volatile, flammable, organic liquids. With few exceptions, organic liquids and vapors catch fire readily, and many organic vapors form explosive mixtures with air. Obviously, organic liquids must not be manipulated near an open flame, and precautions must be taken to avoid the escape of organic vapors into the laboratory. For general safety, you should form the habit of scanning the adjacent laboratory bench space for lighted burners before working with flammable solvents, and it is good practice to look around for fire hazards to yourself and adjacent workers before lighting a match or a burner.

The degree of flammability of organic compounds varies widely. The vapors of diethyl ether, petroleum ether, acetone, and ethanol catch fire quite readily, and the manipulation of these liquids requires careful attention at all times to fire hazards. Methylene chloride (bp 40°) is a much safer solvent. Carbon disulfide is so readily ignited (even by a hot steam pipe) that it should *never* be used by an inexperienced worker.

Chemical Burns and Cuts. Specific precautions for handling particularly dangerous chemicals are noted in the directions for procedures in which they are used, but any ordinary chemical or piece of apparatus can be dangerous if manipulated carelessly. It is important to develop a general awareness of dangers and accidents that can arise from carelessness in simple routine, operations. To cite two examples, a severe cut or laceration may result from carelessness in pushing rubber tubing over a glass tube; a severe explosion and fire may result from attempting to distill a substance in a completely closed system.

Procedures to be followed in case of accidents are given in the Appendix and also are printed on the inside back cover of this manual.

Toxic Chemicals and Mutagens. Many common organic chemicals, particularly those containing nitrogen, are toxic or even lethal when ingested in amounts as small as a few tenths of a gram. A major rule of safe laboratory practice is *never* taste any compound.

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