Roger Adams
John R. Johnson
Charles F. Wilcox, Jr.

Laboratory Experiments in

# ORGANIC CHEMISTRY

SEVENTH EDITION

# Laboratory Experiments in ORGANIC CHEMISTRY

SEVENTH EDITION

**Roger Adams**
LATE OF THE UNIVERSITY OF ILLINOIS

**John R. Johnson**
CORNELL UNIVERSITY

**Charles F. Wilcox, Jr.**
CORNELL UNIVERSITY

MACMILLAN PUBLISHING CO., INC.
NEW YORK

COLLIER MACMILLAN PUBLISHERS
LONDON

Printed in the United States of America



Macmillan Publishing Co., Inc.
866 Third Avenue, New York, New York 10022

Collier Macmillan Canada, Ltd.

Library of Congress Cataloging in Publication Data

Adams, Roger
Laboratory experiments in organic chemistry.

First published in 1928 under title: Elementary laboratory experiments in organic chemistry.
Bibliography: p.
Includes index.
1. Chemistry, Organic—Laboratory manuals.
I. Johnson, John Raven joint author.
II. Wilcox, Charles F joint author.
III. Title.
QD261.A2 1979 547'.0028 78-4482
ISBN 0-02-300590-4

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

This Seventh Edition of
LABORATORY EXPERIMENTS
IN ORGANIC CHEMISTRY
is presented as a tribute
to the memory of
ROGER ADAMS
who has played a major role
in the progress of synthetic
organic chemistry during the
past half century

# Preface to the Seventh Edition

Since the appearance of the sixth edition of this manual notable advances have been made in the applications of chromatography and spectroscopy in the undergraduate laboratory. Equipment for ultraviolet, infrared, and nuclear resonance spectroscopy has become available at relatively moderate cost and affords enhanced opportunities for characterization and identification of organic materials. The discussions of these physical methods have been enlarged and examples of their uses have been added in the new edition.

A special feature of this edition is the modification or omission of a number of experiments with the object of minimizing exposure of students and instructors to noxious reagents and to chemicals that may be carcinogens (or mutagens) or may be difficult for inept or inexperienced students to handle safely. Solvents eliminated or minimized are chloroform, carbon tetrachloride, and benzene. Reagents eliminated or minimized are bromine, sodium metal, sodium cyanide, benzidine and naphthylamines, phosphorus, phosphorus and sulfur halides and oxyhalides, and fuming sulfuric acid. As in earlier editions, warning of a hazard is indicated by a ➤**CAUTION** inserted in the text.

Experiments deleted for reasons of safety include ethyl iodide, acetyl chloride, valeronitrile and valeric acid (cyanide), bromobenzene, *p*-bromoaniline, *m*-bromotoluene, benzenesulfonic acid, and a few others.

Several experiments have been removed because we think they can be replaced by new ones having more significance and greater current interest. Methoxychlor replaces DDT; an aminobenzothiazole and isatin (plus a cinchoninic acid) replace quinoline, fluorescein, and others. An experiment using N-phenylmaleimide and maleic anhydride as dienophiles (4 + 2 cycloaddition) has been added and also the preparation of ferrocene and acetylferrocene. Simple experiments on kinetics have been introduced.

It is a pleasure to express our thanks to several teachers of organic chemistry who have given us thoughtful criticism and offered many appropriate suggestions for improving this manual. We have missed the advice and help of Roger Adams in preparing this new edition.

John R. Johnson
Charles F. Wilcox, jr.

# General Preface

These laboratory experiments are intended for undergraduate students of organic chemistry who may be specializing in chemistry and chemical engineering, or studying the subject because of its relationship to biology, medicine, engineering, food science, agriculture, the graphic arts, and other fields.

The more important basic operations and procedures encountered in the organic laboratory are set forth in the first section of the manual, with details of correct manipulation and illustrations of typical assemblies of apparatus. The intent is to emphasize important principles rather than to present merely the laboratory technique. The current tendency to curtail laboratory work often makes it desirable to introduce a particular operation in conjunction with an experiment in which it is used, rather than as a separate exercise.

The primary objective in selecting preparative experiments has been to choose syntheses that illustrate general reactions and furnish pure products in satisfactory yields. Laboratory work should encourage a student to be realistic—to consider the merits and faults of different routes to a particular goal.

In a few experiments the product is a mixture that is to be examined by chromatographic and/or spectroscopic methods. If time and instrumentation are available the instructor may wish to extend this practice.

Preference has been given to the use of relatively inexpensive reagents and chemicals when this can be done without sacrificing other desirable features. Many sequences of preparations are available so that a student can gain experience with multistep syntheses that are so important in organic laboratory work. Examples are: *n*-butyl bromide–2-methyl-2-hexanol–2-methylhexenes (Experiment 15); aniline–acetanilide–1-nitroaniline–Para Red or *p*-nitrostilbene (Experiments 27 and 35b or 40);

aniline–acetanilide–*p*-acetamidobenzenesulfonyl chloride–sulfanilamide (Experiments 27 and 29). A short list of *Suggestions for Supplementary Experiments* has been provided to encourage students who are qualified for further synthetic work. The section on *Literature of Organic Chemistry* should also be useful.

In many instances two or more examples involving the same type-reaction are presented. This permits students in the same class to use different examples to illustrate the same general reaction and emphasizes that aspect of synthetic work. Moreover, this allows changes in class assignments from one year to another that may be desirable.

Experimental procedures are described in detail, particularly in the first part of the manual, even to specifying the amount of washing liquid or drying agent to be used. This approach is believed to be a good one, especially if the experiments are accompanied by questions concerning the procedures used and the principles involved. Later the student will be able to exercise good judgment in assembling apparatus and using reagents. Laboratory conferences covering general instructions and some discussions of reactions and procedures, with occasional demonstrations, are effective in developing an intelligent attitude toward experimental work. The use of televised laboratory demonstrations has been quite successful.

Questions given after completion of an experiment can contribute in an important way to laboratory instruction. The instructor should indicate to a class which questions are to be answered, since this will depend upon the extent of the theoretical organic chemistry presented.

The instructor can select easily a sequence of laboratory experiments that suits the pattern in which the subject matter is presented in the lecture course. Good correlation of lecture and laboratory work is highly desirable. Although aliphatic compounds happen to be emphasized in the earlier experiments, aliphatic and aromatic compounds are usually included in the experiments illustrating characteristic reactions of the functional groups. Experiments are available to permit the student to acquire experience in the purification and characterization of organic liquids as well as solids.

A judicious combination of syntheses and test reactions is desirable, since small-scale reactions in which a crystalline product is isolated serve to illustrate an important phase of organic laboratory work. Furthermore, if the time available is quite limited, a broader coverage of topics can be obtained this way. The test reactions and accessory preparations of solid derivatives enhance the student's familiarity with characteristic reactions of the functional groups and acquaint him with some of the special reagents developed for identification purposes.

Identification of simple unknowns, within limited classes of compounds, is suggested in the experiments on alcohols, aldehydes and ketones, amines, phenols and others. This aspect is usually liked by

students. A more extensive outline of traditional procedures for identification of simple organic compounds, by means of solubility and chemical tests, has been included (Experiment 58). It is intended that this outline be used in conjunction with the test reactions and small scale preparations mentioned above. To supplement this brief treatment one of the good texts in this field should be consulted (see the section on *Literature of Organic Chemistry*).

Recent advances in instrumental methods have made possible a fruitful integration of structural information derived from spectroscopic methods with that from chemical reactions (Experiment 59). The use of spectroscopic methods is of tremendous importance in university research laboratories and in industrial chemical work.

Convenient procedures for students to follow in keeping notes and recording experimental results are described but other methods may be devised to suit the individual instructor's approach. Standard taper glass-jointed apparatus is neat and saves time; it is now generally used.

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

The authors acknowledge gratefully their indebtedness to many colleagues and instructors throughout the country for suggestions and friendly criticism—and to *Organic Syntheses* and other laboratory manuals for ideas and procedures.

J. R. J.
C. F. W., jr

# Contents

## Experiments on Separation and Purification

## Preparation and Reactions of Typical Organic Compounds

# Experiments on Separation and Purification