EXPERIMENTS IN
ORGANIC CHEMISTRY

SECOND EDITION

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IN
ORGANIC CHEMISTRY

Part I

BY
LOUIS F. FIESER
Sheldon Emery Professor of Organic Chemistry
Harvard University

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PREFACE

A brief statement of the general policy adopted in the construction of this book perhaps will reveal most easily the points of departure from the manuals already available for use in laboratory courses of elementary organic chemistry. It has become the practice in this country to provide the beginning student with carefully standardized and detailed directions, in order that a good technique may be acquired with the greatest possible economy of time and materials, and to this policy I subscribe wholeheartedly. There is no novelty in the preference for preparations rather than experiments involving only test reactions, or in the opinion that the most stimulating and useful preparations are those which proceed smoothly and in good yield. It is hardly necessary in these days to state that every effort has been made to keep the cost of chemicals at a minimum, and a few preparations which have become old favorites have been abandoned regretfully for this reason. Careful attention has been given to the matter of utilizing the products accumulating from one experiment as starting materials for other preparations, for this plan is both economical and instructive.

Less orthodox is the view that some of the reactions of aliphatic chemistry can be illustrated perfectly well, and to considerable advantage, with the use of aromatic compounds. Some of the transformations characteristic of the aldehydes, acids, halides, and esters proceed particularly well when simple aromatic substances are employed as the starting materials, and the use of such substances permits greater diversity and often provides a welcome change from the succession of preparations involving only liquid reagents and liquid products. The early introduction of compounds containing the "mysterious" phenyl group does not appear to be at all confusing to the students or to detract from their interest, at a later period, in the chemistry of the benzene nucleus. It may be said in this connection that the Grignard reaction offers no great difficulties when introduced at a time corresponding to the elaboration in the lectures

of some of the striking applications of the synthesis, and that it is a distinct event to the student.

In the belief that a truly helpful manual should attempt to answer, rather than to ask, some of the many questions which arise in connection with the experiments, the quizzing of the student on his preparation and reading has been left in the hands of the laboratory instructors, and an effort has been made to provide the student with useful reading matter. To this end prefaces introducing and explaining the experimental procedures have been included, and it is hoped that this may be of assistance in encouraging intelligent preparation in advance of the laboratory period. Another function of the introductions is to emphasize the value of test reactions in identification work and in the separation of mixtures. Experiments with carbonyl compounds and with amines develop further the theme of qualitative analysis and a special experiment placed at the end of Part I is devoted to the identification of unknowns. This provides a review and a practical application of nearly all the tests previously studied. Only a limited number of types are included, and the average student can identify about six unknowns in four afternoon periods. Over one hundred inexpensive chemicals have been used with success for the purpose and the list will be furnished gladly to interested teachers. It is most enlightening to use as unknowns some of the student's own preparations! One gram of material is usually more than adequate, and the outlay of test reagents is very modest.

Some provision for the particularly interested and gifted students has been made by the inclusion of special experiments and alternate preparations. Some of these are of more than the usual difficulty, some are too expensive or too hazardous for general class use, and some may be assigned for the purpose of supplying a chemical desired for use by the class. The "Martius Yellow" experiment properly belongs in the group of special preparations, and it may be used as the basis for an interesting form of competitive test. Other special experiments can be assigned in connection with the rather elaborate discussions of steam and vacuum distillation. In order to meet further requirements in this direction, and in order to make the book useful to students in advanced courses and to beginners in research, a number of notes, suggestions, and references have been incorporated in Part II of the manual in a somewhat condensed form.

Preliminary versions of nearly all the experiments of Part I have been used in course work at Bryn Mawr and Cambridge, and the reactions and comments of the students have been very helpful. The present directions are based both upon these experiences and upon a considerable amount of experimentation. Although a certain measure of novelty may be claimed for some of the experiments, the book as a whole is based upon the work of many distinguished predecessors, whose number is too great to permit individual acknowledgments.

A number of friends have contributed helpful suggestions, and I am glad to acknowledge the valuable counsel of Professor E. P. Kohler, the assistance of Dr. C. L. Bickel in the preparation of the chapter on semi-microanalysis, and the criticisms and suggestions kindly offered by Dr. G. H. Carlson, Dr. N. Weiner, Dr. G. F. Wright, and by several of the assistants in "Chemistry 2." The method of making rubber stamps is the contribution of Mr. A. M. Seligman. I am greatly indebted to Mary Fieser for valuable technical assistance, for the drawings from which the wax plates were constructed, and for a preliminary draft of the scheme of qualitative analysis.

LOUIS F. FIESER

CAMBRIDGE, MASSACHUSETTS
April, 1935

PREFACE TO THE SECOND EDITION

In this edition the experiments designed for a first course in organic chemistry have been revised in certain details and extended by the inclusion of directions for the preparation of sulfanilamide, for the synthesis of vitamin K_1 and related compounds, and for the isolation of the principal acid constituent of rosin. The material of a more advanced character included in the second part of the book has been expanded considerably, and Parts I and II are now available in separate printings.

Part II constitutes a miscellany of notes on procedure and technique designed for the general guidance of advanced students. Although certain specific experiments are indicated, the general plan has been to provide a broad foundation of information and references on the

basis of which illustrative experiments can be selected according to individual or local interests and with reference to the equipment and starting materials available.

Much of the new material of Part II is based upon the experiences, observations, and opinions of my collaborators in recent researches. I take pleasure in acknowledging particularly the invaluable assistance and advice of Dr. E. B. Hershberg, who kindly contributed the section on glass blowing and who is responsible for the design of the majority of the pieces of apparatus illustrated in the engravings. For other contributions and suggestions, I am indebted to Drs. J. Cason, H. J. Creech, Max Tishler, J. K. Wolfe, J. L. Wood, and R. B. Woodward, and to W. von E. Doering, R. C. Clapp, E. R. Coburn, W. H. Daudt, and H. Heymann. Mary Fieser again has contributed generously to the book by editing the manuscript, checking the references, reading the proof, and compiling the indexes.

LOUIS F. FIESER

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