HETEROCYCLIC COMPOUNDS

THIOPHENE

AND DERIVATIVES

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THIOPHENE
and Its Derivatives

This is the third volume published in the series
THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER, *Consulting Editor*

THIOPHENE
and Its Derivatives

HOWARD D. HARTOUGH
Socony-Vacuum Laboratories
Paulsboro, New Jersey

With Special Chapters by
F. P. HOCHGESANG
Socony-Vacuum Laboratories, Paulsboro, New Jersey
and F. F. BLICKE
University of Michigan, Ann Arbor, Michigan

1952
INTERSCIENCE PUBLISHERS, INC., NEW YORK
INTERSCIENCE PUBLISHERS LTD., LONDON

LIBRARY OF CONGRESS CATALOG CARD NUMBER 51-13781

INTERSCIENCE PUBLISHERS, INC., 250 Fifth Ave., New York 1, N. Y.

For Great Britain and Northern Ireland:
Interscience Publishers Ltd., 2a Southampton Row, London W. C. 1

PRINTED IN THE UNITED STATES OF AMERICA BY MACK PRINTING CO., EASTON, PA.

INTRODUCTION TO THE SERIES

The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

Research Laboratories
Eastman Kodak Company
Rochester, New York

ARNOLD WEISSBERGER

Preface

Since thiophene was discovered in 1882 by Victor Meyer its importance has increased at an accelerating rate. Although there has not been a year from 1883 to the present without publications concerning thiophene or its derivatives, there are three main periods in which the greater proportions of the publications were issued. The first of these was the Victor Meyer period of 1883 to 1888, which culminated in Victor Meyer's book *Die Thiophengruppe* (Braunschweig, 1888). The second period, which should be classified as the Steinkopf period, began in 1918 and continued until 1941. Again the work was summarized in a book by Wilhelm Steinkopf, *Die Chemie des Thiophens* (Verlag von Theodor Steinkopff, Dresden, 1941). The present period of accelerated research, initiated by the commercial availability of thiophene, began in 1945 and promises to continue into the next decade.

The rapid strides in thiophene chemistry between 1944 and 1950 have created the need for the present volume. For example, the subject matter of Chapter IX, one of the longest in the book, is covered in less than a page in *Die Chemie des Thiophens*. I once commented before an American Chemical Society meeting that thiophene chemistry was merely in its infancy, since there were still so many problems to be undertaken and solved before we could know its true character. The remark came back from the floor that, while this was probably true, thiophene chemistry was certainly enjoying a robust and healthy childhood.

The present book was begun in 1947 but so many references appeared in 1947 and 1948 that it was necessary to rewrite most of the chapters as many as three times. The text originally included references up to January 1, 1949. Several hundred references appearing in *Chemical Abstracts* between January 1 and October 1, 1949, were inserted into the completed text but in a number of cases it was not possible to handle these later references in detail. Since October 1, 1949, about four hundred additional articles and patents have been published.

The treatise was designed to cover critically all phases of thiophene chemistry and to point out some of the existing problems yet to be solved. In order to achieve this goal, Dr. F. F. Blicke, Head of the Pharmacy School, University of Michigan, contributed Chapter II on toxicological and pharmacological properties of thiophene, and Mr. F. P. Hochgesang of the Physics Division of the Socony-Vacuum Laboratories reviewed the spectrochemical and related properties of thiophene. In addition,

Chapter IV includes a complete summary of the unpublished data obtained in the Socony-Vacuum Laboratories. These data should be of particular value to petroleum chemists, as well as to organic chemists, in identifying natural-source thiophenes and synthetic thiophenes. The literature was reviewed with the intention of including every significant reference and every derivative of thiophene. It will be appreciated that this is a rather formidable task, and I shall be most grateful to those users of the book who will bring to my attention deficiencies of which they become aware.

In addition to the contributions mentioned above, I am deeply indebted to Drs. A. A. O'Kelly and D. E. Badertscher for their encouragement during the writing period. Dr. S. L. Meisel and Dr. E. M. Crane were especially helpful in proofreading the manuscript and in offering critical comments. Great credit goes to Dr. W. P. Hawthorne for his painstaking proofreading and critical review of the contents of this volume which have immeasurably improved its quality and organization. Special thanks are due to Dr. R. Bulkley, Dr. L. A. Hamilton, and Mr. J. J. Dickert, Jr., who graciously volunteered to help in the tedious task of checking references.

The writing of this book was greatly facilitated by private communications to the author from friends in this country and abroad. Sincere thanks are due Dr. Robert Levine of the University of Pittsburgh, Dr. C. D. Hurd of Northwestern University, Dr. F. F. Nord of Fordham University, and many others. Dr. Otto Dann of the University of Erlangen, Germany, was instrumental in maintaining contact for the author with Dr. Steinkopf and in supplying biographical data about Dr. Steinkopf. He also transmitted information concerning his own work in thiophene chemistry. Dr. Frederick Challenger of the University of Leeds, England, has been helpful in forwarding copies of his articles submitted for publication in English journals many months prior to their availability in this country.

Originally this volume was to include fused ring systems containing thiophene rings such as thianaphthene and dibenzothiophene. To expedite publication of thiophene data, the data on condensed ring systems containing thiophene rings are now scheduled for publication in a separate volume by the present author and Dr. S. L. Meisel which should appear in 1952 or 1953.

Hercules Experiment Station H. D. H.
Wilmington, Delaware
August, 1951

Contents

IX. Thiophene Compounds Containing Nitrogen in the Side Chain (*continued*)