
 BOOK REVIEWS

The Chemistry of Heterocyclic Compounds. Volume 15. Heterocyclic Systems with Bridgehead Nitrogen Atoms. Part Two. By WILLIAM L. MOSBY, American Cyanamid Company, Bound Brook, New Jersey. ARNOLD WEISSBERGER, Consulting Editor. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1961. 719 pp. 16 × 23.5 cm. Price, \$48.00.

Dr. Mosby has classified over a thousand systems as belonging to the class of heterocycles having bridgehead nitrogen atoms. In this second part of Volume 15 he has completed the section on fused ring systems begun in part one, and has dealt with the subject of bridged ring systems.

Bridgehead nitrogen makes a poor common denominator for relating such a multiplicity of structural types, and the casual reader will feel less at home with either part of this volume than with preceding ones which deal with traditional and well-defined topics such as pyridine or thiophene. One is reminded of an attic, full of unrelated things, items that are out-of-season, abandoned projects and unidentifiable gadgets. As readers of part one will recall, Dr. Mosby is systematic in sorting out the various systems through use of the "Ring Index" classification. He has secured the help of Dr. L. T. Capell of "Chemical Abstracts" in providing systematic names for several hundred systems previously unnamed. The occasional lapses from "Chemical Abstracts" nomenclature, such as calling the quinolininium ion the dehydroquinolininium ion (p. 1001), are easily forgiven.

The work is more than a simple catalog of systems and reactions. It is a critical review, and Dr. Mosby is to be admired for proposing alternatives to some of the dubious structures which have appeared in the literature. For the person interested in the proof of structures, this volume provides more problems than could be solved in several man-decades.

Just as every attic has items which should simply be thrown out, we suggest to Dr. Mosby that in any future revision of this work he eliminate those "ring systems" which are actually betaines. Granted that the editors of "Ring Index" may still have doubts as to the permanence of the concept of electrovalence, this reviewer feels that Dr. Mosby insults the intelligence of his readers; for example, he suggests (p. 1309) that the betaine 1-methyl-3-sulfo-pyridinium is even formally a representative of the tricyclic system 7-oxa-6-thi-1-azabicyclo[3.2.1]octane.

Dr. Mosby has done a good job with a large quantity of difficult material, and all who work in this field will be grateful to him. It is unfortunate that not every such worker will be able to afford his own personal copy of Volume 15.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, N. C.

C. K. BRADSHAW

Advances in Fluorine Chemistry. Volume 2. Editors, M. STACEY, F. R. S., Mason Professor and Head of Department of Chemistry, University of Birmingham, J. C. TATLOW, Ph.D., D.Sc., Professor of Organic Chemistry, University of Birmingham, and A. G. SHARPE, M. A, Ph. D., University Lecturer in Chemistry, Cambridge. Butterworths Inc., 7235 Wisconsin Avenue, Washington 14, D. C. 1961. 220 pp. 16 × 25.5 cm. Price, \$8.00.

This book, which follows along the same general lines as the first volume of the series, consists of six separate chapters, each by a different author, which are not closely related to each other except that each contains a reasonably up-to-date discussion of some phase of the chemistry, physical chemistry, occurrence, preparation and utilization of fluorine and its compounds.

The first chapter by Patrick deals with the thermochemistry of fluorine and its compounds. Items are discussed such as bond energies, heats of formation and dissociation, the thermodynamics of the reactions of fluorine compounds and

the thermal decomposition of fluorine polymers, together with an outline of the emerging pattern of the thermochemical relationships between these fluorine compounds, which should help to explain their unusual stability. Comparisons are made with similar properties of related classes of compounds, and a considerable table of heats of formation is included. A significant feature of this chapter is the effort which has been made to correlate the many scattered and varying data, and to evaluate their reliability and utility.

The next article by Finger has to do with the sources, world reserves and industrial utilization of fluorine compounds. The mineral sources of these compounds, such as fluorspar and the enormous reserve of fluorine-containing phosphate rock among others, are evaluated, and their distribution in many parts of the world has been outlined. Also, considerable attention has been given to the processing of the various ores for industrial use. Great quantities of fluorspar are consumed in the chemical manufacture of hydrogen fluoride, in the steel industry as a "flux," and in the ceramic industry. Many of the industrial processes involved are described in some detail in this chapter. It appears that there are a surprising number of major and minor applications of fluorine compounds, from the preparation of elemental fluorine, refrigerants, propellants and oxidizers on the one hand, to the synthesis of non-combustible anesthetics and fluorinated steroids on the other. This interesting and fairly complete account can leave no doubt in the mind of the reader that fluorine and its compounds, not so long ago mere academic curiosities, are big business today.

The next section by Majer deals with the fragmentation of many types of fluorine compounds in the mass spectrometer, and the use of the data obtained in the evaluation of the structures of these compounds, as well as in the analysis of complex mixtures, especially when only small amounts of sample are available. The electron impact method is also used in measuring the ionization potentials of these molecules and in the determination of the bond energies involved. Some 33 Tables and 6 Figures are given to illustrate in detail the mass spectra and ionization potentials of a large number of aliphatic and aromatic fluorine compounds, including many comparisons with corresponding hydrocarbons and with molecules containing halogens other than fluorine. Again data from many literature sources are collected, correlated and evaluated, and the coverage appears to be quite satisfactory. The material presented here should be of substantial service in the identification and estimation of new fluorine compounds, especially when available only in minute amounts.

The following chapter by Tedder discusses the direct fluorination of organic compounds with elemental fluorine. The theoretical, experimental and practical aspects of this subject have been considered in detail, including methods for direct fluorination in a cold solvent; in the vapor phase over a divided metal packing; and in the vapor phase without packing as in the jet fluorination reactor. Recent studies in reaction kinetics have been included, and comparisons have also been made of the directive effects and selectivities exhibited by the different halogens in their reactions with organic compounds. There follows a summary of the typical reactions which take place when about a dozen different classes of organic compounds are fluorinated under various operating conditions. It appears that the results which have been achieved by most of the important groups of workers in this field, both here and abroad, have been adequately covered over a period of some 75 years. Technical details have been well illustrated, apparently with but few errors, and many useful cross references have been included.

The next article by Hodge presents a comparative and in larger part descriptive and detailed survey of the chemistry of the fluorides of the actinide elements, actinium, thorium, protactinium, uranium, neptunium, plutonium, americium and curium, the greater part of the space being devoted to uranium and plutonium. Topics such as electronic structures, oxidation states, complex ions, methods of preparation and chemical reactivities and stabilities are discussed, to-

gether with numerous physical properties, such as solubilities, melting and boiling points, phase systems, crystal lattices, crystal habits and numerous others. Questions of the relative importance of these elements and their fluorides have not been neglected, and the presentation is well illustrated by numerous tables, phase diagrams, mechanisms and similar material. The data are presented in a clear and orderly manner, the coverage would appear to be good, and the documentation is very satisfactory.

The last chapter by Saunders on the physiological action of fluorine and its compounds begins with a discussion of the toxic properties of elemental fluorine, hydrogen fluoride and the fluoride ion. Acute and chronic poisoning by sodium fluoride, as well as the highly controversial question of the fluoridation of drinking water supplies to aid in the control of dental caries, have been discussed at some length. Following this, the preparation, structures and physiological properties of the various alkoxy- and alkylamino phosphorofluoridates containing the P-F link are described. The powerful effects of some of these compounds upon the autonomic, voluntary and central nervous systems in animals and humans are elucidated. This is followed by a description of the occurrence of salts of fluoroacetic acid in certain plants which are very toxic to animals. It is believed that this acid substitutes for acetic acid in the well-known Krebs cycle, which accounts well for this toxicity. It is also found that only the alternating members of the homologous series of ω -fluorocarboxylic acids, which can yield fluoroacetic acid by β -oxidation, are toxic. This furnishes good support for the accepted theory of β -oxidation in the animal organism. Some mention is also made of the toxicities of certain fluorinated hydrocarbons. Finally, the author expresses his hope that in the future at least, toxicity studies may be conducted, not to take, but rather to save lives.

In sum, this highly technical volume, which has little central theme, may be aptly described as all meat, to be read and appreciated chiefly, it is presumed, by those who can assimilate this kind of intellectual diet with equanimity and profit. In the reading it should be remembered that certain of the areas involved are advancing so rapidly as to make it well nigh impossible for any book of this kind to be completely up-to-date. On the other hand, this work constitutes a mine of information, gathered from widely scattered sources, which has been condensed into a reasonable space, on the whole clearly presented and carefully evaluated. The material is also very well documented with no less than 675 references to the original literature. For these good reasons, this book is well recommended for the reference shelf of every fluorine chemist.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA

LUCIUS A. BIGELOW

Heterocyclic Compounds. Volume 7. Polycyclic Compounds Containing Two Hetero Atoms in Different Rings. Five- and Six-Membered Heterocycles Containing Three Hetero Atoms and Their Benzo Derivatives. Edited by ROBERT C. ELDERFIELD, University of Michigan. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1961. vii + 878 pp. 15.5 × 23.5 cm. Price, \$37.50.

This volume of the Elderfield Heterocyclic Compounds series starts with an excellent chapter on compounds with two heteroxygen atoms in different rings by W. Basil Whalley. Since this subject has not been reviewed previously, the author has treated in a comprehensive manner the degradation and synthesis of both the naturally occurring and synthetic members of this class. This chapter is well worth investing the time required to read its 197 pages. The naphthyridines are treated briefly in a chapter by M. J. Weiss and C. R. Hauser. The carbolines and phenanthrolines are discussed by W. O. Kermack and J. E. McKail. These two chapters were originally submitted in 1950 and were brought up to date by the Editor to include the major English and German language periodicals through 1959 and partially into 1960. Excellent chapters on the triazoles and oxadiazoles were contributed by J. H. Boyer. The chapter on thiadiazoles was written by W. R. Sherman, and the chapter on s-triazines by E. J. Modest. A very nice chapter on the 1,2,4- and 1,2,3-triazines was contributed by J. P. Horowitz and one on oxadiazines and thiadiazines by G. W. Stacy.

This volume, in common with the previous volumes of this series, provides an excellent introduction to the chemistry of the classes of heterocycles treated. In certain instances, such as the contribution of W. Basil Whalley, the class of compounds has not been reviewed or has undergone much development since its last review, and the article is very valuable. In certain other cases review articles, and in fact entire comprehensive books, have been published recently on the topics treated here. Although it is often valuable to have on hand several reviews of the same material treated from different points of view, it is unfortunate that the Editor could not omit these in order to try to lower the high price of the book.

The Editor and the authors deserve to be congratulated on the excellence of the book they have produced. The articles in general appear to be authoritative and up-to-date. They are clearly written, although, in a few instances, more liberal use of numbered structural formulas would have aided comprehension. I feel sure that this volume will take its place along with its predecessors as one of the first places one looks when a problem in heterocyclic chemistry arises.

RESEARCH AND DEVELOPMENT DIVISION
SMITH KLINE AND FRENCH LABORATORIES
PHILADELPHIA 1, PENNSYLVANIA JOSEPH WEINSTOCK