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BOOK REVIEW

The Chemistry of the Sulphonium Group. Part 1 and 2, Edited by C. J. M. Stirling (In the series: *The Chemistry of Functional Groups*, Edited by S. Patai). John Wiley and Sons, Chichester-New York-Brisbane-Toronto. 1981. XIV + 847 pp. £75.

The illustrious family of books entitled "The Chemistry of Functional Groups", fathered by Professor S. Patai, can proudly announce another addition to its rank: this time twins, happily delivered through the competent midwifery of Professor Stirling. This most recent offspring appears as two stately volumes on the chemistry of the sulphonium group, together comprising 17 chapters authored by 22 individuals, including several distinguished members of the international community that has contributed significantly to our present knowledge about this restricted, but important area of modern chemistry.

Sulphonium compounds have a long but curiously intermittent history going back more than a hundred years. In 1942, the sulphonium compounds, including their stereochemical properties, could be dealt with on five out of more than one hundred pages devoted to organic sulphur compounds in Gilman's comprehensive "Organic Chemistry". Now, in 1981, we are confronted with a total of 847 pages to cover the same topic. This dramatic development is conditioned primarily by two lines of interest: (i) the synthetic applicability and usefulness, and (ii) the biological significance of sulphonium compounds, both requiring, at least partly, a detailed knowledge of their stereochemical properties.

It would have been helpful if it had an authoritative introductory chapter tracing the history of sulphonium compounds from their infancy to the present full bloom, with brief stops at important milestones. This monumental work deserved such an overture to help unfold a fascinating piece of scientific history and, at the same time, present the reader with a vantage point from which to recognize the overall pattern made up of chapters ranging from orbital theory to enzyme specificity. Other items of general significance such as problems associated with definition, naming, and indexing of sulphonium compounds could have been profitably treated in the same introductory section, thereby reducing a number of inconsistencies noted from chapter to chapter. Thus, the definition of a "sulphonium compound" in the present work ranges all the way from a tri-carbon-ligated species to an entity possessing as little as one carbon atom attached to a tricoordinate, charged sulphur atom. Some introductory comments on this varying practice would have been in order.

The reviewer's need for an introductory section should not, however, blur the picture of the present monograph as a substantial, comprehensive and inspiring addition to our chemical literature. We are undoubtedly dealing here with *the* book on sulphonium compounds for a long time to come. The book addresses itself not only to the specialist seeking precise information on details but also to the chemist for whom sulphonium compounds constitute less familiar but potentially fertile ground.

The ensuing exposition of the individual chapters endeavours to disclose the new monograph as a veritable treasure box of facts and inspiration.

The opening chapter by M. Simonetta and A. Gavezzotti on general and theoretical aspects points to sulphur as an element "that forms a variety of compounds escaping simple dot-and-dash description". The authors present the first extended Hückel calculations of simple sulphonium ions and thus provide insight into the shape of their molecular orbitals. The subsequent paper by E. F. Perozzi and I. C. Paul succinctly reviews our present knowledge about the structural chemistry of sulphonium compounds including ylides and some selenium analogues. A detailed presentation of all the structures which have been subjected to X-ray analysis is beautifully illustrated with numerous stereoscopic views and is accompanied by a competently commented survey of the established molecular dimensions.

Five shorter chapters follow dealing with various properties of sulphonium compounds: M. R. F. Ashworth outlines the numerous problems associated with the detection, isolation, identification, and quantitative determination of the highly polar sulphonium ions; R. Shaw reviews the thermochemistry, and J. D. Coyle the photochemistry, demonstrating, by way of examples, the often deep-seated and potentially useful transformations brought about upon interaction of sulphonium substrates with light. Anyone interested in chiroptical properties of sulphonium compounds must be grateful to G. C. Barrett for his excellent review of our knowledge about the electronic spectra, mandatory to correct interpretations of ORD- and CD-curves of chiral sulphonium substrates. A well-written chapter by J. Grimshaw provides surprises, notably, it is believed, to the less informed reader by demonstrating the potential usefulness of electrochemical processes in synthesis, often regarded by the average organic chemist as a specialist's corner.

Two chapters reflect on the inductive character of the sulphonium grouping. The multitude of reactivities embedded in sulphonium ions (elimination, ylide formation, rearrangement and several other types of reactions) has aroused considerable interest, also on the part of the biochemist, concerning mechanistic details. As a useful tool in studies towards this end isotopes have been widely invoked. Hence, it is useful and timely that L. F. Blackwell has presented us with an excellent exposé on isotopically labelled sulphonium compounds and their reactions. Somewhat in the same vein is the subsequent chapter on the electronic effects of the sulphonium group, authored by J. Shorter; here, many useful data relating to important reactions such as electrophilic and nucleophilic substitution and stabilization of adjacent carbanion centers in ylides can be found.

In an authoritative review K. K. Andersen succeeds, on well-nigh 40 pages, to give the reader a comprehensive account of the important stereochemical aspects of sulphonium ion chemistry, a field of considerable current interest, both in organic synthesis and in a biochemical context. The chapter serves as sort of a prerequisite for the two ensuing chapters on the synthesis and reactivity of sulphonium salts. P. A. Lowe succinctly reviews the synthetic aspects and teaches the less versed reader that numerous alternatives exist to the classical sulphide alkylation. On about 60 pages, A. C. Knipe discusses the reactivity of sulphonium salts in a well-organized review. The scope of the task is reflected in the fact that the reader is confronted with 508 (!) literature references.

The second volume opens with a mammoth chapter on cyclic sulphonium salts, authored by D. C. Dittmer and B. H. Patwardhan. Here, 861 references are listed to support the competent and ordered discussion of sulphonium salts ranging in ring-size from three to seven and more members. The discussion encompasses many of the more spectacular results from the last few years and is a veritable well of inspiration for novel discoveries. A chapter on organosulphur cation radicals, by H. J. Shine, appears at first glance to be slightly off the main road. Closer scrutiny, however, reveals much of interest to the "sulphonium ion chemist". S. Oae, with the colleagues T. Numata and T. Yoshimura, have undertaken the formidable task of reviewing the heterosulphonium salts. This they do, and do well, on about 100 pages, with 576 references to the literature. The coverage includes oxysulphonium, azasulphonium, thiasulphonium and halosulphonium salts, as well as their numerous modes of reaction, and constitutes another source of inspiration.

Sulphonium salts were introduced as a tool in organic synthesis in 1962 by Corey and Chaykovsky and have since been utilized for this purpose with an ever-increasing elegance and efficiency. The existence of several recent reviews justifies the rather brief, but succinct attention given to this aspect in Block's 30 page chapter. It affords inspiring reading and suggests that the potential is far from exhausted.

The closing chapter on the biochemistry of sulphonium salts by G. A. Maw is a meticulously prepared and very comprehensive account of a fascinating development from the historical discovery in 1948 by Professor Challenger of the first naturally occurring sulphonium compound to the detailed studies on the stereochemical intricacies of *S*-adenosyl-L-methionine, the sulphonium compound *par excellence* without which life cannot be sustained.

"Repetitive, redundant, uneven in style and format". These are adjectives frequently applied to multiauthor undertakings, but applicable, to be sure, to only a very limited extent in the present production. "White spots" exist, however; thus, the spectroscopical properties of sulphonium compounds, other than the electronic spectra, are hardly covered in a systematic fashion. The book is well-printed, though not devoid of typographical errors, and is equipped with copious indexes making it relatively easy to find one's way around. Most reviews these days close with a remark to the effect that the price is prohibitively high for personal purchase. The present work is no exception in this respect. For libraries, however, frequented by chemists with even the remotest interest in sulphonium ion chemistry, acquisition ought to be a matter of course.

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