Book Reviews

The Chemistry of Organic Sulfur Compounds. Volume 2. Edited by NORMAN KHARASCH and CAL Y. MEYERS. Pergamon Press, Inc., 44-01 21st St., Long Island City, N. Y. 1966. vii + 465 pp. 17.5 × 25.5 cm. $21.00.

Few have been attracted to the formidable task of writing comprehensive surveys about organic sulfur chemistry. A reason was implied by the most indefatigable such author, E. Emmet Reid. In the first of his five volumes on the organic chemistry of bivalent sulfur, Reid commented that the rate of expansion of organic sulfur chemistry is twice that of the subject as a whole and that the proportion of entries in *Chemical Abstracts* dealing with organic sulfur compounds increased from one-sixth in 1924 to one-third in 1954. A single author may well quail at the thought of supplying a counterpart to Reid's treatise for higher valent classes! C. M. Suter's excellent volume covered part of this complementary ground but appeared in 1944.

There has been great need for protection of those needing information about sulfur compounds from the publication explosion. The key to the defense lies obviously in alliances of authors. Volume 9 of the fourth edition of Houben-Weyl, by such an alliance, contains 915 pages of comprehensive coverage of organic sulfur chemistry, but it appeared in 1955. The chemical community can be grateful for the series edited by Kharasch and Meyers for its notable help in meeting the need, particularly since it is on a continuing and flexible basis.

The approach of the present series is to supply critiques on special areas by experts working in them, rather than systematic coverage of classes after the fashion of Reid, Suter, and Houben-Weyl. As the series grows, though, it will probably embody much of the class-survey aspect. Chapters of the class-survey kind in Volume 2 treat olefin sulfides, polyfluoroalkyl derivatives, 1-alkynyl thioethers, 1,2-dithioles, thiohydantoins, and thiophosgene. There is an interesting chapter on bond properties, and the remainder of the fifteen chapters deal with reactions from a usefully mechanistic viewpoint; the reactions are those of Raney nickel desulfuration, isomerization of thiocyanates, eliminations of sulfur dioxide, thiols (oxidation, additions of radicals), and disulfides, especially cystine (alkaline decomposition, cleavage with cyanide ion, and oxidation). The series makes one think of *Chemical Reviews* restricted to sulfur chemistry with more involvement of authors' views; one might add that occasionally, though not often, these views become a bit dogmatic with the result that demarcation between generally accepted and author-developed theory becomes blurred. The topics are timely and deserve review, although two or three reviews overlap recent ones elsewhere. A few topics seem rather highly specialized but still well worth inclusion.

The experts have been well chosen. They have generally written well, and their treatments are properly critical rather than being mere catalogs of facts. But there are a few instances where particular interpretations of data may not be universally approved. The chapters impressed the reviewers as being about evenly distributed between adequate, good, and outstanding. Coverage usually is good, the number of references per chapter ranging from 40 to over 200. Many references are to 1964, with partial updating into 1965 by an appendix; since some reviews evidently were completed in 1961, and since only six chapters were so updated (perhaps because the others were completed much later), however, it does seem that reduction of the time lag in the future would enhance the value of these useful volumes.

There are several commendable novel features in the series. Volume 2 contains previews of Volumes 3 and 4 (searches of the series would be aided if future volumes listed *earlier* chapters as well). The appendix has an extensive general listing of books, reviews, and symposia and another of papers on reaction mechanisms and structure; these update to 1961–1965 lists in Volume 1. An author index is supplied (one should be aware that a few late references missed inclusion); the subject index has been done with more than usual care.

Printing, paper, and sturdiness are excellent, and the book should stand up well under the hard use it will surely receive. The price per page is about midrange for such books. There are relatively few errors, nearly all of them typographical; a couple of dozen were noticed but none seem serious.

The series will be a chemical classic. One hopes for its continuation at as fast a pace as possible. Not all chemists will want the series in their personal libraries, but those who work often with sulfur compounds are likely to find it a good investment. *All* chemists at least should be aware of the existence of the series, since their dipping into it when working with sulfur compounds will probably be rewarding—the more so, in light of the intent to make the series useful to those interested in physical, inorganic, and biological chemistry, as well as in the primary focus on organic chemistry. The series of which Volume 2 is a part is a "must" for libraries.

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Hydrogen Compounds of the Metallic Elements. By K. M. MACKAY, B.Sc., Ph.D., A.R.I.C. Barnes and Noble, Inc., 105 Fifth Ave., New York, N. Y. 1966. vi + 186 pp. 16 × 24 cm. $10.00.

This readable survey of hydrides, mostly of the metals, does not pretend to be invincibly profound and is unabashedly descriptive in outlook. By assimilating its six brisk chapters, a good chemistry student can get a firm qualitative grasp of hydrides today.

There is not a single crystallographic sketch, an omission which makes the reader strain his senses to interpret verbal descriptions of the arrangements of atoms in compounds like UH_3 (p 66) or K_2ReH_9 (p 138). There are only two generalized phase diagrams, but these are competently explained. Mackay's book summarizes conveniently many of the physical constants of hydrides, although one looks in vain for quantitative data on some systems, such as the Pd–H system. The lack of an author index is frustrating. There are a dozen or so misprints and other unimportant errors.

The presentation of ionic hydrides is clean and quite satisfying. In discussing transition metal hydrides, it was shown that the protonic and hydridic theories are not mutually exclusive. One might have wished for a more far-reaching attempt to formulate a general theory of transition metal hydrides, relating coordination number with structure type and interatomic distances. There is a lucid description of TiH_2 and its polymorphism, and, while the underlying reasons for this behavior are moot, the pertinent questions are presented. The hazy status of the binary hydrides of Fe, Co, and Ni is left as inconclusive as ever. One finds mention of little-known substances such as GeH_2, although some, such as $LiAlH_2$ (Garner and Haycock, 1952), are omitted. The controversy on the position of H^- in the spectrochemical series is reported. Table 5.1 is an unsuspectedly long list of no less than 190 π-bonded complex compounds also containing metal–hydrogen bonds. I would like to impress certain of my colleagues indelibly with the tart warning on page 100, to the effect that not all differences between carbon and nitrogen and their heavier congeners are attributable to participation of d orbitals.

The book does have its share of inadequacies, in factual errors, opaque phrasing, and omissions. Some of these are detailed here. Kinetic and thermodynamic stabilities of some complex hydride solutions seem to be confused (p 169). Trimethylplumbane is described as decomposing above $-100°$ on page 121 and above $-37°$ on the next page. The description of copper hydride is far better than that found in any other summary, but suffers from errors, such as calling a suspension a solution, or that CuH can be made using atomic hydrogen (which is unproven). Wiberg's allegation (1952) that a pyridine-soluble CuH can be made was not cited. The statement (p 88) that palladium hydride affords the only case where the hydrogen-poor and hydrogen-rich phases have metal lattices of the same symmetry is not really true, as some rare earth metals constitute other examples. Europium and ytterbium dihydrides do show considerable metallic character, contrary to the information on page 36, and ytterbium has not yet been coaxed into forming a trihydride, contrary to page 61. The presentation of chromium hydrides is uncommonly skillful, but the magnetic study by Albrecht and Perthel (1964) was inadvertently omitted. No quantum mechanical computations of the type carried out by

Takeuchi and Suzuki (1962) were mentioned in connection with continuous-phase hydrides, such as PuH_2–PuH_3. The oxo process might have been included in the section on cobalt carbonyl hydride. A well-known preparation of stibine (Berka, *et al.*, 1960) was unaccountably overlooked. Gaylord's book on reductions with complex hydrides was referenced, but not that of Micovic and Mihailovic (1955). Organic purists will shudder at phrases such as "monovalent carbon as in the alkyl group" (p 11) and "a strongly coordinating ether such as triethylenediamine" (p 111).

No chemist in the field of hydrides can ignore this volume with profit; it generates too many ideas for that. In some places, it communicates thrill with the subject, maybe even a little awe. I like the book.

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Benzenoid-Metal Complexes. Structural Determinations and Chemistry. By H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, Monsanto Research S. A., Zurich. The Ronald Press, Co., 15 East 26th St. New York, N. Y. 1966. v + 101 pp. 15.5 × 23.5 cm. $7.00.

Since the discovery of ferrocene and the development of carbon–metal bonding theories in the early 1950's, the area of organotransition metal chemistry has developed at an exceedingly rapid rate. An appreciable part of this growth has concerned the synthesis, properties, and reactions of organometallic compounds containing arene or benzenoid groups which are π-bonded to various transition metals. The present monograph constitutes a reasonably comprehensive and critical review of this branch of organometallic chemistry, dating from the original studies of Hein in 1919 until January 1965.

The book is divided into three major parts. The first chapter is relatively short and discusses single-crystal X-ray diffraction studies which have been carried out on various arene–metal complexes. This chapter on structural determinations is followed by successive chapters on bis-arene–metal complexes, as exemplified by bis-benzene–chromium, and on arene–metal carbonyl complexes, as exemplified by benzene–chromium tricarbonyl. Each of these latter chapters contains useful tables which list the molecular formulas, melting points, and original literature references of the many complexes which fall into each category. The book also contains a Nomenclature Index as well as Author and Subject Indexes.

The chapter on structural determinations discusses complexes in which the arene unit is bonded to the metal either by weak van der Waals forces, by charge-transfer forces, or by stronger π-bonding interactions. The controversy concerning the symmetry and structure of bis-benzene–chromium is the major topic of discussion of this chapter, and additional refinements of reflection data made by the present authors are included. It is unfortunate that the important papers of Bailey and Dahl concerning the structures of benzene–, thiophene–, and hexamethylbenzene–chromium tricarbonyl, briefly referred to on page 13, were not available for more general discussion. Equally unfortunate is the omission of Haaland's electron diffraction studies on bis-benzene–chromium, although the latter work is briefly mentioned on page 34 in Chapter Two. One is left with the impression that most of the π-arene rings in these complexes show little if any threefold distortion toward "cyclohexatriene" systems, but that such a conclusion can by no means be generalized.

The chapter on bis-arene–metal complexes is essentially an extension of a previous chapter written by Zeiss in "Organometallic Chemistry" (Reinhold Publishing Corp., New York, N. Y., 1960). The earlier chapter dealt primarily with the elegant structural elucidations of bis-arene–metal complexes which were conducted by Zeiss and Tsutsui in the 1950's. The present chapter describes in more detail the various synthetic routes leading to bis-arene–metal complexes, as well as a discussion of their physical properties, spectra, and chemical reactions. The chapter is well written and is reasonably complete, although a reference to the "Inorganic Syntheses" procedure (Volume 6, 1960) for the formation of bis-benzene–chromium and bis-benzene–chromium (I) iodide is noticeably absent. The formation and properties of arene–metal carbonyl complexes are covered in detail in the final chapter, and there is a discussion of mechanistic studies relating to these substances. The chapter contains a large number of structures and illustrations which aid immeasurably in comprehending the text. The book is remarkably free from typographical errors, although several were noted in the Nomenclature Index on page 94.

This book should serve as a useful reference for scientists actively engaged or contemplating research in organotransition metal chemistry. It may also find use as a reading supplement on arene–metal complexes in various graduate courses in inorganic and organometallic chemistry. Perhaps the biggest criticism of the book is that the material would have logically fitted into one of the several excellent organometallic review journals available rather than to have appeared as a monograph.

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