Book reviews

Synthetic Methods of Organometallic and Inorganic Chemistry W. A. Herrmann (ed) Volume 3, Phosphorus, Arsenic, Antimony, and Bismuth H. H. Karsch (Vol. Ed) Georg Thieme Verlag, Stuttgart, 1996

228 pages. DM185 ISBN 3-13-103041-0 (Georg Thieme Verlag, Stuttgart) ISBN 0-86577-654-7 (Thieme Medical Publishers, New York)

Synthetic Methods of Organometallic and Inorganic Chemistry is a series of eight volumes covering both the synthesis and the spectroscopic data useful for identifying the most important compounds in inorganic or organometallic chemistry.

Volume 3 deals with organic compounds of group 15 elements. It contains only orginal contributions from top specialists in this field, i.e. synthetic methods that have been tested in their own laboratories.

A brief but consistent introduction explains the importance of these compounds, especially those of phosphorus, and presents a complete list of the compounds containing phosphorus, arsenic, antimony or bismuth discussed in the first two volumes.

The material is organized in six chapters, including the introduction. Chapters 2–5 concern phosphorus compounds, while the last one (Chapter 6) deals with substances containing arsenic, antimony and bismuth. Either common synthetic routes for classes of related (similar) compounds, or specific procedures for each derivative, are given.

For each compound the most suitable procedure is described in detail and, where necessary, the authors insist on caution to avoid risks in handling the substances. Alternative methods of synthesis are presented for many compounds, but these are not discussed in detail. When necessary, synthetic methods for starting materials are also specified. In many cases, the equipment used for the synthesis is illustrated. A representative literature list accompanies each preparative method.

IR and NMR (frequently ¹H and ³¹P, sometimes ¹³C) data are given to allow the identification of the compounds. Often, other physical data are available (conductivity measurements, solubility etc.).

Chapter 2 is devoted to acyclic phosphorus(III) compounds. The compounds are classified in three groups, according to the coordination number at phosphorus: one, two, or three. From the first group, methylidynephosphane (H–C \equiv P) and some of its derivatives R—C \equiv P, as well as lithium salts of [O–C \equiv P] $^-$ and [S–C \equiv P] $^-$ and compounds containing cationic [Ar–N \equiv P] $^+$ or bis(amino)-phosphenium and -arsenium, are discussed. From the second group, compounds with one P=N or P=C bond are presented; for coordination number three,

preparative methods for RPH₂ and R₃P, as well as for halogenated compounds RPCl₂ or R₂PCl, are described.

Chapter 3 deals with acyclic phosphorus(V) compounds, referring to different compounds with three-(phosphorane derivatives) or four-coordinated phosphorus atoms, while Chapter 4 gives details on acyclic compounds containing two or more phosphorus atoms, i.e. compounds with single P-P or double P=P bonds, as well as compounds containing P-Se-P, P=C=P, or P=CH-P fragments.

The next chapter is devoted to mono- and poly-cyclic phosphorus compounds containing one or more phosphorus atoms. Only heterocyclic compounds are described.

Chapter 6, on the compounds of arsenic, antimony and bismuth, contains preparative methods and NMR data for some R_3E (E=As, Sb, Bi) and halogen-containing compounds of organoantimony(III) and (V), organoarsenic(III) and organobismuth(III).

The book is completed by a Subject Index and a Formula Index indicating all the compounds mentioned in the book and those for which specific preparative procedures are given.

The material presented here, providing a high level of information and applicability, will be an excellent tool for chemists, research workers and students involved in synthetic work, teaching or study at universities or in industrial laboratories, and for those interested in Group 15 element chemistry and generally in organoelement chemistry.

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Organotin: Environmental Fate and Effects M A Champ and P F Seligman (eds) Chapman and Hall, London, 1996 623 pages. £195.00 ISBN 0-412-58240-6

This monograph is divided into 29 chapters with contributions from 49 authors.

Organotin compounds have many applications in industry, the largest being as PVC stabilizers. This book is concerned with the uses of tributyltin derivatives over the past 30 years as paint additives, where they function as antifouling agents for the protection of marine and freshwater ships from organisms such as barnacles, tube worms and seaweeds, which otherwise increase the frictional resistance of the underwater parts of vessels. The organotin may be in the form of (Bu₃Sn)₂O or, more effectively, Bu₃SnO- groups bonded to a polymer chain. The discovery that very low concentrations of Bu₃Sn-(nanograms per litre) are also toxic to molluscs such as oysters and mussels resulted in a ban on their use as paint additives except for ocean-going vessels. Several chapters are devoted to regulatory policies for the use of organotin compounds, and to the acute effects of Bu₃Sn- compounds on aquatic biota.

A number of chapters are devoted to the difficult task of developing reliable analytical methods for these low concentrations of organotin compounds; these include conversion to organotin hydrides using NaBH₄ or to tetraorganotins using RMgX, followed by a separation technique (usually chromatography) and detection by atomic absorption or mass spectrometry. ¹⁴C-labelling of Bu₃Sn– has also been employed; in addition, mussels have been used as bioindicators in order to overcome some of the limitations of chemical analysis.

Other chapters are concerned with the complex problem of the fate and persistence of Bu₃Sn– in aqueous ecosystems. Both aquatic plants and animals possess enzyme systems responsible for successive loss of butyl groups; this loss may be accompanied by biomethylation, since Bu₃SnMe and Bu₂SnMe₂ have been detected. Free-radical biological hydroxylation of Bu–Sn groups also occurs, giving for example [CH₃CH₂CH(OH)CH₂SnBu₂]⁺. Metabolic studies on fish using ¹⁴C-labelled Bu₃Sn– have revealed a short residence time of about three days.

Further chapters are concerned with the ways in which these varied chemical reactions occur and the time scale involved. Reactions take place in the organic-rich surface film of natural waters, the bulk aqueous medium and in sediments. Biodegradation in sediments is possibly catalysed by clay minerals but is slow, and sediments provide a short-term sink for Bu–Sn compounds. Photolytic decomposition is probably confined to the surface layer. It has been firmly established that bacteria, algae and fungi can degrade Bu₃Sn–. A further point of general interest is that the persistence of Bu₃Sn– in aqueous ecosystems is measured in months, whereas many toxic chemicals such as DDT persist for years.

Chemists may be a bit dismayed by the number and nature of errors in representing structural formulae, e.g. in Figs 1.2 and 18.2 and on p. 4 (the TBT⁺⁺) cation, but the general organization of this book is good and individual chapters are both stimulating and readable. A substantial and well-organized index is included.

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Symmetry and Structure

S. F. A. Kettle 2nd edition, John Wiley and Sons, Chichester, 1995 430 pages. £19.99 ISBN 0-471-95476-4

The first edition of this book, subtitled *Readable Group Theory for Chemists*, appeared in 1984, and the major changes in this new edition are added chapters on crystal symmetry and space groups. The main competing text is Cotton's *Chemical Applications of Group Theory* and it is interesting to compare the authors' different approaches. Whereas Cotton launches quickly into formal definitions of groups and the classification of point groups, Kettle starts much more gently and leads the reader along with specific examples rather than formal ideas. This has some consequences which are surprising at first sight. For example, the identification of molecular point groups is not discussed until the end of Chapter 7, by which time most of the ideas about representations and character tables have been fully developed.

For those who like a gentle approach, Kettle's book certainly justifies its subtitle, and gives an excellent introduction to the basic priniciples. The new chapters on space groups follow a rather different format, being more abstract and less based on examples, but are nevertheless very clear and useful. I do find some disadvantages, however, with Kettle's approach. The range of examples discussed is very limited (often one molecule per chapter); in point groups these are mostly concerned with molecular orbitals; vibrations and spectroscopic selection rules are treated much more briefly. Readers of this journal will be disappointed to find no reference to organometallic compounds. Also, it is not easy to look things up in this book—it really is intended to be read from the beginning. In summary, I recommend it as a very good book for students, but much less useful for reference purposes.

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