

Book reviews

S-Centered Radicals

Zeev B. Alfassi (ed.)

John Wiley, New York, 1999

382 pages. £120

ISBN 0-471-98687-9

My scientific career has been focused on free radicals, yet in its many aspects sulphur-radical chemistry has been something of a blind spot. Therefore, the opportunity to comment on this new text edited by Zeev Alfassi was especially welcome, and for the most part I have not been disappointed. An initial search for recent data on the structure and ease of formation of sulphur-centred radicals quickly revealed all that I wanted to know. And although not all of the detail which I was seeking was to be found in the two chapters specifically devoted to Structure and to Thermochemistry, the excellent subject index led me quickly to further pertinent information.

The general standard of production is high. The contributors have themselves all added to our current knowledge of the field, and therefore write with authority; their coverage usually includes references well into 1998. In several instances, however, contributors have imposed explicit constraints on the extent of subject coverage. Where this entails omission of the older literature, any deficiency is made good by comprehensive referencing of alternative review sources; in these cases I found no difficulty in following the presentation. Where, occasionally, selectivity has instead excluded certain topics entirely, this may be less satisfactory, although sometimes it is compensated for in other chapters. In this respect, the editor seems to have succeeded in avoiding unnecessary duplication, though a curious omission is the absence of any Editor's Preface—which might have assisted the reader in gaining some impression of the planning and ordering of the book. Perhaps that lot was intended to fall to the reviewer, in which case.... Although the last three chapters cover the structure and organic chemistry of sulphuranyl radicals (X_3S^+), the roles of thiyl radicals in biological systems, and the application of sulphur-centred radicals in organic synthesis, the emphasis in much of the earlier part of the book has a distinctly 'physical' flavour. The general discussions of sulphur-centred radical structures and of thermochemistry start things off, but the middle chapters comprise a series of rather specialized reviews, for which it must have been quite difficult to create a coherent order. These are concerned with: SO_x anion radicals; gas-phase reactions of sulphur-centred radicals—including atmospheric sulphur chemistry; the use of radiation chemical techniques

in the context of sulphur-radical chemistry; aromatic thiyl radicals—with an emphasis on fast reaction kinetic techniques; thiyl radicals in the solid phase; and finally, sulfoxyl radicals—again emphasizing physical aspects.

I believe the omission of an author index from a specialist text of this kind is a mistake. It would also have been helpful if the contents list had included major chapter subdivisions. Nevertheless, Alfassi has managed to compile a book into which chemists from diverse fields will dip with advantage. As such, it can be recommended, but the price is probably too high for more than the most affluent to include in their personal libraries.

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Activation of Unreactive Bonds and Organic Synthesis Topics in Organometallic Chemistry, Vol. 3

S. Murai (ed.)

Springer-Verlag, Berlin, 1999

272 pages. £76

ISBN 3-540-64862-3

The title of this book is rather disarming. As the editor writes in the preface, he was hesitant to use the term 'activation' to describe the type of reaction being reviewed here. The term 'hydrocarbon activation' is well known and is used by organometallic chemists to mean metallation of a hydrocarbon C–H to give C–M. This is the meaning of activation in this book. Another point not clear from the title is that the book is mainly concerned with transition-metal complexes. The material in this monograph is made especially stimulating by describing applications to organic synthesis. As such it is a very useful and informative book, and the editor deserves praise for bringing together such an interesting range of topics.

This is a multi-author book, with ten chapters, but the only index is to previous volumes in the series. The

chapters cover the following subjects: General Survey, Stoichiometric C–H Activation, Catalytic C–H Activation, Catalytic Activation of Methane and Ethane, C–C Bond Cleavage, Activation of Si–Si Bonds, Activation of C–O Bonds, Activation of C–Cl Bonds, Dinitrogen in Organic Synthesis, and Activation of C–F Bonds. These topics are in different stages of development as techniques for practical organic synthesis.

Anyone reading about this area of chemistry for the first time will be struck by the apparent obsession of the investigators with the importance of transition metal–carbon bonds. Admittedly they are important, but the cobalt-catalysed oxidation of cyclohexane is a commercial process involving C–H activation, which probably does not involve M–C bonds although it is catalysed by a transition metal. However, I found very few errors in the book, although I was surprised to see on p.2 the derivation of the word ‘agostic’ being attributed to Crabtree, rather than to M. L. H. Green.

A detailed examination of the chapters reveals an up-to-date survey of the various areas. For example, in the chapter on C–C single-bond cleavage by M. Murakami and Y. Ito, the authors have found a surprisingly large number of examples of this reaction. This type of reaction is less developed than C=C cleavage (olefin metathesis), and a large proportion of the examples involve strained (three and four-membered) rings. There are also reactions involving a pincer-type chelating ligand, and several types of rearrangement or migration reactions. Some elements which are familiar in polymerization reactions such as lutetium, zirconium and hafnium, also undergo reverse insertion reactions, which involve C–C cleavage. Both stoichiometric and catalytic reactions are described in this chapter.

The most challenging system discussed in the book is the triple bond in dinitrogen. However, it is now emerging that the chemistry of coordinated dinitrogen is possibly more varied than the chemistry of coordinated carbon monoxide.

To summarize, this book contains the basis of much important future work which will result from developing the themes presented here. It is not so much a record of what has already been achieved, as a signpost to the areas where future developments lie.

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X-ray Fluorescence Spectroscopy

R. Jenkins

2nd edn. John Wiley, Chichester, 1999
xviii + 207 pages. £65
ISBN 0-47-129942-1

This book provides a complete introduction to the subject, from the basic physics of the process through

to industrial applications. The theory sections have been significantly embellished since the first edition, with a new chapter on X-ray spectra. They are, however, pitched at a level that will make them accessible to any interested reader.

There is also a new section on the historical development of XRF, which provides an interesting insight into the way the technique has matured from an esoteric exercise in physics into a general-purpose industrial tool.

In my opinion, the book is primarily targeted at practical users of the technique, particularly newcomers. It includes, for example, chapters on specimen preparation, qualitative and quantitative work.

I felt that the book does not really do the title justice in that it also provides useful introductions to a number of related techniques such as X-ray lithography, tomography, astronomy etc. There is a full chapter devoted to X-ray diffraction. A surprising omission in this respect is the use of X-ray spectrometry in conjunction with electron microscopy, which receives scant mention.

Overall, I found the book to be very easy to read and a worthwhile addition to the literature on the subject. I am sure that, like the first edition, it will find widespread use both as a teaching aid as well as a reference book for more experienced practitioners

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Interrelations Between Free Radicals and Metal Ions in Life Processes

Metal Ions in Biological Systems, Vol. 36

A. Sigel and H. Sigel (eds)
Marcel Dekker, New York, 1999
848 pages. \$250
ISBN 0-8247-1956-5

There is so much of interest in this book that it is difficult to know where to begin the review. The central theme is radicals in biology, in particular the interaction of these radicals with metal ions. A wide range of radicals is considered, including superoxide and nitric oxide. There are also chapters on radical processes such as lipid peroxidation, metal-induced carcinogenesis and organo-cobalt-induced radical formation. In all there are 21 chapters, written by different authors, and five of them are concerned with aspects of the nitric oxide story. The remaining 16 cover a range of topics, some of which have been mentioned already. Although the quality of the contributions to a multi-author work varies, all the chapters are written by acknowledged experts with an air of authority and will be of particular aid to those newly entering a field of research. There is also much of interest