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Book reviews

Free Radicals; Ed. by J.K. Kochi, Wiley, New York, 1973, Vol. I, xvii + 713 pages, £18.75; Vol. II, xx + 906 pages, £21.50.

Most of the topics of current interest in free radical chemistry are covered in this impressive two volume work in the "Reactive Intermediates in Organic Chemistry series". The editor and the leading authorities who wrote individual chapters are to be congratulated on avoiding the pitfalls usually associated with multi-author works: the result here is a broad, balanced coverage with little wasteful overlap.

The chapters are organized into four theme areas, one of which is "Free Radicals with Hetero-atoms". Two very substantial chapters on phosphorus and on Group IVB centred radicals in this section, along with a chapter on S_H2 reactions at metal centres, will be of greatest interest to readers of this Journal.

W.G. Bentrude gives a comprehensive coverage of the structure and reactions of the various possible types of phosphorus centred radicals including radical cations and anions, but with phosphino ($Z_2P\cdot$), phosphinyl [$Z_2P(O)\cdot$], and phosphoranyl ($Z_4P\cdot$) radicals receiving most of the attention. Stereochemistry is highlighted, reflecting the considerable configurational stability of phosphorus-centred radicals and also the nuclear spin of ½ possessed by ^{31}P which is useful in ESR studies. Much of the experimental data, particularly on reactions involving phosphoranyl intermediates, is discussed in terms of the thermochemistry of the reactions involved: in situations where alternative reactions are feasible, this approach often offers insight into why one reaction is more favourable than the others.

Group IVB radicals, reviewed by H. Sakurai, provide fewer different reaction types, the main radicals of importance being of type $R_3M\cdot$. An important feature of their chemistry is the comparison, both in structure and reactivity, with carbon-centred radicals. Methods of formation of $R_3M\cdot$ radicals are discussed comprehensively: many of the differences between preparative methods for these radicals and organic radicals reflect thermochemical differences, which are also important in affecting reactivity. The (non-planar) stereochemistry of silyl radicals is discussed in some detail. In the section on reactivity, particular emphasis is given to aromatic substitution, cyclizations and rearrangements of Group IVB containing radicals, and also to S_H2 reactions at Si—Si linkages, areas of research in which Japanese research groups are prominent.

A.G. Davies and B.P. Roberts, in their chapter on bimolecular homolytic substitution reactions at metal centres, review a relatively new area of research to which they themselves have contributed outstandingly. S_H2 reactions at metal centres are most facile for radicals centred on electronegative atoms: the longest section in the chapter is devoted to alkoxy radicals, whilst alkyl and aryl radicals rate only two pages. Attack by alkylperoxy radicals is important in autoxidation of organometallic compounds, and these autoxidations form an instructive contrast to hydrocarbon autoxidations (a topic also considered in the separate chapter on autoxidation by J.A. Howard). Many of these reactions have been studied kinetically by ESR methods, and structural features affecting reactivity are becoming better understood.

The way in which organometallic radical reactions have become part of the fabric of free radical chemistry is shown by the wide occurrence of organometallic reactions in the discussions in the other chapters of the book. Although only three chapters out of 26 are devoted entirely to radical reactions of organometallic compounds, discussion of structure or reactivity of organometallic radicals, especially those centred on tin or silicon, occurs in no less than 14 of the remaining chapters of the work.

In summary, this work is likely to remain for many years the best and most comprehensive monograph on Free Radical Chemistry available. Although its price may appear to put in the "library purchase" category, the utility of "Free Radicals" will ensure that a large number of individual researchers on free radical chemistry, including the growing number working on organometallic radicals, will wish to have their own copies.

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Gmelins Handbuch der anorganischen Chemie. Ergänzungswerk zur 8. Auflage. *Band 10. Zirkonium-organische Verbindungen* (88 pp.). *Band 11. Hafnium-organische Verbindungen* (22 pp.). Gmelin Institut für anorganische Chemie und Grenzgebiete in der Max Planck-Gesellschaft. A. Moulik (reporter); A. Slawisch (senior editor), Verlag Chemie, Weinheim/Bergstrasse, 1973, DM169.

This slim book which contains both of the mentioned volumes continues the Gmelin Institut's coverage of organotransition metal chemistry with an exhaustive review of the C-bonded organic derivatives of zirconium and hafnium. In contrast to the volumes on chromium, vanadium and cobalt [1,2] which are in German, this book is in English. (It would be nice indeed, and it would make practical sense, if all future Gmelin volumes were published in English). Marginal notes in German serve to aid the German user, and the preface which explains the organization of these volumes is given in German as well as in English. The organization is the same as that followed in the previous volumes [1,2] and useful compound and ligand formula indices are provided.

Over 400 compounds of zirconium and hafnium are described. Their types are not numerous, compared with those of other transition metals. Some σ-bonded alkyls, benzyls and aryls are reported, but π-bonded derivatives