Advances in Carbene Chemistry. Volume 3. Edited by Udo H. Brinker (Universitát Wein). JAI Press, Inc: Stamford. 2001. x + 322 pp. $295.00. ISBN: 0-444-50892-9.

This is the third volume of a valuable series on carbene chemistry. Continuing the tradition of previous volumes, a number of leading researchers in the field have written chapters on areas in which they have made major contributions. For the most part, this useful volume provides important examples of the application of techniques of modern physical organic chemistry to the study of a significant reactive intermediate.

The chapter by Merrer and Moss contains an extensive discussion of the kinetics of intramolecular carbene rearrangements. A wealth of data both from laser flash photolysis (LFP) kinetic investigations and from product analysis is presented. The authors focus on three main factors affecting the kinetics of singlet carbene rearrangements: the role of carbene precursors, mainly rearrangements in excited states (RIES) of precursors; the effect of quantum mechanical tunneling; and substitutent effects at the migration origin. The important issue of the intervention of RIES and carbene-alkene complexes in carbene reactions is dealt with clearly and fairly. Of great value is an appendix containing an extensive compilation of rate constants and activation barriers, both experimental and calculated, for carbene rearrangements. In some cases, the rather large discrepancy between experimental and calculated values should provide considerable impetus for further investigation.

The question of the protonationation of carbenes to form carbocations is discussed in an interesting chapter by Kirmse. As the author points out, the issue of carbene protonation is tricky, because products can also arise from protonation of carbene precursors. This is especially true when diazo compounds are employed. The reader is led through a clear discussion of the problems and their resolution through the use of controls and LFP studies of reaction intermediates and rates. This chapter concludes with a useful discussion of the proton affinities and basicities of carbenes.

A contribution by Maier and Reisenauer entitled “Carbenes in Matrices: Spectroscopy, Structure and Photochemical Behavior” chronicles the achievements of this remarkably prolific group at Giessen. A description of the carbenes that have been matrix-isolated by the Maier group is presented. These carbenes range from cyclopropylidenes through stable nucleophilic carbenes to C_nO species. The authors make clear the utility of matrix isolation for investigating these reactive intermediates and illustrate the extraordinary value of calculated IR spectra in such studies.

The chapter by Sander and Bettinger is an extensive examination of the chemistry of 2,5-cyclohexadienylidenes. Beginning with a concise discussion of current computational techniques as applied to carbenes, this chapter chronicles both matrix isolation and LFP studies of cyclohexadienylidenes. The rich chemistry of these triplet carbenes makes fascinating reading and represents a perfect example of the use of modern matrix isolation and LFP in conjunction with calculations to study an interesting reactive intermediate.

Perhaps the carbene reaction that has received the most attention, both experimental and computational, is the phenylcarbene rearrangement. In a chapter titled “Differences between Phenylcarbene and Phenylnitrene and the Ring Expansions They Undergo”, Karney and Borden discuss this reaction and the related interconversion of phenylnitrene and the pyridylcarbenes. The experimental differences between phenylcarbene and phenylnitrene are clearly described along with sophisticated calculations that rationalize these differences. A valuable aspect of this contribution is the lucid discussion of the reasons for these differences. Computational results are translated into solid chemical principles that should be easily understood by those not versed in the complex jargon of computational chemistry.

One of the beauties of the chemistry of carbenes is that their high energy can be channeled into the synthesis of highly strained species. Frequent targets are bridgehead alkenes. Szeimies has summarized his work in this area in a nice chapter describing his experimental and computational studies of carbene → bridgehead alkene → carbene rearrangements. A useful synthetic aspect of carbenoid chemistry, selective insertion into the α-C−H bonds of alkoxides, is discussed in a chapter by Oku and Harada. The use of the exotic but important technique of photoacoustic calorimitry to determine heats and rates of carbene reactions is described by Goodman, whose research group has pioneered this technique in the area of carbene chemistry.

Although much of the material contained in this book is familiar to specialists in carbene chemistry, they should still find it extremely useful to have so much information collected in one place that is easily accessible. Those researchers with a more general interest in reactive intermediates will also find this volume useful. The modern physical organic techniques described here for a mature reactive intermediate are certainly applicable to newly emerging reactive species.

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JA0153823

10.1021/ja0153823

Synthetic Macromolecules with Higher Structural Order. Edited by Ishrat M. Khan (Clark Atlanta University). American Chemical Society: Washington, DC (Distributed by Oxford University Press). 2002. x + 230 pp. $125.00. ISBN: 0-8412-3728-X.

This book is based on a symposium by the Division of Polymer Chemistry held during the 219th National Meeting of the ACS in San Francisco in March 2000. Synthetic macromolecules with secondary and tertiary structural order constitute a highly interdisciplinary area that includes "organic and polymer synthesis, peptide design and synthesis, self-assembled

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macromolecules, computational studies to complement spectroscopic higher structural order determination, interaction of conformational (or higher structurally) organized oligomers and polymers with biological systems", to quote the editor. Accordingly, the chapters are organized into the following subtopics: Higher Ordering in Synthetic Polymers, Synthetic Peptides, and Macromolecular Assemblies. References are current to 2000. Author and subject indexes complete the book.

JA025260Q

10.1021/ja025260q

Organometallics in Synthesis: A Manual. 2nd edition. Edited by Manfred Schlosser (Université de Lausanne). J. Wiley & Sons: Chichester. 2002. xii + 1244 pp. $149.95. ISBN: 0-471-98416-7.

The second edition of this handy reference book strives to maintain the goal of the original volume, i.e., to teach the basic concepts and techniques of organometallic reactions through, in the words of the editor, "useful hints, rules of thumb, and last but not least, carefully selected working procedures". This second edition features not only updated and reworked chapters to incorporate new applications and protocols, it also includes four additional chapters on the chemistry of tin, zinc, zirconium, and chromium and iron.

JA025261I

10.1021/ja025261i

Combinatorial Materials Development. Edited by Ripudaman Malhotra (SRI International). American Chemical Society: Washington, DC (Distributed by Oxford University Press). 2002. xii + 184 pp. $125.00. ISBN: 0-8412-3772-7.

This book is based on a symposium on combinatorial approaches to materials development held during the 219th National Meeting of the American Chemical Society in San Francisco in March 2000. The symposium was focused on four areas of combinatorial materials development: parallel synthesis, rapid-throughput screening, robotics, and informatics. References are current through 2000. Author and subject indexes complete the book.

JA025259R

10.1021/ja025259r

Chirality: Physical Chemistry. Edited by Janice M. Hicks (Georgetown University). American Chemical Society: Washington, DC (Distributed by Oxford University Press). 2002. xii + 356 pp. $140.00. ISBN: 0-8412-3737-9.

This book grew out of the symposium entitled Physical Chemistry of Chirality held in San Francisco in March 2000. To paraphrase the editor, the book covers new instrumental and theoretical techniques to examine the "structure, recognition, and optical response of chiral systems". Its 22 chapters are divided into the following sections: Introduction, Vibrations of Chiral Molecules, Advances in Chiral Spectroscopy, New Approaches in Chiral Recognition, and Surface Chirality and Chiral Nanostructures. Author and subject indexes complete the book. References are current to 2000.

JA025246D

10.1021/ja025246d

Environmental Electrochemistry: Analyses of Trace Element Biogeochemistry. Edited by Martial Taillefert (Georgia Institute of Technology) and Tim F. Rozan (University of Delaware). American Chemical Society: Washington, DC (Distributed by Oxford University Press). 2002. xii + 412 pp. $145.00. ISBN: 0-8412-3774-3.

This book was developed from the symposium on Electrochemical Methods for the Environmental Analysis of Trace Element Biogeochemistry held in Washington, DC in August 2000. According to the Editors, the goal of the symposium was to show the usefulness of electrochemical techniques in environmental research, including "trace metal measurements in the water column of freshwater and marine environments, redox chemical species at hydrothermal vents, in anoxic water bodies, sediments and microbial mats, major cations and anions in extraterrestrial systems, metal complexing properties of natural waters, and mineral−water interface processes". The book's 19 chapters are organized under the following sections: Introduction, In Situ Measurements in the Water Column, On-Line Measurements in the Water Column, In Situ Measurements at the Sediment−Water Interface, Sediment Porewaters and Microbial Mats, New Technologies in Electrochemistry, and Trace Metal Complexation. Author and subject indexes complete the book. References are current through 2000.

JA025245L

10.1021/ja025245l

Metal−Oxygen Clusters. The Surface and Catalytic Properties of Heteropoly Oxometalates. By John B. Moffat (University of Waterloo). From the Series: Fundamental and Applied Catalysis. Kluwer Academic/Plenum Publishers: New York. 2001. xiv + 308 pp. $150.00. ISBN 0-306-46507-8.

A book on this subject is timely and warranted for two clear reasons: (1) the collective research effort in all aspects of catalysis by polyoxometalate clusters continues to grow and is now at a substantial level, and (2) there are no informative and comprehensive monographs on this subject currently available. Chemists and chemical engineers specializing in heterogeneous catalysis and polyoxometalate and solid-state chemistry could benefit from a good reference volume on the title subject. This monograph goes a long way toward fulfilling this need.

The book is focused on Keggin-type heteropolyanions. Other classes of polyoxometalates are covered in only the briefest possible terms, but this parallels their relative importance in heterogeneous catalysis. Homogeneous catalysis by polyoxometalates is mentioned only occasionally and not addressed formally.

The book begins, logically, with chapters on the history (Chapter 1), synthesis (Chapter 2), characterization (Chapter 3), and structural and bulk properties (Chapter 4) of polyoxometalates. These chapters do not constitute the strength of the book but are of some value to the novice in polyoxometalate chemistry. They are brief and leave out some key findings, techniques, and many papers as a result.

Chapters 5−7 address, respectively, polyoxometalate stability, supported heteropoly acid derivatives, and microporosity in polyoxometalate-based solids. These subject areas have been and remain today important aspects of heterogeneous catalysis by polyoxometalates. The chapter on microporosity is particularly well-elaborated and insightful.

In Chapter 8 the author gives an overview of the acid and oxidation (frequently reversible redox) properties of polyoxometalates, the two types of properties that underlie the value of this sizable and growing class of compounds in heterogeneous catalysis. The chapter is largely focused on the techniques used and sets the stage for the subsequent two chapters, which address specific systems and reactions: acid-catalyzed processes (Chapter 9) and oxidation processes (Chapter 10). Chapter 8 could have benefited from an evaluation of the fundamental findings from homogeneous systems. There is far more known about polyoxometalate acid−base and redox properties from studies of polyoxometalates in solution, and these findings clearly relate to polyoxometalate solid state and heterogeneous catalytic properties. Both Chapters 9 and 10 are good compilations of exemplary systems.

The final chapter, “Environmentally Related Processes”, like many of the others, is selective rather than comprehensive in its coverage. There are brief descriptions of polyoxometalate applications in the conversion of nitrogen oxides, hydrodesulfurization, and polymerization chemistry.

In summary, the value of this monograph would have been increased by the inclusion of findings directly relevant to heterogeneous catalysis by polyoxometalates that have appeared in the fairly recent and voluminous literature on polyoxometalates in solution, including their homogeneous catalytic chemistry. In addition, a more critical analysis of the data and its interpretation in some, but not all, sections of the book would have been welcome. Inconsistencies in how formulas of the same compounds are written and a lack of a list of abbreviations are distractions but not serious criticisms of this book. The index is too brief to be of much value. On the positive side, this is reasonable and welcome reference volume on the title subject and definitely helps bring some intellectual and programmatic clarity to a field that is per force very phenomenological in nature and consequently beset with ambiguities. It should be mandatory reading for new and seasoned investigators alike with an interest in this area.

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JA015374M

10.1021/ja015374m