Book Reviews

Advances in Supramolecular Chemistry, Vol. 5. Edited by George W. Gokel (Washington University School of Medicine). JAI Press: Stamford, CT. 1999. ix + 365 pp. $109.50. ISBN 1-7623-0447-2.

This book is the fifth in a fine series presenting review articles on recent research in supramolecular chemistry. The volume is comprised of six chapters with each providing an in-depth survey of a particular subfield of supramolecular chemistry. Each of the chapters is clearly written with thorough referencing and logical organization, and I found most of the chapters engaging.

In the first chapter, entitled (Supra)molecular Systems Based on Crown Ethers and Secondary Dialkylammonium Ions, Fyfe and Stoddart provide a detailed account of the recent work out of Stoddart's laboratories. The emphasis is on the synthesis of rotaxanes and pseudorotaxanes, where cyclic crown ethers are threaded by linear molecules that contain one or more dialkyl ammonium groups. The preparation of these assemblies and the determination of the binding constants make up the majority of the chapter, with a brief discussion of device-like systems at the end.

The second chapter, by Schneider and Anslyn, focuses on unnatural oligomers and their synthesis by solid-phase methods. This chapter provides an excellent review of the burgeoning field of unnatural oligomers (e.g., polyamide nucleic acids, PNAs), including a discussion of synthetic methods and the spectroscopic methods used in reaction monitoring. The chapter ends with a review of recent work in the area of combinatorial chemistry and examines how one determines the sequence of a particular (unnatural) oligomer that has some desired activity. This is a nicely focused chapter that provides a thorough treatment of an important new area of chemistry, although it seems a bit out of place in a volume on supramolecular chemistry.

The third chapter, by Brouwer and Ripmeester, examines host−guest chemistry involving calixarene host molecules. The focus of the chapter is on the structure of the host−guest assemblies in the solid state as determined by X-ray crystallography and solid-state NMR methods. The chapter describes how one uses the results of both of these methods to arrive at a clearer understanding of the structural and dynamic features of this particular brand of host−guest system.

The fourth chapter, by Smith and Gardiner, reviews the field of facilitated transport through artificial membranes. This chapter effectively covers the theory of membrane transport and examples of recent transport studies. Recent results involving the transport of saccharides, nucleosides and nucleotides, catecholamines, and amino acids are described. The authors show the reader that, although much has been accomplished in this area, there is still a great deal that we do not understand about the mechanisms of facilitated membrane transport.

Gokel and De Wall primarily describe work out of the Gokel laboratory on the redox control of vesicular aggregation in the fifth chapter. Amphiphilic molecules that have a redox-active headgroup (ferrocene in most cases) and a hydrophobic tail have been examined in order to prepare vesicles that can be electrochemically or chemically "switched off" to collapse the vesicles. This interesting chapter thus outlines a creative method to control supramolecular aggregation.

The final chapter, by Hubin, Kolchinski, Vance, and Busch, is a comprehensive treatment of the area of template control of supramolecular architecture. Far exceeding the other chapters in length, the sixth chapter is a beautifully written review that covers the preparation of interlocked molecules (such as catenanes and rotaxanes), in which a template (in most cases a metal ion) is used to improve the synthetic yield of the desired molecular entity. This impressive chapter thoroughly covers the vast amount of work that has been done in this area in the past decade. Any researcher who is interested in the areas of topological chemistry or interlocked molecules would find this chapter to be invaluable. The authors provide key insight into this field, as they intersperse their commentary into a review of the work of Sauvage, Stoddart, and many others. The chapters ends with a brilliant section entitled "Suggestions for the Future", which is brimming over with novel ideas and perspicacity.

This volume is highly recommended for research libraries and personal collections.

Timothy B. Karpishin, *University of California, San Diego*

JA9956977

10.1021/ja9956977

Advances in Asymmetric Synthesis. Volume 3. Edited by Alfred Hassner (Bar-Ilan University). JAI Press: Stamford, CT. 1998. x + 365 pp. $128.50. ISBN 0-7623-0106-6.

The contents of this latest volume of Advances in Asymmetric Synthesis include seven chapters: 1. Asymmetric Synthesis of β-Amino Acids and β-Lactam Derivatives via Conjugate Addition of Metal Amides; 2. Enantioselective Deprotonation of Cyclic Ketones; 3. Stereoselective Addition of Chiral α-Aminoorganometallics to Aldehydes; 4. Asymmetric Access to Functional, Structurally Diverse Molecules Exploiting Five-membered Heterocyclic Siloxy Dienes; 5. Asymmetric Catalysis using Heterobimetallic Compounds; 6. Palladium-Catalyzed Enantioselective Allylic Substitution Reactions; and 7. New Achievements in Asymmetric Synthesis of Organophosphorus Compounds.

Chapter 1 (conjugate addition of metal amides) begins with a discussion of various aspects of reactivity and selectivity of the racemic variant of the reaction. Topics include the effects of the structure of the nitrogen nucleophile and the electrophile on reactivity; 1,2-diastereoselectivity with γ-substituted α,β-unsaturated esters; stereoselective formation of both *E*- and *Z*-γ-amino silylketene acetals; inter- and intramolecular trapping of the γ-amino ester enolate intermediate; and applications to natural product synthesis. In the latter part of the chapter, several asymmetric variants of the reaction are described, including the addition of chiral nonracemic amines to achiral acceptors, the addition of achiral amines to chiral nonracemic acceptors, and the addition of chiral amines to chiral acceptors.

Chapter 2 (enantioselective deprotonation) starts with a concise summary of approaches to the synthesis of enantiomerically pure compounds and how enantioselective deprotonation fits into that scheme. The deprotonation reaction is discussed in considerable depth, including the effect of substrate and amide structure, solvent, and additives. Various applications of the method to the synthesis of tropane alkaloids, some simple terpenoids, and carbohydrates are described.

Chapter 3 (α-aminoorganometallics) begins with a concise discussion of issues of stereoselectivity in the addition of nucleophiles to aldehydes and then focuses on the those issues with respect to α-aminoorganometallics. The first half of the chapter discusses various mechanistic topics, including polar vs SET pathways and the effect of electrophile structure on the stereochemical outcome of the reaction. The latter half of the chapter describes the applications of the method to the asymmetric synthesis of various phthalide−tetrahydroisoquinoline alkaloids.

Chapter 4 (siloxy dienes) contains a very thorough review of the applications of siloxydienes in natural product synthesis, followed by a brief discussion of possible mechanisms of addition of siloxydienes to various C═X electrophiles. An addendum updates the review through 1997.

Chapter 5 (heterobimetallic catalysis) describes the synthesis, reactions, and synthetic applications of BINOL-derived heterobimetallic enantioselective catalyst systems. The asymmetric reactions discussed include the nitroaldol reaction, the Michael addition, aldehyde and imine hydrophosphonylation, epoxide opening, epoxidation, and the aldol addition.

Chapter 6 (allylic substitution) begins with a brief description of the fundamental features of Pd-catalyzed allylic substitutions. The remainder of the review focuses on the considerable efforts that have been directed at asymmetric variants thereof. There is substantial overlap with a review of this area by Trost and Van Vranken (*Chem. Rev.* **1996**, *96*, 395−422). It is worth noting that because of the intense synthetic efforts in this area, a number of significant contributions to the field have been made in the years since these reviews were written.

Chapter 7 (organophosphorus compounds) opens with a brief

discussion of the general features associated with the synthesis of chiral phosphorus compounds. The majority of the chapter is taken up with the asymmetric synthesis of tri- and tetracoordinate phosphorus compounds and reactions involving transfer of chirality from phosphorus to other centers.

The topics that are covered in this volume are timely and of general interest to the synthetic community, although in some cases the reviews focus on a somewhat narrowly defined topic or focus heavily on the authors' contributions. The reviews typically cover material through 1996. Overall, the text is readable and well organized. The structures are, in general, clearly depicted, although a few figures did not reproduce well. In Chapter 7 a number of structures have multiple bonds drawn too closely, making it difficult to tell if a bond is single or double. Also, a larger font size should have been used for some atom labels.

In summary, this volume would be a worthwhile addition to any chemistry library, but the reviews are probably too specific for its purchase to be recommended to individuals unless they are working in the specific areas that were reviewed.

Matthias C. McIntosh, *University of Arkansas*

JA995701E

10.1021/ja995701e

Aerosol Processing of Materials. By Toivo T. Kodas and Mark J. Hampden-Smith (Superior Micropowders, Albuquerque, NM). Wiley-VCH: New York. 1999. xxx + 656 pp. $175.00. ISBN 0-471-24669-7.

As stated in its opening sentence, this book describes the science, engineering, and technology involved in the synthesis and processing of powders and films by gas-phase aerosol techniques. This includes a wide variety of processes, with examples ranging from spray pyrolysis of multicomponent ceramic powders to aerosol-assisted chemical vapor deposition of thin films. The depth of coverage given to each technique varies, in most cases reflecting the maturity of the technique.

The first half of the book deals with fundamental processes related to aerosol processing. Chapter 1 provides an introduction and overview. Chapters 2−7 present the fundamentals of aerosol physics. The sequence of topics in these chapters is similar to those in earlier texts (e.g., transport phenomena related to aerosol particles, the kinetics of particle growth and coalescence, and the evolution of particle size distributions). The level of development is appropriate for an introductory text, with frequent references given for more detailed treatment of individual topics. Chapters 8 and 9 cover topics that are unique to materials processing, namely the chemistry involved in producing various final products and the characteristics of nanostructured powders.

The second half of the book describes specific technologies for powder production and film formation. The chapters are paired, dealing first with the fundamentals and then with process examples. Chapters 10 and 11 deal with gas-to-particle conversion. The latter is the longest chapter in the book and presents examples ranging from the tubular flow reactor used for commercial production of TiO_2 to a brief discussion of laboratory-scale laser-assisted photochemical processes. Chapters 12 and 13 cover liquid-to-solid and solid-to-solid conversion, with spray pyrolysis receiving the greatest attention. Chapters 14 and 15 describe film formation processes, including aerosol-assisted CVD. The book concludes with separate chapters on aerosol reactor components and powder measurement techniques.

The book is written and organized in a simple, readable fashion. This includes a decision to repeat some of the introductory material in more than one chapter. The table of contents is detailed and well-organized, a table of nomenclature is included, and the index is very complete. Chapters 11, 13, and 15 contain an excellent collection of tables that summarize the existing literature examples for each processing technique, including references. It should be noted that most of these examples are laboratory studies or small-scale production processes, many of which are taken from the coauthors' previous academic research or from one of their two start-up companies. The book contains relatively little detailed information about the three major commercial aerosol processes for powder synthesis (i.e., carbon black, TiO_2, and flame SiO_2).

Overall, the book succeeds quite well in presenting a thorough overview of the scientific and technological aspects of the field, while giving a somewhat more limited treatment of the engineering aspects of commercial processes. The book will be a good starting point for anyone considering a new project in the area. It may also serve as a useful collection of references for established researchers.

Gregory L. Griffin, *Louisiana State University*

JA995709O

10.1021/ja995709o

Introduction to Flavonoids. Volume 2. Chemistry and Biochemistry of Organic Natural Products. By Bruce A. Bohm (University of British Columbia). Harwood Academic Publishers: Amsterdam. 1998. 503 pp. $145.00. ISBN 90-5702-353-9.

Plants accumulate a variety of organic natural products such as alkaloids, flavonoids, and terpenoids, to mention a few. These compounds are synthesized in plants, as protective agents, in response to various environmental stimuli and genetically programmed developmental signals. It is no wonder that there is an increasing awareness in the scientific community of the importance of the chemistry, biochemistry, and pharmacology of natural plant products. This is because of the realization that, in addition to their historical efficacity in herbal folklore medicine, pharmacological studies with purified compounds have been found to impact mammalian biology in their effects on immunity, inflammation, antimicrobial activity, and carcinogenicity, among others.

The eight chapters of this book focus on the major aspects of flavonoid compounds, one of the most ubiquitous classes of plant natural products. Topics include their occurrence and distribution in plants, their purification and structure determination, their chemical synthesis and interconversions, and their biosynthesis, enzymology, and genetics, as well as their possible roles in the plant and their impact on humans. In its comprehensive coverage of these topics, this book is by no means an introduction to the subject matter, except to distinguish it from the series, *The Flavonoids: Advances in Research* (Chapman & Hall), to which the author is a regular contributor.

The book starts with a historical background on how and when flavonoids became recognized as a distinct class of structurally related and fuctionally relevant compounds, although much remains to be discovered about this important class of natural plant products. In fact, the author refers to a number of research problems that may challenge the organic chemist and plant biochemist.

The first two chapters deal with the nomenclature and structural features of the major groups of flavonoids, as well as their patterns of oxygenation, alkylation, glycosylation, acylation, and sulfation that result in a myriad of structural variations. The distrubution of flavonoids among plant species and taxa is discussed in the third chapter using a multidisciplinary approach that combines plant biosystematics, genetics, evolution, biochemistry, and natural product chemistry with references to books, journals, conferences, and symposia that are relevant to the subject. The author also describes the criteria for the use of flavonoid compounds as taxonomic markers, as well as specific parameters for the analysis of flavonoid data and cladistic analysis to assess the evolutionary relationships of flavonoids in putatively related taxa, as exemplified by several case studies from the plant kingdom.

Chapters 4 summarizes the methods used for the extraction, chemical degradation, and identification of flavonoids, including spectroscopic methods, which are illustrated by 14 case studies. Chapter 5 gives an overview of the general strategies used for the chemical synthesis and interconversions of the different groups of flavonoids. Both chapters should be extremely useful for those starting their research work in this field. Chapter 6, which deals with the enzymatic synthesis and genetics of flavonoids, is preceded by a historical introduction of the early isotopic work that established the nature of the precursors involved in the biosynthesis of the flavonoid skeleton. This chapter considers the enzymes involved in the assembly of the flavonoid ring system, in the modification of the heterocyclic ring, and in flavonoid substitution. It is unfortunate that neither the genetics of flavonoids nor the molecular aspects of the genes encoding their enzymes could be discussed in any detail, probably because of space limitation in this otherwise exhaustive volume.

The roles of flavonoids in Nature are discussed in Chapter 7, including their function as shields against UV light, as attractants for pollination and oviposition, as signals for N-fixing bacteria, as antimicrobial/antiviral agents, and as plant defensive compounds

(phytoalexins). The last chapter considers the human uses of flavonoids in foods and beverages, with reference to their medicinal value and their putative benefits and risks.

The book fulfills its objectives as it covers the most important aspects of flavonoids under one cover. It is well written, elegantly produced, and well documented with more than 1500 citations, 1000 chemical structures, 28 tables, and 50 schemes, including indexes of the general topics and compounds and plant families and genera of all the organisms cited. The book is obviously a very useful document to the chemical community, including researchers in natural product chemistry, phytochemistry, plant biochemistry, pharmacognosy, food science, and chemical ecology. It also provides an excellent basis for graduate students and young researchers who intend to indulge in research on flavonoids.

Ragai K. Ibrahim, *Concordia University*

JA995759T

10.1021/ja995759t

Magnetic Properties of Organic Materials. Edited by Paul M. Lahti (University of Massachusetts at Amherst). Marcel Dekker Inc.: New York and Basel. 1999. xix + 728 pp. $195.00. ISBN 0-8247-1976-X.

This book attempts to provide a comprehensive overview of the contribution of organic chemistry to the field of magnetism. Beginning with a chapter by Harden M. McConnell detailing the source of his often cited proposed models for ferromagnetic exchange, the book proceeds through sections detailing theoretical and experimental ground states of organic diradicals, magnetic properties of polyradicals and paramagnetic liquid crystals, and theoretical and experimental properties of organic radicals in condensed phases, finishing with a pair of summary chapters.

Though the book provides a good overview of the current research in the field, it is not a good introduction to the study of magnetic properties. Little space is devoted to general concepts of magnetism and magnetic measurements. For such information, other texts are recommended by the editor.

There is significant overlap of theoretical material between chapters, partly because many of the contributors are developing research along similar lines. This does not detract from the book; rather, it provides different perspectives on a common theory. Some of the more noteworthy chapters detail less well known or utilized techniques, such as electron spin transient nutation spectroscopy and heat capacity studies, or approach the problem of magnetism from a different perspective, such as band theory. It is unfortunate that more was not included from a physicist's perspective since research in magnetism spans both chemistry and physics; however, communication between the disciplines is hindered by differences in approach and terminology, and considerable effort is required to span the gap.

David J. R. Brook, *University of Detroit Mercy*

JA9957581

10.1021/ja9957581

Fluid Metals: The Liquid−Vapor Transition of Metals. By Friedrich Hensel (University of Marburg) and William W. Warren, Jr. (Oregon State University). Princeton University Press: Princeton, NJ. 1999. xii + 243 pp. $69.50. £42.50 international. ISBN 0-691-05830-X.

This book is an introduction to the physics and chemistry of liquid metals in general, and in particular to the liquid−vapor and metal−nonmetal transition of metals. Both authors are considered to be experts in the area, having pioneered the field to a large extent in the past few decades. Since then, physicists and physical chemists have made great strides in understanding the basic principles of the physical properties of liquid metals over a large range of thermodynamic conditions. Yet, there has not been a book that brings together the latest ideas and findings in the field. The existence and experimental accessibility of the liquid−vapor critical point of several metals makes it possible to study their continuous transition from a dilute atomic vapor to a dense metallic liquid. Thus, one set of experiments on a single pure material, such as cesium or mercury, takes one from the chemistry of a reacting molecular species in the dense vapor state to the domain of condensed matter physics on the liquid side. Certainly, the nature of the interatomic forces drastically changes along this pathway. Hence, it has been a long-standing challenge in the field to find a framework for both a molecular level understanding and a unified theoretical description of this entire, continuous process. As can be deduced from reading the book, many of the underlying principles seem to be understood.

In brief, the book covers the electronic, magnetic, optical, structural, and thermodynamic properties and the metal−nonmetal transition of liquid metals and semiconductors (alkali metals, mercury, mercury−helium and mercury−indium mixtures, selenium and its alloys). The physical properties presented have been obtained at conditions from the melting point up to the critical point and beyond to the dense vapor state of these materials. In addition, the book covers related and new aspects of condensed matter and cluster physics, such as the metal−nonmetal transition in clusters, critical point fluctuations, and interfacial phenomena, such as wetting and the prewetting transition of fluid metals and the homogeneous nucleation of supersaturated metal vapors. The book closes with a chapter on high-temperature/high-pressure experimental techniques. Because of the inherently interdisciplinary nature of the subject, the authors also present tutorial material (for example, the magnetic properties of liquid metals and a survey of important theoretical approaches and concepts of the metal−insulator transition) as the need arises.

As clearly stated, the authors' approach to the subject of fluid metals is not an encyclopedic one: it is based on the experimental results of a few selected and well-studied systems. Hence, they did not attempt to present results for all systems studied; their goal is to present the underlying concepts. In most cases, they described the results of their own research.

Because the electronic transition occurring near the liquid−vapor critical point of fluid metals is related to the metal−nonmetal transition occurring in disordered solid materials and other classes of liquid systems (for example, many binary alloys, metal−ammonia solutions, and metal−molten salt mixtures), these concepts are also of interest in many other fields of liquid-state physics and chemistry. In many cases, the studies on liquid alkali metal systems also serve as model cases for systems of geophysical and astrophysical interest, such as the metallization of hydrogen in large planets.

There are several groups of potential readers to whom this book is addressed, including researchers concerned with fluid metals and alloys, the metal−nonmetal transition of materials, critical point phenomena, nonideal plasmas, and high-temperature molecular spectroscopy. It will also be of great value to engineers interested in the practical applications of fluid metals, for example, as a high-temperature working fluid. For this purpose, the authors have tabulated in the Appendix the fundamental thermodynamic parameters of cesium, rubidium, and mercury. Owing to the clear presentation and printing, the book should also serve as a useful source for students pursuing graduate study in these and related fields.

In all, it is an inspiring book for anybody investigating fluid metals and a valuable source of information about the general properties and applicability of liquid metals. I believe that it is a "must" for all scientists—physicists, chemists, materials scientists, and engineers—interested in the properties of fluid metals and the metal−nonmetal transition of disordered materials.

Roland Winter, *University of Dortmund*

JA995765P

10.1021/ja995765p