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BOOK REVIEWS

Hydrogen Bonding in Organic Synthesis. Edited by Petri M. Pihko (University of Jyväskylä, Finland). WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim. 2009. xii + 384 pp. $215. ISBN 978-3-527-31895-7.

In the chemical community, the general perception of H-bonding evolved from an esoteric curiosity provocatively referred to as "bivalent hydrogen" by G. N. Lewis to a key structural force implicated in many chemical and biochemical phenomena (for an engaging discussion, see: Weinhold, F. W.; Landis, C. R. *Valency and Bonding: a Natural Bond Orbital Donor−Acceptor Perspective*; Cambridge University Press: Cambridge, 2005; p 583). A unique combination of properties distinguishes H-bonding from other supramolecular interactions: (1) H-bonds are tunable—their strength varies from a very weak contact to a partially covalent bond; (2) due to their partial covalency, H-bonds have a useful stereoelectronic component (i.e., they are directional and programmable); (3) because H-bonds are created dynamically and reversibly, they form predictably, repair themselves when broken, and often coexist with other interactions in a "noninvasive" manner; (4) although H-bonding is solvent-dependent, some H-bonding patterns work reliably even in water; and (5) conveniently, formation of H-bonds is often associated with characteristic spectroscopic signatures and can be monitored in a time-resolved fashion.

This unique combination of properties renders H-bonds indispensable for the creation of intricate supramolecular assemblies. It is high time that organic chemists also take advantage of those properties for achieving better control of reactivity and selectivity in organic synthesis. Research in this area has developed explosively in recent years, especially with the rapid development of noncovalent organocatalysis. A monograph dedicated to this fascinating topic should be a timely addition to the library of any practicing organic chemist, and this book aims to address the clear need for a comprehensive treatise of this emerging field.

Although the title suggests that synthetic organic chemists are the main target audience, the aim of the book is to go beyond merely a compendium of organic reactions by providing useful initial connections to topics beyond the usual concern of organic chemists by addressing the fundamental nature of H-bonding (Chapters 1 and 2), the relationship between H-bonding and Brønsted acid catalysis (Chapter 2), computational approaches to modeling of H-bonded systems (Chapter 3), and the role of H-bonding in enzymatic catalysis (Chapter 4).

The first two chapters provide a rather general introduction to H-bonding, but their authors unfortunately neglect to describe the covalent hyperconjugative component of H-bonding and treat it as an essentially electrostatic interaction. This simplification not only contradicts the modern computational analysis of this phenomenon but also fails to incorporate the stereoelectronic nature and directionality of H-bonding, which are essential to the design of programmable, well-defined H-bonding patterns in reliable supramolecular catalytic systems (for example, see: Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973−5987). An expert analysis of those fundamental features of H-bonding, which are crucial in its application for the control of organic structure and reactivity, would have strengthened the introductory material.

The main part of Chapter 2 deals with the gradual transition between H-bonding catalysis and Brønsted catalysis. Factors that favor one mode of reaction vs the other are discussed clearly and illustrated with a few well-chosen examples. This chapter would benefit from a short discussion on why such a distinction is important. One can argue that since H-bonding precedes full proton transfer from the Brønsted acid, the two types of species coexist on the same potential energy surface and their contributions can be assessed by a Curtin−Hammett type analysis. Overall, the content of the first two chapters is superficial, and most readers with a basic chemical knowledge may go directly to Chapters 3−7.

Chapter 3 is the first chapter that would benefit a Ph.D.-level organic chemist. It begins with a short recap of different modes of covalent and noncovalent organocatalysis and a useful short survey of the most common computational techniques for those interested in gaining additional insight into experimental observations through computational studies. A brief comparison of different catalytic functions of H-bonds concludes the introductory part. The main component of this chapter is dedicated to detailed descriptions of several complex examples where computational analysis provides rich structural and mechanistic information. Although the set of examples is rather limited, the general questions raised in their analysis will be very useful to any computationally inclined organic chemist who is interested in entering this rapidly developing field.

Chapter 4 is dedicated to oxyanion holes, the key elements of many H-bonding enzymes. This well-written chapter provides a very interesting contrast to the small-molecule-based H-bonding catalysts. The active sites of such enzymes were molded by extensive evolutionary pressure for finding optimal solutions to complex chemical challenges. Reverse engineering of such highly efficient systems will undoubtedly inspire molecular design of artificial catalytic systems for specific problems facing modern organic synthesis. After the authors of this chapter set the needed foundation via outlining thermodynamic factors operating in such systems and briefly covering the possible role of low-barrier H-bonds, they provide insightful analysis of oxyanion holes for tetrahedral and enolate intermediates in enzymes and their designed mimics.

The three chapters that speak directly to the synthetic organic audience are Chapters 5−7. Chapter 5 concentrates on Brønsted acid catalysis with chiral phosphoric acid derivatives, catalytic systems based on N−H hydrogen bonds, and combined systems where Lewis and Brønsted-type interactions are synergetic. The authors carefully analyze mechanism, selectivity, and chiral induction in a large number of important organic reactions with

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10.1021/ja103155b © 2010 American Chemical Society

commendable depth and breadth of coverage. The material is well-organized and recent.

Chapter 6, dedicated to organocatalysis using thioureas, is a real gem! It is encyclopedic in its coverage and provides a treasure trove of well-organized information, much of which will be useful even to an expert in this field. The historical timeline of the development provides a fascinating excursion in the complex path involved in the growth of a scientific idea, from its conception through germination, reappearance, and explosive growth. Overall, this chapter offers everything one needs to know about this type of catalysis, including background, history, fundamental forces and phenomena, scope, limitations, mechanistic details, and control of enantioselectivity. The literature is not simply quoted, it is critically reinterpreted and creatively integrated into a tightly organized, logical, and comprehensive discussion. The chapter is self-contained and could be easily reprinted as a separate book.

The highlights of H-bonding in total synthesis of natural products in the final chapter include several very interesting and tastefully chosen examples. Unfortunately, the discussion is not systematic—the selection is mostly *ad hoc* with only a few recent examples, post-2005. This short chapter has the feel of a lost opportunity—an appetizer instead of a full meal.

Quite a few typos crept through to the final version. Some of them are harmless, e.g., “nucelophiles”, but others distort and misrepresent chemical information and should have been caught at the editorial stage. Lewis structures of ammonium salts suffered the most, with the plus sign either missing or moved to the adjacent carbon atom. On a number of occasions, reaction schemes are not synchronized with their discussion but instead are separated from it by at least a couple of pages.

Overall, this is an uneven but useful book. Its educational utility may be limited, but it can serve as a good source of advanced information on selected topics. For those who are interested in noncovalent organocatalysis, this book is well-worth reading.

Igor Alabugin, *Florida State University*

JA103155B

10.1021/ja103155b

Miniaturization of Analytical Systems: Principles, Designs and Applications. By Angel Ríos (University of Castilla-La Mancha, Ciudad Real, Spain), Alberto Escarpa (University of Alcalá, Madrid, Spain), and Bartolomé Simonet (University of Córdoba, Córdoba, Spain). John Wiley & Sons, Ltd: Chichester. 2009. xii + 372 pp. $120. ISBN 978-0-470-06110-7.

Miniaturized systems have emerged as a major component of analytical chemistry and have reached a level of maturity that now attracts a broad audience. *Miniaturization of Analytical Systems: Principles, Designs and Applications* covers exactly what would be expected from the title. The bigger picture is drawn well, plus the topics are explored with sufficient detail and clarity that this book should be of practical use to students and researchers in the lab. The text is generally well-written and readable. Over 1200 references are included, with an appropriate mix of recent and earlier literature, and are relevant, well-chosen, and incorporated well into the flow of the text. Numerous figures are included to illustrate key principles and designs. The reader should be aware of occasional typographical errors in terminology, particularly in the first couple of chapters.

The book begins with a discussion of the philosophy of miniaturization. Chapter 1 tends to be difficult to follow, but the content and perspective are valuable. The next few chapters present excellent reviews and discussions of the components of microanalytical devices. Chapter 2 contains an excellent treatment of valves, pumps, mixing, and the basics of microfabrication techniques, and Chapter 3 provides a valuable and accurate discussion of sample acquisition and treatment methods, including solid-phase microextraction, liquid-phase microextraction, and others. These discussions provide a good balance between theory, operation, advantages, variations, commercial efforts, and integration with separation devices. Factors important to consider when selecting or designing new devices are presented. Substantial practical information is provided, reflecting the authors’ knowledge and experience on the subject.

In Chapters 4 and 5, the authors discuss separation devices, including microchip-based gas chromatography (GC), high-performance liquid chromatography (HPLC), and capillary electrophoresis. These chapters are not nearly as comprehensive as are Chapters 3 and 4 but nonetheless provide substantial information about the principles and applications of these methods. Historical details are relevant and well-integrated with recent results. The Agilent HPLC chip is discussed in detail.

The discussion of detection focuses on laser-induced fluorescence, electrochemical detection, and mass spectrometry. Less common approaches to detection are discussed in appropriate detail—from surface plasmon resonance to NMR—including their relative strengths and weaknesses. The chapter does not focus on the miniaturization of these detection methods *per se*, but rather their use as detectors for microfluidic systems. Efforts to develop portable mass spectrometers are mentioned briefly in a subsequent chapter.

In the remaining chapters of the book, the authors address several additional topics in somewhat less detail. Sensors, including quantum dots, nanoparticles, and electrochemical sensors, are reviewed, and a few applications are provided. Fluid flow and mixing at the micro scale are discussed, including scaling principles. Microfluidic devices for several specific applications, including analysis of DNA, clinical samples, environment, and food, are presented. The case is made that the ability to handle complex, real samples is indicative of the maturity of the methods developed. Portable GC, optical, and electrochemical systems are reviewed.

Overall, this is a valuable monograph, written fairly broadly, but with substantial detail. The assortment of topics and devices covered is reasonably thorough. The book is readable and should be a valuable resource for anyone wanting to become more familiar with the field of miniaturized and microfabricated analytical systems.

Daniel E. Austin, *Brigham Young University*

JA102715S

10.1021/ja102715s

Recoverable and Recyclable Catalysts. Edited by Maurizio Benaglia (University of Milan, Italy). John Wiley & Sons, Ltd.: Chichester. 2009. xviii + 472 pp. $160. ISBN 978-0-470-68195-4.

Many books concerning catalysis have been published during the past decade, with topics ranging from a general treatise of the field to more specialized volumes concerning “hot topics” including asymmetric synthesis, biocatalysis, organocatalysis, C−H bond activation, and alternative reaction media. Another challenging and rapidly growing area of research is that of recyclable catalysts. This book fills a niche and builds on previous reviews and special journal issues concerning this exciting field of research. Indeed, if ever a book was needed to collect ideas together in an important, interdisciplinary area, this one is it.

The editor of this book wants it “to be a ‘catalyst’ for the development of new recyclable catalysts,” and time should see his goal fulfilled. The book is inspirational, and the editor has collected a group of recognized authorities in the field along with rising stars to contribute chapters. Furthermore, these authors bring varied expertise to the book from the fields of organometallic, polymer, and organic chemistry to chemical engineering. The chapters are arranged in such a way that it is surprisingly easy to read for a reasonably large book, with related areas grouped into sequences of chapters. For example, details on engineering aspects of the field, e.g., flow reactors and microreactor technologies, are discussed in neighboring chapters. Recent research involving alternative solvents in this field, e.g., immobilization of fluorous catalysts, biphasic catalysis involving water and/or supercritical carbon dioxide, and ionic liquids, is covered in three sequential chapters. Furthermore, there is little repetition of material covered in the chapters, which must have been a challenge for the editor given the interdisciplinary nature of the field. In many chapters, the authors provide excellent insights in their conclusions. For example, in the chapter “Asymmetric Catalysis in Ionic Liquids”, the lack of mechanistic understanding on the molecular level in these alternative solvents is highlighted and therefore presents an important opportunity for future research.

The first chapter of this book will be particularly valuable to newcomers in the field of recoverable and recyclable catalysts as it clearly outlines some of the common pitfalls in this area, such as how to evaluate catalyst recovery, and it defines some common catalyst terms and measurements used throughout the book. It also comes with the valuable warning to keep a “skeptical eye on the literature” and encourages researchers not to pursue research in this field with an “all or nothing” attitude. These are also important reminders to accomplished investigators. The final chapter would be a good second “port of call” for newcomers, as its author encourages the reader to think about the different priorities of the academic and industrial researcher in this field and also to contemplate why we are exploring it in the first place.

Because this is a book with 26 authors, there are understandably discrepancies in the style of writing among the different chapters, including the formatting and number of references in each. However, all the authors include very timely references with at least 50% of them coming from the five years prior to publication. The areas of organometallic and organic catalysts are treated in detail by the authors, although the recovery and recycling of biocatalysts are not covered sufficiently, especially considering the immense challenges associated with their stability and cost.

In summary, *Recoverable and Recyclable Catalysts* covers this broad, important, challenging, and interdisciplinary area of modern chemistry in an accessible and detailed way. This means that the book will be suitable for beginners and graduate students in the field, in addition to more established practitioners in this exciting area of research.

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JA103058K

10.1021/ja103058k

Handbook of Cyclization Reactions, Vols. 1−2. Edited by Shengming Ma (Shanghai Institute of Organic Chemistry, People’s Republic of China). WILEY-VCH Verlag GmbH & Co, KGaA: Weinheim. 2010. xxi + xxiv + 1265 pp. $430. ISBN: 978-3-527-32088-2.

Cyclic organic molecules are ubiquitous in natural and unnatural products, and a vast ensemble of methods have been developed for their synthesis. In this expansive, 25-chapter collection of reviews, the editor has endeavored to identify the main strategies for preparing cyclic structures. As acknowledged in the Preface, the enormous amount of work directed toward cyclization reactions cannot fully be captured even in a collection of this magnitude. The editor and authors of the chapters, however, have done an impressive job at assembling an informative and thorough, if not all-inclusive, account of the state of the art for cyclization methods.

The book has several chapters on classical approaches to cyclization, including Diels−Alder and other cycloaddition reactions, intramolecular 1,2- and 1,4-additions, radical cyclizations, Friedel−Crafts annulations, and acylations that largely focus on advances in the past 5 to 10 years. Newer strategies based on several aspects of transition-metal-mediated and organocatalytic cyclizations make up the remainder of the volumes. This set provides a plethora of spectacular demonstrations of creativity in the field of organic synthesis and serves as a good resource to illustrate the scope of a wide range of reactions. Most chapters show how the methods have been applied to natural product synthesis, and all of them have useful experimental sections that illustrate the experimental ease or difficulty of the key transformations.

One weak point of this collection is that several chapters are too dense with examples and too light on organization and discussion. Although these chapters serve a role in highlighting the applications of a given process, their pedagogical value is limited. The editing of the chapters is also somewhat spotty, with grammatical errors being common and graphical errors appearing occasionally. Overall, however, this book would be a worthy addition to chemistry libraries. It provides an abundance of recent examples that illustrate the manner by which a wide range of reactions can be utilized and includes hundreds of references. In an academic setting, the books could be a valuable resource for topic outlines in a course on modern synthetic methods, although the lack of depth in many chapters precludes its use as a textbook for such a course.

Paul E. Floreancig, *University of Pittsburgh*

JA103004F

10.1021/ja103004f

Macromolecules Containing Metal and Metal-Like Elements, Volume 9: Supramolecular and Self-Assembled Metal-Containing Materials. Edited by Alaa S. Abd-El-Aziz (University of British Columbia Okanagan, Kelowna, BC, Canada), Charles E. Carraher, Jr. (Florida Atlantic University, Boca Raton, FL and Florida Center for Environmental Studies, Palm Beach Gardens, FL, USA), Charles U. Pittman, Jr. (Mississippi State University, Mississippi State, MS, USA) and Martin Zeldin (University of Richmond, Richmond, VA, USA). John Wiley & Sons, Inc.: Hoboken, NJ. 2009. xxii + 528 pp. $195.00. ISBN 978-0-470-25144-7.

Volume 9 of the series *Macromolecules Containing Metal and Metal-Like Elements* focuses on supramolecular inorganic chemistry, i.e., covalently bound metals and metalloids, and contains 10 review chapters by different authors. The first chapter covers supramolecular assemblies with inorganic tectons for lipid-like hybrid thin films that combine lipid thin films and inorganic frameworks; layer-by-layer assemblies; and functional mesoporous hybrids based on silica, boron nitride, carbon, and carbon nitride. Chapter 2 addresses interesting polyoxometalate macro-ions that are hydrophilic, yet associate into spherical aggregates and thus have some colloid-like properties. In the next chapter, supramolecular aspects of isopolyoxometalate and heteropolyoxometalate transition metal complexes and their crown ether and water complexes are reviewed. Supramolecular-layered and -nonlayered networks with sulfonate and, to a lesser extent, phosphonate linkers and the resulting open-framework solids are discussed in Chapter 4. The interesting family of ligand-supported and unsupported linear, i.e., 1D, transition metal chain compounds with ≥3 metal ions is reviewed, primarily from a synthetic and structural perspective, in Chapter 5. Supramolecular architectures based on boronate ester linkages from boronic acid and diols and extensions to self-repairing (because of reversibility in boronate ester formation) and wide band gap semiconductors are the main topics in Chapter 6.

The notably extensive Chapter 7 covers the coupling and photophysics of metal-based—primarily Ru(II) complexes—redox-active light-absorbers to Rh(III), Pt(II), and Pd(II) centers relevant to photodynamic therapy, DNA photocleavage, water splitting, and solar energy conversion, among others. Supramolecular signaling based on changes in redox, fluorescence, and visible absorbance for the development of chemosensors is described in Chapter 8. Molecular recognition via coordination or H-bonding between supramolecular receptors—primarily framework metal oxalates—and nucleobases is the subject of Chapter 9. The final chapter covers coordination polymers based on concepts in synthetic and topological crystal engineering. Each chapter has an extensive list of references and is independent of the others but integrated by a thorough, comprehensive index.

This book is a nice complement to several older reviews, encyclopedias, and series on supramolecular chemistry, specifically with regard to the metal coordination aspects of supramolecular chemistry and polymers. Researchers with interests in the topics covered by the individual chapters will find this volume particularly useful.

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JA103005B

10.1021/ja103005b

Quantum Tunnelling in Enzyme-Catalysed Reactions. Edited by Rudolf K. Allemann (Cardiff University, U.K.) and Nigel S. Scrutton (University of Manchester, U.K.). From the RSC Biomolecular Series. Royal Society of Chemistry: Cambridge. 2009. $249. ISBN 978-0-85404-122-0.

The editors of *Quantum Tunnelling in Enzyme-Catalyzed Reactions* assembled an impressive team of contributors for this very interesting monograph. Its first 13 chapters focus on interpretations of observed and calculated kinetic isotope effects in hydrogen-, proton-, and hydride-transfer reactions. Chapters on long-distance electron tunnelling in proteins (Stuchebrukhov), proton-coupled electron transfer reactions (Reece and Nocera), and the foreword by the Nobel laureate, Rudolph A. Marcus, demonstrate considerable relevance and depth. The cogency of these chapters more than compensates for less-extensive coverage of electron tunnelling in this book.

The main subject of the book—nuclear quantum effects as an enzyme catalytic feature—emanates tremendous hype and broad appeal, as evidenced by its recent prominent exposure in *Nature* and *Science*. Many authors of these landmark articles, e.g., Klinman, Hammes-Schiffer, Kohen, Truhlar, and Gao, contributed interesting mini-reviews to this monograph, all citing many up-to-date references from the field. Their offerings make it easier for readers to jump on the bandwagon. If readers are inspired to delve further into this topic, they will likely need to study one of several enzymes detailed in this monograph because finding new enzymes where H^+, H, or H^- tunnelling significantly contributes to the rate-limiting step of an enzyme-catalyzed reaction is not an easy task. A particularly attractive system is dihydrofolate reductase (DHFR). Hydride tunnelling in this protein is likely promoted by long-range coupled motions of its amino acid residues; this is an appealing concept that brings together protein dynamics and catalysis. Hammes-Schiffer (Chapter 4), Dybala-Defratyka, Paneth, and Truhlar (Chapter 3), Sen and Kohen (Chapter 7), Loveridge and Allemann (Chapter 8), Pang, Scrutton, and Sutcliffe (Chapter 9), and Liu and Warshel (Chapter 11), all propel the compelling, albeit controversial, story of DHFR through this book.

The chapters are loosely connected by several common themes and contain sufficient introductory materials to support the use of this book as a resource for a graduate-level special topics course. The thoughtful ordering of chapters, which include an exciting dissenting article entitled “Tunnelling Does Not Contribute Significantly to Enzyme Catalysis, but Studying Temperature Dependence of Isotope Effects Is Useful”, supports enjoyable reading. The book should be a valuable resource for university libraries and scientists interested in physical biochemistry.

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JA103114Z

10.1021/ja103114z