Book Review

Organic Reactions in Water: Principles, Strategies and Applications Edited by U. Marcus Lindström (McGill University). Blackwell Publishing: Oxford. 2007. xvi + 406 pp. $199.99. ISBN 978-1-4051-3890-1.

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BOOK REVIEWS

Organic Reactions in Water: Principles, Strategies and Applications. Edited by U. Marcus Lindström (McGill University). Blackwell Publishing: Oxford. 2007. xvi + 406 pp. $199.99. ISBN 978-1-4051-3890-1.

Lindström published his much-cited *Chemical Reviews* article "Stereoselective Organic Reactions in Water" in 2002, and what has followed has been an enormous growth in peer-reviewed publications on aqueous organic chemistry. Now he has organized a team of leading scientists in the field and has provided this monumental monograph, *Organic Reactions in Water: Principles, Strategies and Applications*. This book showcases the milestones that have been achieved in the past 10 years. It was not intended to be exhaustive in its coverage but rather to provide the reader with a means for future exploration on various topics. Most references are within the past 10 years and include those up to 2006. Here, the conventional wisdom that water is deleterious to many organic reactions is questioned, and many examples of reactions that one would not normally conduct in aqueous media are provided. In addition, the authors emphasize new reactions and selectivities that have been discovered only when conducted in water.

The book opens with a personal account of chemistry in water by Breslow, which showcases his 50 years of research on cyclodextrins as artificial enzymes and covers many important biologically relevant reactions. Chapter 2 by Engberts is a lucid review on the structure and properties of water. A major portion of the chapter is devoted to our current understanding of the hydrophobic effect, which many practitioners in the field may find valuable. Ogawa and Kobayashi describe organic reactions catalyzed by acids in aqueous solutions in Chapter 3. Although Brönsted acid and heterogeneous catalysts are discussed, a large portion of the chapter is devoted toward Lewis acid-mediated asymmetric catalysis in water. Li reviews metal-mediated C−C bond formation in aqueous media in the succeeding chapter. After a brief account on why traditional organometallic reagents fail, he discusses a plethora of metal-mediated reactions that include allylation, propargylation, benzylation, arylation, vinylation, alkynylation, alkylation, aldol, Reformatsky, and conjugate addition reactions with carbonyls and imines. The chapter finishes with a discussion of metal-mediated coupling reactions.

Pericyclic reactions in aqueous media is the focus of Chapter 5 by Fringuelli et al. Interestingly, an emphasis is placed on cycloaddition reactions that proceed by using biomolecules as highly stereoselective catalysts. The two subsequent chapters focus on reductions and oxidations in water. Thus, a major emphasis in Chapter 6 is the development of chiral, water-soluble ligands for asymmetric hydrogenation, whereas the use of hydrogen peroxide and dioxygen as green oxidants is reviewed in Chapter 7. Sinou then discusses nucleophilic additions and substitutions in water in Chapter 8, much of which is devoted to enolate chemistry under Lewis acid catalysis; consequently, sections of this chapter are redundant with the material covered in Chapter 3. The properties and practical use of near-critical water are then reviewed in Chapter 9 as an alternative to ambient water. In Chapter 10, Nakamura and Matsuda describe the potential of using biocatalysts for organic synthesis, and in the following chapter, Narayan et al. overview the recent advances in conducting organic reactions in aqueous suspensions and illustrate the fallacy of precluding water from organic reactions due to insolubility. The concluding chapter by Wiebus and Cornils provides a practical perspective on the industrial use of water in aqueous biphasic solutions.

Lindsröm should be commended for his efforts in organizing a much-needed monograph on organic reactions in water. The book should serve the general chemical audience as an introduction to a blossoming field of chemistry. It should eliminate the misconception that water cannot be used as a solvent for organic reactions and instead show that it provides a new viable alternative. I highly recommend the book to those interested in green chemistry as well as to those who aim to further unite the paradigms of organic chemistry and biochemistry.

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Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications. Volumes 1−4. Edited by Krzysztof Matyjaszewski (Carnegie Mellon University, Pittsburgh, PA, USA), Yves Gnanou (Université Bordeaux I, Pessac, France), and Ludwik Leibler (Ecole Supérieure de Physique et Chimie Industrielles, Paris, France). Wiley-VCH Verlag GmbH & Co. KGa: Weinheim. 2007. 2982 pp. $675. ISBN 978-3-527-31446-1.

Ever since I coined the expression "macromolecular engineering" (Kennedy, J. P.; Marechal, E. J. *Carbocationic Polymerization*; J. Wiley & Sons: New York, 1982), the term has been used by the polymer science community to connote the precision synthesis of *all* the structural details and complexities of macromolecules. These four hefty volumes written by 155 authors, styled by three editors, and running close to 3000 pages stretch the concept of macromolecular engineering (ME) far beyond the synthesis of polymers. Although some of the chapters are real gems of synthesis-oriented polymer science, others are not relevant to the subject. As opposed to the misleading title on the cover, the title spelled out in the Preface, "Macromolecular Engineering: *From* Precise Macromolecular Synthesis *to* Macroscopic Materials *and* Applications" (italics added), is better in line with the intent of the editors. An even better title would be "Select Topics of Contemporary Synthesis-Oriented Polymer Science".

Although the first volume, subtitled "Synthetic Techniques", contains plenty of ME, it also includes topics that have little to do with synthetic techniques. Among the 16 excellent chapters that make up this volume, the fifth, entitled "Radical Polym-

Unsigned book reviews are by the Book Review Editor.

erization", is a particularly outstanding, all-encompassing modern review of the subject.

The emphasis of the second volume, "Elements of Macromolecular Structural Control", is still mainly on ME, but it also contains a great deal of ancillary material only remotely connected to ME. Whereas the first volume focuses on more traditional synthetic techniques, e.g., anionic, cationic, ring opening, radical, coordination, condensation, enzymatic, mechanistic transformations, etc., the second volume emphasizes more complicated techniques for the synthesis of telechelics, multisegmented blocks/grafts, cyclic polymers, stars, hyperbranched structures, microgels, dendrimers, brushes, core−shell particles, polyelectrolytes, bioinspired blocks, and other complex structures. The second volume is definitely not for the novice but rather for the specialist in synthesis who is interested in the state-of-the-art of this field and the way ME may evolve in the foreseeable future.

Inevitably, there will be repetition and overlap in such a massive multiauthor treatise: for example, controlled/living radical polymerizations — ATRP, NMP, RAFT — are explained at least three times. The nomenclature is sometimes inconsistent among the individual chapters: "hairy rods" in one chapter become "brushes" in others; M_n in one place is described as D in another, etc. Also, the text in Chapter 10.3.1 regrettably propagates the misuse of the term "grafting through" to describe the copolymerization of macromonomers with conventional small monomers, a conceptually simple polyaddition reaction. This was a term coined by me (together with the widely accepted terms "grafting from" and "grafting onto") to describe the grafting of a monomer through in-chain unsaturations (see Kennedy, J. P. An Introduction to the Synthesis of Block and Graft Copolymers. In *Recent Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Polymer Science and Technology, Volume 4; Plenum Press: New York, 1974 and *Cationic Graft Copolymerization*; Kennedy, J. P., Ed.; Journal of Applied Polymer Science: Applied Polymer Symposia, 30; J. Wiley & Sons: New York, 1977).

Turning to Volume 3, "Structure−property Correlation and Characterization Techniques", I find the 15 chapters to be a hodge-podge of topics only remotely or not at all connected to ME. They oscillate between characterization techniques, such as AFM, scattering, TEM, scanning calorimetry, chromatography, and NMR spectroscopy; topics in select engineering (not macromolecular), like dynamics and rheology, predicting mechanical properties, and reactive blending; and other subjects not easily fitted with ME, such as simulations, morphology diagrams, transport and electro-optical properties, and networks. Mind you, the individual chapters are well-conceived and well-crafted contributions intended for the advanced student and the specialist; however, the cognoscenti will not look for these chapters in a compilation concerning ME.

The same holds true for Volume 4, "Applications", which includes authoritative contributions on a variety of subjects that are only tenuously related to ME, e.g., nanocomposites, polymeric dispersants, surfactants, microelectronics, lithography, semiconducting polymers, membranes, sensors, polymeric drugs, bioconjugates, gels, and tissue engineering. The last chapter, incongruously, concerns IUPAC terminology and nomenclature. The work ends with a good ~80-page subject index.

In my opinion, this set of four volumes is smaller than the sum of its parts. It comprises outstanding, timely, occasionally brilliant individual chapters, which, as a whole, just do not mesh. The first and second volumes represent an excellent up-to-date comprehensive treatment of contemporary ME, but the balance of the work only tenuously connects to the precision synthesis of macromolecules. The latter volumes compile a large variety of subjects far beyond ME and are not for the synthesis-oriented polymer scientist. The extraneous chapters do not contribute much to ME but dilute the overall thrust of the mission and, most regrettably, become lost among the multitude of unrelated topics.

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Discrimination of Chiral Compounds Using NMR Spectroscopy. By Thomas J. Wenzel (Bates College, Lewiston, ME). J. Wiley & Sons, Inc.: Hoboken, NJ. xxiv + 550 pp. $110. ISBN 978-0-471-76352-9.

In this book, Wenzel presents an exhaustive and up-to-date account of strategies employed in the study of chirality by means of NMR spectroscopy. Instead of following the approach commonly found in various literature reviews in which methods of chiral discrimination are arranged based on the functionality of the analyte, the volume is organized by class of the chiral derivatizing and/or solvating reagent. Following a brief introductory chapter in which the differences between derivatizing and solvating agents are explained, the author presents a detailed review of methods used in the determination of absolute configuration based on derivatizations with Mosher's acid and related aryl-containing carboxylic acid reagents (Chapter 2). Approaches using other carboxylic acids as derivatizing and/or solvating agents, such as amino acids and acids with axial chirality, are presented in Chapter 3. This is followed by examples of the use of alcohol-, thiol-, and amine-bearing reagents, including cases detailing the use of carbohydrates and peptides, in Chapters 4 and 5. Strategies based on amides, aldehydes, ketones, and other miscellaneous organic compounds are then outlined in Chapter 6, and the application of chiral auxiliaries bearing phosphorus, selenium, boron, and silicon, nuclei that in some cases can be used as NMR-active probes in the studies, is reviewed in Chapter 7. Chiral recognition through the use of host−guest complexes, particularly those involving cyclodextrin-based compounds, crown ethers, calixarenes, and calixaresorcarenes as hosts, is summarized in Chapter 8. Methods relying on the differential interactions of chiral compounds with paramagnetic and diamagnetic metal complexes, ranging from classical approaches involving lanthanide chemical shift reagents to those based on transition metals, are presented in Chapter 9. In the final chapter, a variety of chiral discrimination methods based on highly ordered systems are reviewed, including examples of the use of nematic liquid crystals, ionic liquids, micelles, and solid-state NMR.

Wenzel's monograph is arguably the most complete review written to date on the subject of NMR-based methods for chiral discrimination. Virtually every strategy available is summarized, and in all cases a wealth of examples from the literature is

presented. Indeed, the number of articles cited, totaling nearly 1700, is impressive. Furthermore, and not counting historical references to the development of a particular method or reagent, the vast majority of the citations are recent. Perhaps as important, many of the examples presented involve nontraditional stereochemical problems, including the study of molecules displaying axial chirality or asymmetry owing to slow rotation. Apart from describing a large variety of approaches, Wenzel also emphasizes their advantages and limitations. For instance, he points out that despite their continuing high popularity, methods that rely on lanthanide chiral auxiliaries can be problematic at the higher magnetic fields found nowadays in average high-resolution NMR spectrometers. Similarly, distinctions between techniques that can be employed to reliably establish absolute configuration and those that can solely be used to determine optical purity are clearly stated, and comparisons among variants within a particular approach are presented.

Although the text is clear and well-written for the most part, there are a number of minor errors that deserve mention. For example, there is some repetition between chapters as well as cases in which terminology is defined after being used earlier in the volume. In addition to a few typos, some of which were likely introduced during editing (including 55.7° being cited as the magic angle instead of 54.7° in Chapter 10), a considerable number of chemical structures are incorrectly drawn, e.g., the structure of the *t*-Boc group in one of the schemes is incorrect, a nitrogen instead of a phosphorus is drawn on one of the bridgehead positions of a spirophosphazene, and some structures show bonds on the back of the structure going over those on the front or through rings, to mention a few. Finally, this reader would have appreciated it if more spectra showing typical results for selected examples were included. However, these are mostly trivial issues that do not take away from the overall quality of the work and are likely to be addressed in future editions of the monograph.

In summary, this book constitutes a comprehensive, well organized, and timely account of chiral discrimination methods by NMR spectroscopy written by an important contributor to the field. It is thus likely to become a valuable reference to a wide range of researchers involved in the study of chiral systems from natural or synthetic sources.

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Springer Handbook of Enzymes, Volume 36: Class 2, Transferases IX, EC 2.7.1.38−2.7.1.112, 2nd ed. Edited by Dietmar Schomburg and Ida Schomburg and Coedited by Antje Chang (Technical University Braunschweig, Germany). Springer: Berlin, Heidelberg, New York. 2007. xxii + 624 pp. $369.00. ISBN 978-3-540-47807-2.

This handbook represents the printed version of the enzyme data information system BRENDA, which was created in 1987 at the German National Research Centre for Biotechnology in Braunschweig and is currently updated at the Technical University Braunschweig. The second edition of this handbook contains descriptions of more than 4000 enzymes than have been "sufficiently well characterized". Entries are arranged according to EC-number sequence, and each entry includes the following types of information about the featured enzyme: Nomenclature; Source Organism; Reaction and Specificity; Enzyme Structure; Isolation/Preparation/Mutation/Application; Stability; and References. There is no index.

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In Situ NMR Methods in Catalysis. Edited by Joachim Bargon (University of Bonn, Germany) and Lars T. Kuhn (Oxford University, U.K.). Springer: Berlin, Heidelberg, New York. 2007. xii + 170 pp. $179.00. ISBN 978-3-540-71426-2.

In Situ NMR Methods in Catalysis is part of the Springer series *Topics in Current Chemistry*. The book contains five chapters and a helpful author and subject index. The chapters are on homogeneous catalysis in ionic liquids, transfer of parahydrogen-induced polarization (PHIP) to heteronuclei, investigations in supercritical fluids, continuous asymmetric hydrogenations, and how to exploit chemically induced nuclear polarization (CIDNP) in the investigation of free radical reactions. This is a diverse set of topics with little or no overlap that will expose the uninitiated reader to a variety of research areas.

The contents of this compilation are driven by the necessity of identifying intermediates in order to elucidate reaction mechanisms, and the editors identify both PHIP and CIDNP as powerful tools for this purpose. They further opine that the chapters on ionic liquids, supercritical solvents, and asymmetric hydrogenation augment the content.

The title, *In Situ NMR Methods in Catalysis*, seems to promise the reader a collection of topics that is focused on nuclear magnetic resonance (NMR) techniques and, in particular, on *in situ* NMR techniques useful for catalytic investigations. Unfortunately, it does not accurately reflect the content as two out of the five chapters—those on ionic liquids and asymmetric hydrogenations—have nothing to do with NMR, and this acronym does not even appear in the text contained in them. In addition, the chapter on CIDNP focuses on radical reactions that are not catalytic in nature. Thus, three out of five chapters bear only a tangential relation to the book's title. As the editors state, all contributing authors were affiliated with the University of Bonn at an early stage in their careers, which seems to have prompted the selection of this wide spectrum of topics.

For a volume titled *In Situ NMR Methods in Catalysis*, names such as A. T. Bell and J. F. Haw come to mind, to name only a select few. None of their pioneering work is included in this compilation. In fact, the focus of this volume is much narrower than the title suggests, as all contributions deal solely with homogeneous catalysis. In addition, as mentioned in the Preface, some of the chapters allude to other applications such as MRI and biological questions—applications that are unrelated to catalysis.

Chapter by chapter, the individual contributions are well written and structured, although some of them have a strong emphasis on the authors' own work rather than providing a review of the field. In particular, one of the chapters presents a

case study with a lot of experimental detail—unrelated to NMR—that would have been more suitable as a journal publication. I greatly enjoyed reading the chapter on supercritical fluids, which contains an excellent introduction, practical advice on how to conduct *in situ* NMR experiments, and interesting examples from a wide range of catalytic applications.

I was disappointed by the fact that the references are quite old; less than 20% of the references are from 2002−2007. The PHIP chapter is most up-to-date, while the CIDNP chapter is the least. It may well be that little has been published in a particular field in the past years. However, if this is the case, one cannot help but wonder if a topic warrants attention in a series titled *Topics in Current Chemistry*.

In summary, the book is not recommended for the enthusiast ready to delve into the field of catalytic investigations using NMR. The book presents an excellent resource for the reader who is interested in a diversity of topics related to homogeneous catalysis, some of which can be investigated by NMR. Other topics, such as PHIP and CIDNP, rely on NMR as a method of detection and are thus limited to specific systems, such as hydrogenations and radical reactions.

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Peptide Characterization and Application Protocols. Methods in Molecular Biology, 386. Edited by Gregg B. Fields (Florida Atlantic University, Boca Raton, FL). Humana Press: Totowa, NJ. 2007. xii + 342 pp. $99.50. ISBN: 978-1-58829-550-7.

This book is "dedicated entirely to the characterization of peptides and their application for study of biochemical systems", to quote from the Preface. It is divided into two parts. Part I, "Characterization" addresses some of the latest techniques for studying peptides, including high-performance liquid chromatography for their purification and evaluation and mass spectrometry for their analysis. Part II covers various applications for synthetic peptides, such as the use of conformationally constrained peptides as potential ligands, substrates, and enzyme inhibitors, to name one. Each chapter follows the usual sequence of sections in the series: summary and key words, introduction, materials, methods, notes, and references. A brief index concludes the book.

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Organic-Chemical Drugs and Their Synonyms, Extensively Enlarged 9th ed., Volumes 1−7. By Martin Negwer and Hans-Georg Scharnow (Berlin). Wiley-VCH Verlag GmbH and Co. KGaA: Weinheim. 2007. xviii + 5656 pp. $2000. ISBN 978-3-527-31939-8.

The latest edition of this seven-volume handbook includes approximately 163,000 synonyms for some 20,000 organic chemical drugs, including 4,000 new drugs. The volumes are organized into five parts: a list of organic chemical drugs and their synonyms arranged by increasing molecular formula (Volumes 1−5); an index of synonyms (Volumes 6−7); an alphabetical group index, which provides a listing of the various groups of compounds included in Volumes 1−5 and the entry numbers of the compounds that belong in those groups, and a reference group index, which lists the entry numbers of the compounds in numerical order, categorizing each, using a letter-digit combination, according to the keywords under which they have been subtitled (Volume 7); an index of CAS Registry Numbers (Volume 7); and an index of microorganisms, plants, and animal tissue (Volume 7).

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