Book Review

Book Review of The Chemistry of Organomagnesium Compounds, Parts 1#2: R#Mg

Robert E Mulvey

J. Am. Chem. Soc., **2008**, 130 (45), 15217-15217 • DOI: 10.1021/ja807539s • Publication Date (Web): 08 October 2008

J|A|C|S
BOOK REVIEWS

The Chemistry of Organomagnesium Compounds, Parts 1−2: R−Mg. Edited by Zvi Rappoport (The Hebrew University of Jerusalem) and Ilan Marek (Technion-Israel Institute of Technology, Haifa). From the Patai Series: The Chemistry of Functional Groups edited by Zvi Rappoport. John Wiley & Sons, Ltd.: Chichester. 2008. xx + 890 pp. $990. ISBN 978-0-470-05719-3.

If your impression of modern organomagnesium chemistry is that it is limited to the study and application of Grignard reagents in mainstream organic synthesis, then you should cast your eyes over this impressive and extensive two-part volume. An excellent and, for the synthetic chemist, indispensable companion to *The Chemistry of Organolithium Compounds* and *The Chemistry of Organozinc Compounds* in the same series, this new book emphasizes the growing popularity and breadth of research in organomagnesium chemistry as well as its international appeal—the contributing authors, who are leaders or at least active in the topics they review, come from 11 different countries. Striking a good balance between traditional Grignard "RMgX" and less well-known diorganomagnesium "R_2Mg" compounds, this book offers even greater scope than *Grignard Reagents: New Developments*, which appeared in 2000, and provides new, mostly up-to-date detailed material. It is the most comprehensive book yet on the organometallic chemistry of this fascinating group 2 metal.

The scene is set by a short historical perspective in the opening chapter on the chemistry of organomagnesium structures. This chapter in particular captures the excitement and novelty of the recent advances in the area with over a hundred carefully drawn figures illustrating the rich diversity of formulations—homometallic, heterometallic, homoleptic, heteroleptic—and structural types found for both neutral and charged—cationic and anionic ate—species. Reflecting where the major activity lies, most chapters are rightly dedicated to synthetic issues, for example of magnesium enolates, functionalized organomagnesiums, iron-catalyzed Grignard reactions, carbomagnesiation methodologies, catalytic enantioselective addition reactions, and more. Analytical, electrochemical, spectroscopic, thermochemical, and photochemical aspects receive decent coverage too, providing the reader with a more comprehensive insight into the area rather than simply a long list of synthetic transformations. There is also an enlightening chapter on the biochemistry of magnesium. For me, only a chapter on the supramolecular chemistry of magnesium is missing, although aspects of the subject do appear in some other chapters.

Technically, the book is aesthetically pleasing with ample, clearly presented figures, schemes, and tables that support and illuminate the text, although oddly the beautiful color plates associated with biomolecules in Chapter 8 appear erroneously in Chapter 9, which deals with unrelated theoretical chemistry. Containing substantial author and subject indexes, the book is easy to dip in and out of to locate specific information, and there is an extensive bibliography to enable readers to quickly find original papers.

In summary, this book continues the high standard of *The Chemistry of Functional Groups* series and is an essential resource for professional organic and inorganic chemists and their research groups who have an interest in organometallic chemistry. It could also prove useful in postgraduate teaching for designing a modern course on the subject. With the recent report of the first crystallographically characterized Mg−Mg bonded compound, this area is likely to increase in popularity and research activity; thus, the publication of this book is timely. A copy should be made available in every library that houses a section on advanced chemistry at the postgraduate level and above.

Robert E Mulvey, *University of Strathclyde*

JA807539S

10.1021/ja807539s

Multidimensional Liquid Chromatography: Theory and Applications in Industrial Chemistry and the Life Sciences. Edited by Steven A. Cohen(Waters Corporation, Milford, MA) and Mark R. Schure (Rohm and Haas Company, Springhouse, PA). John Wiley & Sons: Hoboken, NJ. 2008. xx + 456 pp. $125.00. ISBN 978-0-471-73847-3.

Chromatographic analysis of samples from biomedical, petrochemical, environmental, and natural products as well as food and other important entities encounter great challenges due to enormous compositional complexities. The conventional one-dimensional approach is often inadequate to provide satisfactory separation of thousands of components present in such samples. Although high-efficiency columns may improve the separation to some extent by keeping the chromatographic zones narrow, one-dimensional chromatograms of such complex samples are even then crowded with overlapping peaks. Multidimensional chromatographic systems are appropriate for the separation of such complex samples.

This book brings a wealth of information on the latest developments in multidimensional liquid chromatography (MDLC) with a distinctive focus on liquid-phase separations in the areas of the life sciences and industrial chemistry. The editors have assembled an able group of well-renowned scientists to cover various aspects of MDLC and capillary electrophoresis (CE), and they have produced a book that complements the information already available in the literature, e.g., *Multidimensional Chromatography: Techniques and Applications*; Cortes, H. J., Ed.; Marcel Dekker: New York, 1990 and *Multidimensional Chromatography*; Mondello, L., Lewis, A. C., Bartle, K. D., Eds.; John Wiley & Sons: Chichester, 2002.

A multidimensional chromatographic system uses two or more columns (dimensions) with orthogonal mechanisms of separation. The peak capacity, and hence resolving power, of such a system is greatly enhanced compared to that of a one-dimensional system and may theoretically become as high as the product of peak capacities for individual dimensions. Thus, a multidimensional separation system possesses a higher resolv-

Unsigned book reviews are by the Book Review Editor.

ing power than a one-dimensional system. Excellent overviews of the theoretical aspects of multidimensional chromatography—dealing with peak capacity, resolution, orthogonality, etc—as well as statistical approaches to decoding individual components of complex two-dimensional (2-D) chromatograms are presented in Part I of the book (Chapters 2−4).

The simplest and most commonly used multidimensional chromatographic techniques are 2-D techniques. Instrumentation and method development for 2-D separations are more demanding than in the case of 1-D separations. In the former, partially resolved chromatographic zones from the first dimension are transferred to the second dimension for further analysis using two different approaches: (1) heart cutting and (2) comprehensive 2-D methodologies. Technical details of instrumentation and column technology for MDLC are presented in Part II of the book (Chapters 5−8). Especially noteworthy is the chapter on monolithic columns and their applications in 2-D HPLC (Chapter 7).

This book focuses on MDLC applications in two areas: (a) the life sciences (Part III) and (b) industrial chemistry (Part V). Almost half of the book is devoted to these two topics and for good reasons. Rapidly growing areas in the life sciences, including proteomics, peptidomics, metabolomics, and glycomics, have to deal with biological samples of extraordinary compositional complexity. Only a multidimensional approach is in a position to provide the desired separation and decipher the composition of such complex samples. In the area of life sciences, this book provides up-to-date reviews on recent developments in MDLC of complex protein and peptide samples (Chapters 9−13). Especially noteworthy is the liquid mass-mapping technique (Chapter 10) and its application in cancer research. Excellent up-to-date reviews on MDLC applications in the area of industrial chemistry are presented in Chapters 17 and 18, highlighting multidimensional LC analysis of polymer and surfactant samples, respectively.

Liquid chromatography is a versatile analytical technique that is amenable to a wide range of analytes ranging from small molecules to gigantic biopolymers, from very nonpolar to very polar. This explains the popularity of LC and its wide range of use in diverse areas of science and technology. One significant shortcoming of conventional LC is its relatively low separation efficiency, measured in plate numbers, which seriously limits the analytical potential of multidimensional LC. There are two different approaches to overcoming this drawback using (a) ultrahigh pressure liquid chromatography (UPLC) and (b) capillary electrophoresis—two liquid-phase separation techniques that are characterized by extremely high separation efficiencies. Chapters 8, 15, and 16 provide excellent overviews of recent developments in these areas.

Sample preparation is an important step in the analysis of complex material systems like the ones encountered in multidimensional separations. Naturally, the reader would expect this book to contain a separate chapter on recent developments in sample preparation for MDLC, but such a chapter is missing; it would have been a valuable addition. This lack does not undermine the importance and usefulness of this book, however. It is a timely publication and presents a valuable resource of scientific information on MDLC. It presents systematically gathered scientific information from a plethora of articles scattered over a wide range of sources. This effort should be appreciated by a wide audience of scientists and researchers who deal with complex separation problems in biomedical, environmental, and natural products; industrial polymers; food; and other sources.

Abdul Malik, *University of South Florida, Tampa*

JA808005T

10.1021/ja808005t

Expert Systems in Chemistry Research. By Markus C. Hemmer (Fresenius University of Applied Sciences, Cologne, Germany). CRC Press/Taylor & Francis Group: Boca Raton, FL. 2008. xxii + 394 pp. $139.95. ISBN 1-4200-5323-X.

The author describes this book as a "good mixture of scientific literature and a captivating novel" in his attempt to explore both the theory and practice of using expert systems in chemical research. In this book, Hemmer describes the principles behind expert systems as well as the various techniques and tools for developing such systems. He covers various automated intelligence analysis techniques for processing chemical information, discusses applying molecular descriptors, and describes the use of expert systems in fundamental chemistry, in other interdisciplinary areas of research, as well as in the laboratory environment. In the final chapter, Hemmer discusses what expert systems can and cannot do and some of the challenges still facing this ever-evolving field. An extensive subject index completes the book.

JA8078847

10.1021/ja8078847

Organic Synthesis with Enzymes in Non-Aqueous Media. Edited by Giacomo Carrea and Sergio Riva (Istituto di Chimica del Riconoscimento Moleculare C.N.R., Milan, Italy). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xviii + 310 pp. $215.00. ISBN 978-3-527-31846-9.

This monograph is the latest in a series of recent releases by Wiley-VCH that have focused on using enzymes in organic transformations and industrial applications. It is a well-timed addition to the libraries of both academic and industrial scientists interested in harnessing the power of biocatalysts for synthetic purposes. Since the discovery in the early 1980s that many enzymes retained activity in neat organic solvents, even without chemical modification, the field of nonaqueous enzymology has been growing at a swift pace. This text provides the necessary background and perspective to understand why the field has expanded so rapidly and where the future of biocatalytic synthetic methodologies may be headed.

The editors' preface states that their overall objective was to provide a general overview of the field of nonaqueous enzymology since 1996 when Klibanov and Koskinen published their seminal book on the subject. Although the coverage in both texts is similar in many areas and includes contributions by several of the same authors, it is clear that the editors have accomplished their goal without being overly repetitive of the previous work. The current book comprises 12 chapters, written by well-known researchers in the field, that flow extremely well together and is divided into three parts. The opening chapters include a graduate-level introduction to the fundamentals of enzymology when performed in both aqueous and organic

media. Not surprisingly, the citations in this section, albeit relevant, are somewhat dated. This section establishes the language and foundation of many of the guiding principles and objectives of nonaqueous enzymology that are discussed throughout the remaining chapters, including enantioselectivity, kinetics and thermodynamics of biocatalysts in the absence of bulk water, the effect of organic solvents on substrate specificity, and activating enzymes under nonaqueous conditions. Although not intended to be a stand-alone textbook, if supplemented with an additional discussion on protein structure−function relationships or an overview of biocatalysis, the first part of this book could function as the text for a graduate-level half-semester course for students interested in special topics in synthetic organic chemistry.

The second part focuses on the more established and well-studied areas of nonaqueous enzymology, such as enantioselectivity in hydrolase chemistry, chemoenzymatic deracemization for the synthesis of enantiomerically pure chiral molecules, exploiting the specificity of enzyme active sites for chemo- and regioselectivity, and the use of biocatalysts in industrial scale applications. Despite this focus on the more mature areas in the field, the citations are surprisingly current in this section, with most chapters containing 30−40% of their references to literature since 2004.

Although the second section undoubtedly represents the heart of nonaqueous enzymology, it is the final part of the book that sets it apart from any other text on the subject. Within these last five chapters are detailed overviews of the emerging areas in biocatalysis, such as the use of biphasic systems or ionic liquids as the transformation media in enzymatic reactions, solid-phase biocatalysts acting on gas-phase substrates, and biocatalysis with undissolved solid substrates and products. These promising and unusual areas of nonaqueous enzymology are covered in significant detail in the present book and are not found in the previous Klibanov and Koskinen text. The only weakness that detracts from the efficacy of this section in conveying the importance of these rising areas is that the timeliness of the references is highly variable from chapter to chapter, particularly in the last two, in what should have been the most current section.

In summary, *Organic Synthesis with Enzymes in Non-Aqueous Media* provides an excellent overview of the fundamental principles and utility of biocatalysts in organic transformations and represents a comprehensive reference guide for both organic chemists and enzymologists interested in the field. Unfortunately, the moderately high list price of this hardback precludes its use as a graduate-level textbook and may limit its distribution to the shelves of institutional rather than personal or even departmental libraries, particularly when one considers several other titles with somewhat overlapping subject material available from Wiley-VCH.

Reza A. Ghiladi, *North Carolina State University*

JA807826G

10.1021/ja807826g

Organocatalysis: Symposium Proceedings 07.2. Edited by Manfred T. Reetz, Benjamin List (Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany), Stefan Jaroch, and Hilmar Weinmann (Bayer Schering Pharma AG, Berlin, Germany). Springer: Berlin, Heidelberg, New York. 2008. xiv + 340 pp. $119. ISBN 978-3-540-73494-9.

This book was developed from a symposium on the titled subject organized by the Ernst Schering Foundation which took place in Berlin in April 2007. The goals of the symposium and workshop was to give an overview of organocatalytic processes, mechanisms, and applications and to discuss future directions in the field. There are 11 chapters, a sampling of which includes "Biomimetic Organocatalytic C−C Bond Formations" by Enders et al., "Nucleophilic Carbenes as Organocatalysts" by Glorius and Hirano, and "Recoverable, Soluble Polymer-Supported Organic Catalysts" by Benaglia. There is no subject index.

JA8078797

10.1021/ja8078797

Dynamic Stereochemistry of Chiral Compounds: Principles and Applications. By Christian Wolf (Georgetown University, Washington, DC). Royal Society of Chemistry: Cambridge. 2008. xx + 512 pp. $99.00. ISBN 978-0-85404-246-3.

This book provides a feast of fascinating chemistry involving wide-ranging stereochemical studies. The author presents a unique perspective of phenomena involving the intersection of molecular chirality and stereodynamics. Topics include asymmetric synthesis, racemization/diastereomerization, kinetic resolution, molecular devices, topologically chiral assemblies, and other phenomena in which dynamic molecular phenomena are involved. With such an angle, the book transcends traditional divisions of organic chemistry and draws together themes common to diverse chemical phenomena. It is a useful entry into the literature, with over 3000 references. These include a number of papers from 2005 and a couple as recent as 2006.

Such a discussion of stereochemistry and asymmetric synthesis requires the use of accurate terminology and nomenclature. The book provides reasonably comprehensive overviews of the pertinent concepts and terms in a very succinct manner, targeting an audience that has some prior exposure with the material. Many fundamental principles of synthetic and physical organic chemistry are reviewed, including inversion of amino and other heteroatom moieties, hindered bond rotation, reactions giving racemization via achiral intermediates, mechanisms of epimerization of spiro-compounds, enantiomeric integrity of chiral Grignard, organolithium, and other organometallic reagents, conformational analysis, and atropisomerism. Discussion of these foundational topics generally focuses on the phenomena without going into extensive detail and is accompanied by thermodynamic or kinetic data in many cases, although detailed physical rationale is beyond the scope of the volume.

A limited discussion of analytical methods is presented, with a glimpse into chiroptical methods and a bit more detail on the use of NMR—especially dynamic NMR methods—and stopped-flow chromatographic and electrophoretic analysis, including a thorough discussion of dynamic chromatography.

After an introduction to the terms and principles of asymmetric synthesis with broad applicability, the discussion focuses on chemistry in which dynamic behavior plays a role, such as atroposelective synthesis of axially chiral molecules, chirality transfer, and interconversion of chiral elements such as in S_N2' reactions or sigmatropic rearrangements. Transfer of chirality

from one molecule to another is discussed, as is self-generation of stereogenicity and chiral relays. The very interesting topics of asymmetric resolution, dynamic kinetic resolution, and related chemistry are examined. Reactions are typically presented with a mechanistic rationale.

The text also covers stereodynamic phenomena including molecular gears, propellers, switches, sensors, and motors. Topological chirality and isomerism are discussed, with a smattering of studies involving chiral rotaxanes and catenanes. The major missing area is the rich chemistry of dynamic chiral polymers, gels, and liquid crystals, which had to be excluded due to space and time. However, the book contains more than enough organic chemistry to satisfy most readers.

This is a book that people will love to read. The topics are well chosen and interesting, and the writing is succinct and accurate. It could be used as a textbook for an advanced undergraduate or graduate special topics course and will serve as a valuable source of stimulating supplementary material for many courses.

James W. Canary, *New York University*

JA8074055

10.1021/ja8074055