Book Review

Nitrosation Reactions and the Chemistry of Nitric Oxide By D. L. H. Williams (University of Durham, U.K.). Elsevier BV: Amsterdam. 2004. xii + 268 pp. $209.00. ISBN 0-444-51721-9.

Peter C. Ford

J. Am. Chem. Soc., **2005**, 127 (20), 7654-7655• DOI: 10.1021/ja041042g • Publication Date (Web): 29 April 2005

J|A|C|S
BOOK REVIEWS

Synthesis of Biaryls. By Ivica Cepanec (BULUPO Pharmaceuticals, Zagreb, Croatia). Elsevier Ltd: Oxford. 2004. xiv + 350 pp. $140.00. ISBN 0-08-044412-1.

As instructors of undergraduate courses on synthesis should now fully realize, sp^2-sp^2 bonds are no longer made by addition of vinyl Grignards to carbonyl compounds followed by dehydration, but in a regio- and stereoselective manner, by transition-metal-catalyzed cross-coupling reactions. In the case of formation of the aryl−aryl bond, as the author of this timely and useful volume recognizes and documents, the classical Ullmann, Gomberg−Bachmann−Hey, Pschorr, and Gatterman methods have been superceded, modified, and reinvented in the last 30 years into mild procedures that bear the familiar names of Kumada−Corriu, Negishi, Suzuki−Miyaura, Stille, and others which are emerging (e.g., Hiyama) and still not fully explored. This book is a modern and up-to-date discussion of the mechanisms, scope, and limitations of the synthesis of biaryls, which includes experimental sections. There are references to the end of 2003. It will undoubtedly be of value to all medicinal and process chemists who work in labs where >80% of bioactive molecules are aromatic and heteroaromatic, but it should also prove useful to teachers of upper level and graduate courses in the ever-changing field of organic synthesis.

After a brief but useful introduction to the significance of biaryls, classical methods of synthesis are succinctly summarized, and mechanistic and synthetic issues are discussed and amply illustrated in tabular and experimental forms. Critical conclusions are given to indicate that some of these methods (e.g. the Ullmann method) are still competitive with modern methodologies. In Chapter 3, dealing with aryl halide- and sulfonate-coupling reactions, the author emphasizes mechanisms and methods for homo- versus cross-coupling, catalytic versus stoichiometric techniques, and types of metals (Zn, Mg, Al, Mn, Cu, including the recent In). At the end of each chapter, 6−8 procedures are presented in detail for easy transfer into the laboratory.

Chapter 4 covers cross-coupling methodologies extensively according to the named reactions mentioned above, but also deals with the evolving and not yet thoroughly tested aryl reagents of Si, Mn, Ti, and In. Tabular data provide comparative analysis of the effect of aryl substituents and choice of catalyst. Chapter 5, the longest in the book, is devoted to the Suzuki−Miyaura reaction, the "Grignard reaction of the 21st century." Consecutive sections detail the effects of base, solvent, and catalyst (including TONs), provide comparison of coupling partners (e.g., halides, diazonium salts), illustrate the considerable tolerance of this methodology for various functional groups, and include valuable information on the preparation and handling of arylboronic acids and their derivatives.

In the relatively brief Chapter 6, the author instructs the chemist that oxidative coupling of arenes to biaryl and polyaryls, especially intramolecular versions, are valuable mainly for preparing symmetrical structures and indicate the most favorable one-electron metal sources. Chapter 7 is a review of the Meyers and Motherwell approaches to biaryls, using free radical *ipso* substitution and *ortho*-oxazolinyl-driven aromatic nucleophilic substitution reactions respectively. These reactions, in addition to other miscellaneous methods that are described, deserve much more recognition than has been given to them to date, especially as they pertain to synthesis of highly hindered *ortho*,*ortho*′-substituted biaryls. Most appropriately, in terms of the rational progression of aryl−aryl bond-forming methods, the author ends the book with a chapter on methods for constructing axially chiral biaryls. The broad application of cross-coupling methods, especially to drug discovery programs, indicates that axially chiral bioactive molecules will be, if not already (albeit surreptitiously), common, and that this area, while still in its infancy, will be a beehive of activity soon.

The writing and preparation of this book has clearly been a labor of love for Dr. Cepanec. He has provided exhaustive coverage of the old and the new, critically analyzed and compared the methods, provided data on best conditions for first attempts, given mechanistic insight as it relates to synthetic optimization, and listed selected synthetic procedures, some from direct experience, for use in the lab. The text is clear, the equations are instructive, with more than the normal detail of conditions, and the index is substantial and carefully constructed. The field of aryl−aryl coupling is omnipresent in chemical synthesis and is therefore required knowledge for the modern practicing chemist. This volume not only provides that knowledge and examples of its application, it also fosters an appreciation for biaryl synthesis.

Victor Snieckus, *Queen's University*

JA040988N

10.1021/ja040988n

Nitrosation Reactions and the Chemistry of Nitric Oxide. By D. L. H. Williams (University of Durham, U.K.). Elsevier BV: Amsterdam. 2004. xii + 268 pp. $209.00. ISBN 0-444-51721-9.

The chemistry of nitric oxide and related species, such as the one-electron oxidation and reduction products (NO^+ and HNO, respectively) and other NO_x, has undergone a major renaissance over the past 15 years. This follows the discoveries of numerous key roles for these species in the cardiovascular, neurological, and immune response systems in mammalian biology. At first glance, a simple diatomic such as NO would not appear to be an obvious candidate for a biological messenger since it has little regiochemistry and it diffuses readily through all sorts of media. However, the remarkable outpouring of publications focusing on the biomedical roles of NO should certainly dispel such a prejudice.

In the excitement of studying the biological and medical roles of the nitrogen oxides, it is worth remembering that the

Unsigned book reviews are by the Book Review Editor.

10.1021/ja040988n CCC: $30.25

chemistry of these species with organic and inorganic substrates had already received considerable attention before these roles were recognized. One specific example is nitrosation, the addition of an equivalent of "NO^+", usually by replacement of a proton, e.g., $X-H + NO^+ \rightarrow X-NO + H^+$. Nitrosation reactions of various organic substrates were reviewed in the valuable monograph *Nitrosation*, also written by Professor Williams and published in 1988 by Cambridge University Press. The present monograph is largely an updating of that previous publication.

The book is organized into 13 chapters: the first eight are largely focused on the nitrosation of various organic substrates, with specific chapters on *C*-, *O*-, *N*-, and *S*-nitrosation. Chapter 8, for example, is concerned with the synthesis, properties, and reactions of *S*-nitroso thiols (RSNO), compounds that are drawing considerable attention in the biological community as endogenously generated NO carriers and signaling agents. The remaining five chapters include brief discussions of nitrosation reactions involving metals (Chapter 9), the biological chemistry of NO (10 and 11), NO-releasing compounds (12), and the chemistry of the nitroxyl species HNO and NO^- (13). There are 650 references. The real strength of the book lies in its discussion of the formation and reactions of various organic nitrosation products (Chapters 1−8 and parts of 12), which is the research area of greatest familiarity and expertise of the author. With regard to the other chapters, the discussion of the biochemistry and biology of NO is very introductory. For a more detailed treatment, the volume *Nitric Oxide: Biology and Pathobiology* edited by Ignarro and published by Academic Press in 2000 is recommended.

Other than the 1988 volume, I do not know of another source that treats the topic of organic nitrosation as comprehensively or with as thorough a focus on the mechanisms of these reactions as Williams' new book. There is increasing recognition of the importance of nitrosation products in mammalian biochemistry, and for this aspect alone, I would recommend that researchers who have an interest in the chemistry, biochemistry, and/or chemical biology of NO and other NO_x derivatives have this monograph readily available as a reference source.

Peter C. Ford, *University of California, Santa Barbara*

JA041042G

10.1021/ja041042g

Inorganic Materials Chemistry Desk Reference, 2nd ed. By D. Sangeeta (GE Aircraft Engines) and John R. LaGraff (Rensselaer Polytechnic Institute). CRC Press: Boca Raton, FL. 2005. xii + 372 pp. $149.95. ISBN 0-8493-0910-7.

Like its predecessor, the second edition covers the preparation of solid-state inorganic materials by chemical processing techniques. Some of the new features in this book include more than 200 new definitions, anisotropic properties of single-crystal materials, coverage of new chemical precursors and their properties, discussion of new topics, such as combinatorial chemistry, nanostructures, and biomaterials, and a focus on new applications of inorganic materials. A subject index completes the book.

JA0410542

10.1021/ja0410542

Progress in Colloid and Polymer Science, Volume 126: Trends in Colloid and Interface Science XVII. Edited by Valérie Cabuil (Université Pierre et Marie Curie, Paris, France), Pierre Levitz (no affiliation given), and Clande Treiner (no affiliation given). Series edited by F. Kremer and W. Richtering. Springer: Berlin, Heidelberg, New York. 2004. viii + 200 pp. $179.00. ISBN 3-540-20073-8.

This book contains a selection of papers presented at the 16th meeting of the European Colloid and Interface Society, which was held in Paris, France, in September 2003. There are 42 chapters organized under the following sections: Molecular Self-Assemblies; Long Range and/or Weak Interactions in Interfacial Systems; Concentrated Colloids and Rheophysics; Original Ways to Probe Colloidal Systems; and Colloids in Biology. An author/title and a keyword index complete the book.

JA059705X

10.1021/ja059705x

Insect Antifeedants. By Opender Koul (Insect Biopesticide Research Centre, Jalandhar, India). CRC Press LLC: Boca Raton, FL. 2005. xii + 1006 pp. $189.95. ISBN 0-415-33400-4.

This handbook compiles information about various aspects of insect antifeedants, plant defensive chemicals that discourage herbivory, in the following seven chapters: Introduction; Concepts and Mechanisms; Bioassays; Structure-Activity Relationships; Commercialization; Practical Applications and Conclusions; and Bioefficacy Monographs. The last chapter, with its somewhat misleading title, is a series of data sheets on the chemistry and bioefficacy of nearly 900 compounds that are presented in alphabetical order. An extensive subject index completes the book.

JA059703C

10.1021/ja059703c

Gas Adsorption Equilibria: Experimental Methods and Adsorptive Isotherms. By Jürgen U. Keller and Reiner Staudt (Universität Siegen). Springer: New York. 2005. xiv + 442 pp. $139.00. ISBN 0-387-23597-3.

This book presents a comprehensive summary of methods for measuring gas adsorption equilibria and for characterizing materials such as absorbents and gas separation or gas storage media. It consists of seven chapters beginning with coverage of the basic concepts of adsorption and finishing with a detailed description of adsorption isotherms. The latter are very often final deliverables, where adsorption equilibria are concerned.

The organization of the book is based on the physicochemical principles of the method addressed in the specific chapter, beginning with volumetry, gravimetry, a combination of these two methods, oscillometry, and impedance spectroscopy. Each chapter is developed in the same logical way. In reading the book, we learn about measurements and their variations, the theory behind each setting, as well as the limitations of the specific method addressed. A very elegant and useful part of each chapter is the short summary of advantages and disadvantages of each method.

The targeted audience of the book are young experimentalists and those whose work focuses on experimental results. Thus, the authors provide a clear outline for each experimental approach and present examples of the results obtained. This is especially important for young experimentalists, who, having grown up in the era of total computerization, need to understand the source of their data and the reliability of the results obtained.

An especially important aspect of the book is the fact that it addresses multicomponent adsorption from theoretical, experimental, and even applied points of view. To my knowledge, there is no other comprehensive review addressing this problem in a simple and introductory matter. This aspect gives the book a "down-to-earth" flavor, which I think was the idea of the authors.

The figures and tables included in the book are very educational and in many cases self-explanatory, particularly the latter ones, which include useful constants, equations, conditions, and empirical parameters. The way in which the book focuses on each experimental approach is very straightforward, informative, and educational. It certainly fills a gap in the market and should be due for future updates and expansions.

On the negative side, I found the book somewhat limited in references and expected a broader scan. Another deficiency is that it contains many obvious spelling errors, which could have been avoided by more careful editing. Also, some passages are awkwardly worded. Finally, if I were to change something in this book, I would transfer the last chapter, which deals with adsorption isotherms, to the beginning of the book just after the basic concepts in order to show clearly the target for which all of these experimental approaches are used.

Teresa J. Bandosz, *City University of New York*

JA041029W

10.1021/ja041029w

Side Reactions in Organic Synthesis: A Guide to Successful Synthesis Design. By Florencio Zaragoza Dörwald (Novo Nordisk A/S, Malov, Denmark). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2005. xvi + 374 pp. $110.00. ISBN 3-527-31021-5.

I am glad I did not try to write this book. Nearly every organic reaction has at least one side reaction, and one person's side reaction is another's target material. Thus, to explain the intended products of the possible side reactions is to explain organic chemistry twice over. As I read through this work, I could feel the author staggering under the weight of the task he had taken on.

The title of the book is not one that would attract casual readers. Consequently, I was surprised to see that the first few chapters talked of fundamentals and generalities. For example, they cover retrosynthetic analyses and stereoelectronic effects and give an overview of the stabilities of organic compounds. Conversely, there is nothing in this book on design of experiments to minimize byproducts, even though that surely must be a state-of-the-art consideration. In Chapter 4, when the book becomes more specific, the focus is on nucleophilic substitutions. This is interesting material, the content here and in some subsequent chapters reminded me of that excellent old text by Lowry and Richardson, but it is not the type of approach to the subject that I expected to see. That is the problem throughout: the strategy is unclear.

In retrospect, it is clear to me now that a book on side reactions in organic chemistry is primarily going to be a reference text; few readers would read it cover-to-cover, and most would want to look up particular transformations. The table of contents does not indicate it could be used effectively in that way, so I tried the index. As a test, I randomly selected a few likely search terms. Four page entries were listed for "Mitsunobu", but in none of those pages was this reaction described in any detail. There was one entry for "aldol", and the corresponding text was superficial, and there were no entries at all for "Swern" or "Pummerer". Maybe it is not fair to expect named reactions in an index, but the reality is that there is often no better way to look up a transformation.

The text in this book is clear, and the diagrams are well presented. There are lots of references, with titles making it easier for the reader to access the value of a reference before they go to find it. The author has worked hard on this book and made a brave effort. Overall, though, it is one for research libraries, but does not merit a personal investment, in my opinion.

Kevin Burgess, *Texas A&M University*

JA059728B

10.1021/ja059728b

Practical NMR Relaxation for Chemists. By Vladimir I. Bakhmutov (Texas A&M University). John Wiley & Sons, Ltd: Chichester, U.K. 2004. xii + 202 pp. $185.00. ISBN 0-470-09445-1.

As the author indicates in the preface to this modest volume, nuclear magnetic resonance is a versatile analytical tool for chemistry. The versatility lies in the many parameters that affect spectra and their relation to chemical connectivity, structure, and dynamics. Early uses of NMR in chemical studies emphasized chemical shielding and indirect coupling as indicators of chemical state, particularly for determining the type of group and chemical connectivity. In the last 30 years, the use of NMR spectroscopy in chemistry has expanded greatly to include gathering of information on other parameters that delineate chemical and physical states. Since the dynamical state is an important material descriptor and user-friendly spectrometers for gathering data have been developed, chemists have become interested in the evaluation of relaxation times. Bakhmutov's book gives a relatively low-level introduction to relaxation measurements and their uses in describing dynamical processes, particularly for molecular systems in solution.

The plan of the book is rather straightforward. In the first chapter, an explanation of relaxation is given in terms of macroscopic processes, followed by a short discussion of the origins of relaxation in molecular motions. A chapter on procedures for measuring relaxation times and a discussion of errors in the measurement process follows. Subsequently, the author discusses the major mechanisms of relaxation, using macroscopic models that are particularly appropriate to fast motions as one would find in solution. The last half of the book is dedicated to specific examples of relaxation in various systems to determine parameters, such as internuclear distances, quadrupole coupling constants, chemical-shielding anisotropy, the effects of chemical exchange, and relaxation in the presence of paramagnetic materials. Throughout the book, the author avoids complex quantum mechanical calculations and summarizes results in useful equations. As such, a person with only a passing knowledge of quantum mechanics can easily navigate most of the explanations of relaxation and dynamics.

The book focuses on relaxation studies of solutions, with only passing reference to solids. For many chemists, this is an adequate introduction to NMR relaxation theory. However, the mechanisms of relaxation in solid materials raise complex issues that are not addressed in this book. For example, paramagnetic relaxation in solids has been studied by a variety of groups to obtain information on the dynamic state, and the interpretation of the relaxation in many cases is far more complex than simple exponential recovery can predict. The relaxation mechanisms in solids, and the central part spin diffusion (or lack of it) plays in relaxation in solids, are not discussed. Even unusual mechanisms for liquidlike systems, such as those that arise from director fluctuations in liquid crystals, are not mentioned. In addition, some technological aspects of relaxation, such as the description of the spin−echo experiment (the Carr−Purcell experiment), get very light treatment. I suspect that a novice at NMR spectroscopy would have a difficult time understanding the technological significance of the spin−echo experiment from the short introduction given in this book. Finally, there are typographical and grammatical errors that demonstrate a lack of careful editing, but none seem to affect the equations that someone interested in NMR relaxation would find very useful in analyzing data.

This book is not the sort of monograph that Wolf's *Spin-Temperature and Nuclear-Spin Relaxation in Matter* is, but making such a monograph was not the author's intention, as stated in the preface. Surely it will find use by chemists who want a simple explanation of NMR relaxation and a means to analyze relaxation data in solution experiments on common small molecules.

Cecil Dybowski, *University of Delaware*

JA0597247

10.1021/ja0597247

Molecular Light Scattering and Optical Activity, 2nd ed. By Laurence Barron (University of Glasgow). Cambridge University Press: Cambridge, U.K. 2004. xxii + 444 pp. $150.00. ISBN 0-521-81341-7.

Optical activity was discovered early in the 19th century and played an important role in persuading scientists of the reality of 3D molecular structure and the existence of chiral molecules and crystals. In the mid-19th century, Faraday's observations of magnetically induced optical activity implied a connection between light and electromagnetic fields. By the mid-20th century, circular dichroism and optical rotatory dispersion had become essential tools for elucidating the structure of natural products and other biomolecules. Toward the end of the 20th century, the discovery and development of vibrational optical activity, in the forms of circular differential Raman scattering and vibrational circular dichroism, and their magnetically induced counterparts heralded a renaissance in the field.

Barron has provided a personal overview of molecular optical activity, based on his 35 years of research in the field. He provides a generalized mathematical framework for describing the interaction of molecules with electric and magnetic fields that encompasses all of these phenomena and more. The chief strength of this book is that the framework is so general and powerful that it can be used to describe phenomena that have not yet been imagined or discovered. In addition, Barron writes clearly and provides much physical insight into the phenomena he describes.

A complexity of light scattering is that when polarized light or a static field is incident on a molecule, the molecular response is not always proportional to the strength of the applied electromagnetic field, nor is it in the same direction as the applied field. Also, the electric or magnetic field distribution in a molecule is not simply described by a dipole moment, but by higher-order moments as well. To describe systematically these features, one must use mathematical tensors. This book, by necessity, contains more than a thousand equations involving tensor notation. This aspect will likely scare away many potential buyers, but for readers willing to master the math, this book will pay back much more in the tools it provides.

The book also makes considerable use of symmetry arguments to shed light on many phenomena and to simplify many derivations. After the introductory chapters on field-molecule interactions, light scattering, and symmetry, the later chapters go on to treat natural electronic optical activity as well as vibrational optical activity and their magnetic analogues. References are up-to-date, with the most recent from 2004. The book is not meant to be all-encompassing; for example, it does not cover nonlinear optical activity, cholesteric liquid crystals, helical polymers, or new detection techniques for natural optical activity. Nevertheless, this is an important book for any researcher or student interested in a solid physical grounding in chiral optical phenomena.

Bruce A. Garetz, *Polytechnic University*

JA041027B

10.1021/ja041027b

Handbook of Ion Chromatography, 3rd, completely revised and enlarged edition, Volumes 1 and 2. By Joachim Weiss (Dionex GmbH). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2004. xiv + 894 pp. $395. ISBN 3-527-28701-9.

This book is an important, comprehensive reference for anyone in the chemical sciences seeking to use ion chromatography in their research. It is written with the detail of a user's

manual and the clarity of a novel. The *Handbook of Ion Chromatography* is so well written that it is easy to forget it is a translation. It is based on hundreds of citations that acknowledge publications from the 1970s, marking the founding of modern ion chromatography, while at the same time including several references from the last five years.

Chapters 1 and 2 provide a brief history of ion chromatography and a short review of the theory of chromatography that should be particularly useful to the novice. In Chapters 3−6, anion exchange, cation exchange, ion exclusion, and ion-pair chromatography are discussed. Each chapter presents detailed discussions of the stationary phases, suppressor systems, eluent selection criteria, and carefully selected groups of analytes representative of most compounds that an operator may wish to separate. The organization of these chapters, complemented by clearly presented tables and informative illustrations, allows the reader to access quickly practical information that may be useful for method development. Thus, this book should facilitate further advancement of techniques in ion chromatography.

A problem with most reference books is that they are so focused that they are difficult to understand without supplemental references. The author thoughtfully circumvents this problem by providing a nice balance between the concepts described explicitly in the text and the details referenced in the citations. For example, a welcome addition to the third edition is the expanded discussion on hyphenated mass spectrometry techniques in Chapter 7. It is possible for a reader to review this section knowing nothing about either technique and walk away having a basic understanding of both. This basic format is followed throughout the book, making the text easy to read, while providing the reader with more information on demand.

Chapters 8 and 9, written on quantitative analysis and applications, respectively, distinguish this handbook from other reference books. The inclusion of the chapter on quantitative analysis demonstrates once again the author's attempt to make this a truly comprehensive and user-friendly resource. Not only is this section a helpful reminder of the parameters that must be measured for a respectable study of method development, it also addresses the specific concerns of users of ion chromatography. Chapter 9 includes a plethora of applications from which the reader can learn more about specific analyses.

In summary, this book is a must-have for anyone serious about separation science. No single text can include everything. However, this reference is so complete that if it does not address the user's specific need, it should have a closely related application for guiding the operator toward the solution to his or her problem. It is well-organized and timely and has potential to advance the science. Commercially available electrolysis-based eluent generation systems and the availability of application specific stationary phases have initiated exponential growth in the number of practitioners of ion chromatography in the past several years. Consequently, the scientific community is primed for an updated, comprehensive resource on this topic. Dr. Weiss's book does an excellent job of synthesizing the most important developments in the field of over the past 30 years. I highly recommended it to both students and professionals alike.

Krishna L. Foster, *California State University, Los Angeles*

JA041040W

10.1021/ja041040w