Additions and Corrections

Novel Synthesis of Cyclic Alkenylboronates via Ring-Closing Metathesis [*J. Am. Chem. Soc.* **1998**, *120*, 7995−7996]. JOHANNE RENAUD* AND STEPHANE G. OUELLET

Page 7996; During publication a line was dropped in the sentence beginning on line 20 of the right column. The sentence should read as follows: The slower rates of ring closure may result from the formation of intermediate ruthenium complexes, implicating donor atoms of the olefinic precursor and the newly formed ruthenium carbene center.[14]

JA985525U

10.1021/ja985525u
Published on Web 10/28/1998

Book Reviews

Metal-Catalyzed Cross-Coupling Reactions. Edited by F. Diederich (ETH, Zurich) and P. J. Stang (University of Utah). Wiley-VCH: Weinheim. 1998. xxi + 517 pp. $140. ISBN 3-527-29421-X.

This volume includes eleven chapters written by some of the major players in the field of metal-catalyzed cross-coupling reactions which constitute some of the most powerful tools for C−C bond formation in modern organic synthesis. As would be expected, the majority of these contributions focus on palladium-mediated processes. Each chapter emphasizes the synthetic utility of this chemistry, and issues of regio- and stereoselectivity permeate the book. Specific sections on asymmetric methodology are presented in five chapters.

In Chapter 1, E. Negishi and L. Liu survey palladium- and nickel-catalyzed cross-coupling reactions involving organozinc, -magnesium, -aluminum, and -zirconium reagents. Chapter 2 (A. Suzuki) deals with palladium-catalyzed cross-coupling reactions of alkenyl-, aryl-, and alkylboron compounds with organic halides and triflates. Chapter 3 (S. Brase and A. de Meijere) provides a very good overview of the Heck reaction, including various tandem processes that include a Heck step. One drawback is the partial overlap between this chapter and the excellent review of the intramolecular Heck reaction in natural products synthesis by J. T. Link and L. E. Overman (Chapter 6). T. N. Mitchell provides a thorough survey of the use of alkenyl-, aryl- and alkynylstannanes in cross-coupling reactions (Stille coupling, Chapter 4). K. Sonogashira's chapter on alkynyl cross-coupling reactions (Chapter 5) focuses on the synthesis of conjugated alkynes *via* the coupling of unsaturated halides with alkynylmetals or terminal alkynes. I. Marek and J. F. Normant (Chapter 7) provide a well-written account of carbometalation reactions, emphasizing recent applications of carbolithiation, carbozincation, and carbocupration reactions in ring synthesis. J.-E. Backvall (Chapter 8) provides a highly systematic account of palladium(0)- and palladium(II)-catalyzed 1,4-additions to conjugated dienes. One concern is that this chapter deals largely with the formation of carbon−heteroatom bonds, which does not fit well with the intended focus of the book. In Chapter 9, P. Knochel provides an excellent overview of carbon−carbon bond forming reactions using polyfunctionalized organozinc or zinc/copper reagents, including palladium- and nickel-catalyzed processes. Chapter 10 (T. Hiyama) reviews organosilicon compounds in cross-coupling reactions, with a focus on activation of the C−Si bond toward palladium(0)-mediated cross-coupling reactions *via* fluoride ion attack. Finally, J. Tsuji and T. Mandai (Chapter 11) provide a systematic overview of palladium-catalyzed coupling reactions of propargylic compounds.

Many reviews and monographs in the areas covered by this book have been published in recent years, and one challenge for the authors was to provide a unique angle on their topic. This was effectively achieved in most but not all chapters. Of greatest concern are Chapters 2 and 11 which were lifted almost verbatim from recent reviews by the same authors, and Chapter 10 where large portions of a 1994 review are repeated.

The literature coverage in each chapter is largely through late 1996/early 1997, except in Chapter 2 where only one reference after 1995 is cited. The breadth of coverage in most chapters is appropriate, and the writing style throughout the book is largely interesting and informative. Most authors provide a balanced view of the area under review, providing examples from their own work but also including contributions from many other groups. In Chapters 8−10, the heavy emphasis on the authors' own work appropriately reflects the relative importance of their contributions in those areas. With the exception of Chapters 4, 5, 6, and 9, considerable mechanistic insight is provided. All chapters provide a plethora of synthetic applications. In the Foreword, the Editors indicate the synthetic importance of metal-catalyzed cross-coupling reactions in areas ranging from "complex natural products to supramolecular chemistry and materials science"; however, while many illustrative examples throughout the book are taken from natural products syntheses, relatively few applications are discussed from the latter two areas. Several chapters provide insightful conclusions, while others have either a brief and uninformative concluding statement or else no conclusion at all. Each chapter has its own table of abbreviations, many of which are highly repetitive. One such table at the end of the book would have sufficed.

In line with a continuing trend in recent years, a series of 4−17 representative experimental procedures are given at the end of each chapter. There is considerable variability in the types of procedures given (general procedure vs specific preparation), the level of detail provided, and the scale of each procedure (from ca. 30 μmol to 0.5 mol of substrate). Some procedures are provided with an *Organic Syntheses* level of detail, while others are far more abbreviated and are less useful to the nonspecialist. For example, in the preparation of α-farnesene (Chapter 1), the procedure given is more abbreviated even than the original procedure published in a *J. Am. Chem. Soc.* communication; even a warning about the pyrophoric nature of trimethylalane is omitted! The majority of procedures, however, are presented at a level of detail typical for such books (e.g., Schlosser's *Organometallics in Synthesis: A Manual*) which would allow the experiment to be repeated by an experienced organic chemist. In Chapter 6, Overman precedes his experimental procedures with an excellent two page discussion outlining general protocols for the selection and handling of various catalysts and reagents needed for Heck chemistry. The inclusion of similar details in other chapters would have been a valuable addition to the volume. An attractive feature of some chapters is the cross-referencing of these procedures with the body of the chapter, but again this is not done consistently throughout the book. A detailed table of contents and an extensive subject index are included. The short author index is very incomplete and is of

questionable value, only listing authors whose names are *explicitly* mentioned in the body of the text.

The book is typeset, and with the exception of Chapter 3, the figures have been reworked into a common style prior to publication. It is thus all the more remarkable that, with the notable exception of Chapters 6, 9, and 10, an enormous number of errors have been propagated into the final printed version of the book. In the extreme, I found six typographical errors in a half-page listing of abbreviations in Chapter 5. Typesetting errors are also common, including the omission of the edges of some figures and the use of "C C" for a triple bond in several places. Errors of substance are also in evidence, particularly in some schemes where curved arrows are misused, structures are incompletely or erroneously drawn, and stereochemistry is sometimes ambiguous. On p 212, Sonogashira claims that several metal salts are effective at mediating a particular cross-coupling reaction, whereas an examination of the cited literature indicates that the converse is true, while, on p 68, Suzuki misuses the term "S_N2" to describe an addition−elimination reaction of a β-halo enone. Clearly the book would have significantly benefited from more careful editing prior to publication.

Overall, however, in spite of the concerns listed above, this volume does uniquely assemble a number of useful contributions from a broad spectrum of synthetically useful metal-catalyzed cross-coupling reactions. It should prove useful to a wide audience of chemists, including graduate students, who are interested in modern organic synthesis. I would certainly expect to see a copy of this book on the shelves of most chemistry libraries.

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JA985656V

10.1021/ja985656v

Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement. By Krishnan Rajeshwar (University of Texas at Arlington) and Jorge G. Ibanez (Universidad IberoAmericana). Academic Press: San Diego. 1996. $95.00. xvi + 776 pp. ISBN 0-12-576260-7.

This book is an excellent treatise on the fundamentals of modern electrochemistry and its applications to the solution of analytical and remedial environmental problems. The first chapter introduces the topics of environmental chemistry, analysis, and treatment strategies. Chapters 2−5 give an excellent tutorial on electrochemical methodology and could indeed be used as the basis of a short course on the subject. Chapters 6−8 describe specific recent applications of electrochemical methods to environmental cleanup and analysis. References are up to date and numerous, with several chapters having in excess of 300 citations each.

Chapter 2 discusses basic electrochemistry, starting from the very beginning and reaching a moderately high level of sophistication. It also touches upon the important areas of analytical applications, electrochemical reactor design, and semiconductor electrochemistry. Chapter 3 presents a very good summary of the electrochemical reactions which organic and inorganic pollutants undergo, with a focus on the chemistry and mechanisms involved. Chapter 4 presents electrochemical methods of sensing, and features flow-through electrodes, chemically modified electrodes, gas phase measurements, and potentiometric and voltammetric stripping analysis. Chapter 5 focuses on the larger scale electrolysis procedures for pollutant remediation. It includes discussions of direct and indirect electrolysis, electroflotation, electrocoagulation, electroflocculation, engineering design, membrane-assisted processes, and electrokinetic methods. The authors do a fine job of presenting and summarizing the fundamentals of this ever-expanding area at a level suitable for general technically trained readers.

Chapter 6 discusses photoassisted degradation of pollutants, which is often considered "electrochemical" when using heterogeneous semiconductor photocatalysts such as titanium dioxide. Chapter 7 introduces the important topic of water disinfection using electrochemical methods, and also discusses current photochemical and photoelectrochemical technologies. Chapter 8 discusses new and emerging technologies for pollution abatement, and includes some economic analysis.

In summary, I believe that this book is an essential introduction to electrochemical methodology and a valuable practical resource for those working in pollution abatement and related fields. It provides an excellent introduction to the field of electrochemistry and its possibilities in environmental research and remediation, as well as a comprehensive review of environmetal electrochemical research. It is generally readable by engineers, chemists, physicists, biologists, and other technical persons trained at the level of advanced undergraduate students and beyond. It presents quite nicely the considerable capabilities of electrochemical methodologies to solve environmental problems.

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JA975699W

10.1021/ja985699w

Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces. Studies in Surface Science and Catalysis, Vol. 104. Edited by W. Rudzinski (M. Curie-Sklodowska University, Lublin, Poland), W. A. Steele (Pennsylvania State University), and G. Zgrablich (University of San Luis, San Luis, Argentina). Elsevier: Amsterdam. 1996. xviii + 890 pp. $390.75. ISBN 0-444-82243-7.

Surface and/or structural heterogeneity is a common feature of adsorbents and catalysts. It is well known that the majority of solid surfaces is geometrically and chemically nonuniform. In addition, many solids exhibit structural heterogeneity, which is manifested by the presence of pores of different sizes and shapes. Active carbons, silica and alumina, which are commonly used in many areas of science and technology, represent solids of complex surface functionality and not well-defined porous structure. Geometrical, chemical, and structural nonuniformities of these solids are the source of their energetic heterogeneity with respect to adsorbing molecules. Characterization of adsorbent heterogeneity as well as studies of surface phenomena on heterogeneous solids are challenging tasks and still absorb the attention of scientists.

Studies of adsorption processes on heterogeneous solids have proceeded along three somewhat separate lines: (i) adsorption equilibria on heterogeneous solid surfaces, (ii) dynamics and kinetics of adsorption processes, and (iii) adsorption in porous solids. The volume edited by Rudzinski, Steele, and Zgrablich is a first attempt to provide a comprehensive overview of three aforementioned topics and to demonstrate how the surface and structural heterogeneities affect both the equilibria and kinetics of adsorption processes. The book contains 17 chapters written by a team of internationally recognized experts in their fields; some of them have already published books on adsorption. The first two chapters dealing with the description of single- and multiple-gas adsorption equilibria on heterogeneous surfaces introduce the reader to the field and provide foundations for further chapters. The next seven chapters are devoted to the adsorption−desorption kinetics and surface diffusion on heterogeneous solids. The remaining chapters mostly deal with the evaluation of energetic and structural heterogeneity of porous solids. The editors should be complemented for putting a special emphasis on the kinetics and dynamics of adsorption processes on heterogeneous solids. This approach was fully justified because adsorption equilibria have been extensively discussed in earlier books and reviews.

As a whole, this book represents a very useful addition to adsorption on heterogenous solids. In contrast to many edited books, which often are a loose collection of different contributions, this volume contains well-selected and organized chapters that cover many important aspects of adsorption equilibria and kinetics on heterogeneous solids. In addition, the book can be a very useful reference guide for experienced adsorption researchers as well as those entering the field.

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JA975534N

10.1021/ja975534n

Advances in Molecular Structure Research, Volume 3. Edited by Magdolna Hargittai and Istvan Hargittai (Hungarian Academy of Sciences). JAI Press: Greenwich, CT. 1997. xi + 346 pp. $109.50. ISBN 0-7623-0208-9.

This is the third volume of a series of reviews on various topics of molecular structure and its determination written by international

authors, mostly European authors. This volume has a collection of ten review articles on five major topics: (1) theoretical techniques for structural determination (empirical Hamiltonian methods with high-order corrections for extraction of molecular geometry from rotational constants, molecular potential function for equilibrium structure from gas-phase electron diffraction data, and ab initio and density functional theory methods); (2) experimental techniques for structural determination (matrix-isolation absorption spectroscopy, rotation−vibrational spectroscopy, and gas-phase electron diffraction); (3) molecular structures of several groups of compounds (small carbon molecules, compounds containing C−C, C−N, C−O, N−O, and O−O single bonds, carbocyclic π-systems, difuoramines, and binary and ternary Se−N and Te−N species); (4) intermolecular interactions (conjugated hydrogen bonds and contacts of benzene rings and isostructurality of organic crystal); and (5) structure−thermochemistry relationships (congested hydrocarbons, metal complexes, etc.).

Each article begins with a short table of contents and a brief abstract (100−200 words). The style and length, however, vary considerable from article to article. The first article, for example, titled Determination of Reliable Structures from Rotational Constants, by J. Demaison, G. Wlodarczak, and H. D. Rudolph, is a thorough review on structural determination using rotational constants from rovibrational spectra. It covers many new concepts and techniques along with a series of latest literature examples and carefully chosen references through 1997. Most of other articles are generally shorter in length but are thorough and careful with up-to-date research results and references. One of the articles, titled Specific Intermolecular Interactions in Organic Crystals: Conjugated Hydrogen Bonds and Contacts of Benzene Rings, by P. M. Zorky and O. N. Zorkaya, discusses two important types of intermolecular interactions in conjugated organic systems: conjugated hydrogen bonds (CHB) and specific benzene contacts (BzC). The subject matter in this review is carefully presented with ample illustrative examples. The list of references appears unusually short (21 entries; 11 of them are the author's own publications), which might cause the reader to question the thoroughness of the review.

An easily noticeable feature in the majority of the reviews is the frequent reference to ab initio results. Theoretical calculation using ab initio theory or density functional theory has been established as an important source of molecular structure data. The articles recognize this fact and have cited extensive computational data with favorable commentaries.

In general, this volume is a worthy member of the series reporting the recent progress in molecular structure research and will be a useful reference resource for workers interested in the topics covered in the book.

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JA975655N

10.1021/ja975655n

Topics in Fluorescence Spectroscopy. Vol. 5. Nonlinear and Two-Photon-Induced Fluorescence. Edited by J. R. Lakowicz. Plenum: New York. 1997. $135.00, v + 544 pp. ISBN 0-306-45553-6.

Multiphoton excitation and stimulated emission methods for studies of biological species and cellular imaging have become a major focus of research in fluorescence spectroscopy. Predicted as early as 1931, two-photon excitation (2-PE) was observed experimentally first in 1961. Since the 1980s we have witnessed rapid growth in the popularity of 2-PE, particularly in the biological sciences. In 2-PE, molecules that absorb light in the UV and visible only are electronically excited by near-IR laser pulses (thereby violating Vavilov's "law"). This allows selective excitation of chosen volumes and may pave the way to 3-dimensional imaging with suppression of out-of-focus fluorescence comparable to confocal microscopy. 2-PE also has the potential of decreased photobleaching and background fluorescence, as well as excitation to different excited states.

The book is divided into 11 chapters that range from pure theory to experimental studies on (small) fluorophores. Theory prevails throughout. Chapters 1 and 2 cover two-photon-induced fluorescence anisotropy. Chapter 1 gives a brief introduction into this area and describes the properties of several basic fluorophores including benzene, tyrosine, and tryptophan. The second chapter is a more extended and rather theoretical treatment which the nonspecialist probably is unable to follow. Of much larger interest to the chemist and biochemist is Chapter 3 (on multiphoton excitation of fluorescent probes and natural fluorophores). The specific features of two- and three-photon excitation are nicely demonstrated in studies on lipid membranes, stained DNA, and HSA. A final section is on two-color−two-photon excitation. Chapter 4 claims to cover aspects of 2-PE and anisotropy decays in membranes and oriented systems but is purely theoretical and a nightmare to read. The excessive equations are tiring, the results are not at all underpinned by experimental data, and the relationship to membranes is far-fetched. Chapter 5 (2-PIF of proteins) therefore comes as a relief, is a pleasure to read, and also contains numerous interesting experimental results. Chapter 6 contains studies on the weak short-wavelength emission of highly excited molecules created by 2-PE. It also demonstrates the possibilities of transient resonant multiwave mixing experiments for studies of ultrafast molecular photodynamics.

Stimulated emission is treated in Chapters 7, 8, and 10. Highlights include the analysis of the information contained in vibrational population relaxation, the quenching of luminescence by light, and pump−probe time-resolved microscopy. Fluorescence microscopy is also treated in Chapters 9 and 11. A method referred to as "point-spread function engineering", introduced in Chapter 9, increases the resolution in the far field. 4-Pi confocal microscopy appears particularly promising. Multiphoton microscopy of confined volumes and deep imaging are some of the highlights of Chapter 11.

Overall, the book is mainly theoretical and will appeal to physicists more than chemists or biologists. It is the most comprehensive book on the subject at present. Some overlap does exist but is acceptable. Another volume, written for biologists, is desirable.

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JA9856396

10.1021/ja9856396

Studies in Natural Products Chemistry, Volume 19, Structure and Chemistry (Part E). Edited by Atta-ur-Rahman. Elsevier Science Publishers B.V.: Amsterdam. 1997. xi + 627 pp. $250.00. ISBN 0-444-82815-X.

This latest volume of *Studies in Natural Products Chemistry* contains thirteen chapters which span the interface between chemistry and biology. More specifically, the following topics have been surveyed: Recent Advances in the Synthesis of Dendrobatid Alkaloids written by C. Kibayashi and S. Aoyagi, Synthesis of Some Aspidosperma and Related Alkaloids written by G. Kalaus, I. Greiner, and C. Sźantay, Synthesis of Natural Products via Aliphatic Nitroderivatives written by R. Ballini, Stereospecific Cannabinoid Synthesis: the Application of NewTechniques to a Classical Problem written by M. A. Tius, Methods for Construction of Sidechain of Brassinosteroids and Application to Syntheses of Brassinosteroids written by B. Jiang, L. Huang, W. Tian, and W. Zhou, Total Synthesis of Quinocarcin and its Related Compounds written by T. Katoh and S. Terashima, Synthesis of Mannostatins and Cyclophellitols, New Cyclitol Inhibitors for Glycoside Metabolism of Glycoproteins and Glycolipids written by Y. Nishimura, Molecular Rearrangement in the Derivatives of Grandiflorenic Acid [(-)-kaura-9(11),16-diene-19-oic Acid] and Some Related Diterpenes written by T. Nakano, Total Syntheses of Cyclic Halo Ether Compounds from Marine Origin written by A. Murai, Oxidative Ring Transformation of 2-Furylcarbinols in Natural Product Syntheses written by T. Honda, Stereoselective Synthesis of C-Branched Nucleoside Analogues written by P. N. Jørgensen and J. Wengel, Bioactive Marine Macrolides written by T. Higa and J. Tanaka, and lastly Hormones in the Red Swamp Crayfish written by A. Yasuda and Y. Naya. Albeit rather expensive, this latest volume continues the high standards and elements of timeliness for which this long-standing series of texts is known.

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JA985616R

10.1021ja985616r