Additions and Corrections

Enantiospecific Synthesis of Allylamines via the Regioselective Rhodium-Catalyzed Allylic Amination Reaction [*J. Am. Chem. Soc.* **1999**, *121*, 6761−6762]. P. ANDREW EVANS,* JOHN E. ROBINSON, AND JADE D. NELSON

Page 6761, Table 1: the ratio of **2j**/**3j** for entry 1 should read 33:1.

JA995539F

10.1021/ja995539f
Published on Web 12/10/1999

Book Reviews

Lewis Acids and Selectivity in Organic Synthesis. By Maurice Santelli and Jean-Marc Pons (University of Aix-Marseille). CRC Press: Boca Raton, FL. 1995. 334 pp. $125.00. ISBN 0-8493-7866-4.

The authors have taken up the challenge of covering the progress in Lewis acid-promoted reactions. There was an intense activity in this area, especially in the 1980s and early 1990s. Due to the amount of information in this area, the authors have restricted their coverage to (1) Lewis acid−carbonyl complexes, (2) Lewis acid-promoted ene reaction, (3) Lewis acid-promoted allylsilanes and allystannanes addition to aldehydes and ketones, (4) Lewis acid-promoted acetal substitution reactions, (5) the Sakurai reaction (conjugate additions of allylsilane and allylstannane to enones), and (6) Lewis acid-promoted Diels−Alder reactions. Despite the narrower focus, this is still a formidable task, and one they have met admirably. Chapter 1 covers Lewis acid−carbonyl group interactions and their theoretical aspects. The remaining chapters cover specific reactions that have been shown to be useful in stereoselective synthesis of complex organic compounds. Each chapter starts with a historical introduction and mechanistic considerations. Where relevant, comparisons of thermal and Lewis acid-promoted reactions have been made. This is followed by well-organized examples from the literature up to 1993, with the emphasis on stereoselective reactions. Chapters 2 and 6 have good coverage of the use of chiral Lewis acids for ene and Diels−Alder reactions.

The authors have done an excellent job of summarizing the advances in Lewis acid-promoted reactions for the transformations they have chosen. Except for some awkward moments (probably due to the translation), the writing is clear and easy to follow. The amount of material necessitates that some explanations be brief. The index is short but is compensated by a separate Lewis acid index. The only minor drawback is that the references are somewhat dated. With a collection of some of the more recent works, a comprehensive documentation would be at hand. Overall, this book would be an excellent addition to the library of graduate students and practitioners of organic synthesis.

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JA9956831

10.1021/ja9956831

Stereoselectivity in Synthesis. By Tse-Lok Ho (National Chiao Tung University). John Wiley & Sons, Inc.: New York. 1999. xiii + 333 pp. $94.95. ISBN 0-471-32922-3.

This book offers a survey of various strategies for stereoselective synthesis. It is divided into chapters, beginning with one that covers some of the fundamentals of stereochemistry. Chapters 2−4 discuss issues relating to 1,2-, 1,3-, and remote stereocontrol. Chapter 5 offers a review of directed and chelate-controlled processes. Chapter 6 concerns conformational effects, Chapter 7 discusses what the author refers to as "topographical and template effects", and Chapters 8 and 9 are titled "Steric, Electrostatic, and Stereo-Electronic Effects" and "Thermodynamics Control and Kinetic Trapping", respectively.

One of the striking features of this book is that it highlights some of the most important and relatively recent accomplishments in stereoselective synthesis. However, it is not clear why different chapters are organized as they are, and what some of the titles mean. For example, after having read five chapters involving reactions that are stereoselective by the virtue of various conformational, electronic, and steric factors, why are we faced with a chapter on conformational effects? Within the chapter, intramolecular reactions are referred to with the awkward "Group Anchoring", and the subsection "Nonbonded Interactions" further confuses this reader about how these interactions differ from what has already been discussed. It is also perplexing to read a chapter entitled "Steric, Electrostatic and Stereoelectronic Effects" after having read seven chapters of stereoselective reactions that involve such issues! To leave a discussion of kinetic vs thermodynamic control to the last chapter is questionable, as one of the implicit underlying factors related to all the previously discussed processes is whether one is dealing with exactly such issues. The headings within this chapter are unclear, as well (e.g., "Self-Regulation of Configurations").

In brief, it is not totally clear for whom this book was written. A novice would find the book's organization difficult to follow, and explanations for stereochemical outcomes are at times cursory and confusing. (For example, see pages 136, 163, and 223.) The first chapter could be more sophisticated, especially for a book on stereochemistry. In the opinion of this reader, the term "chiral center" is not appropriate, and the assignment of *R* and *S* involves atomic numbers, not masses.

The book would have benefited from the help of a few diligent proofreaders. Some sentences eluded this reader even after multiple readings; atoms are often missing from structures. An author's index would have been most welcome, as well.

The book, nonetheless, is a valiant effort by this prolific author to cover the ever-expanding field of stereoselective synthesis. With a better organization, careful proofreading, and more in-depth coverage of fewer topics, this book would have made a more attractive title.

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JA9957027

10.1021/ja9957027

Organic Molecular Solids: Properties and Applications. Edited by William Jones. CRC Press: Boca Raton, FL. 1998. 441 pp. $145.00. ISBN 0-8493-9428-7.

This book is an elegant selection of contributed chapters focusing on the structure−property relationships in molecular organic solids—materials that have gained popularity due to the potential for functionalization of organic molecules and the consequent impact on tuning properties. Thus, a common theme of the chapters is the systematic variation of the organic building blocks and the resulting effects on crystal packing and properties. Unlike many edited books, this one succeeds in maintaining this theme throughout and consistently presents an up-to-date account of the properties for a wide variety of organic solids from fullerenes, liquid crystals, Langmuir−Blodgett assemblies,

and polymers to molecular crystals of hydrogen-bonded molecules and charge-transfer molecules. Each chapter starts with an informative introduction to the respective area and defines its state of the art, and then a detailed presentation is given of their properties, followed by a section on the applications. Linear optical, nonlinear optical, superconducting, semiconducting, conducting, and magnetic properties of organic solids are discussed in individual chapters. This book also presents, in separate chapters, methods for characterization of organic solids, theoretical methods for crystal structure determination, reactivity, and crystal design in organic solid-state chemistry. The unique combination of science and applications in each chapter makes this book an appropriate candidate as a text of organic materials for a senior or graduate class in a number of departments, including chemistry, physics, materials science, and perhaps electrical engineering as well. Since it gives up-to-date information on each class of materials, accompanied by an extensive and current list of relevant references at the end of each chapter, I expect it will prove useful to researchers in the field and others embarking on projects in these areas.

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JA995689Q

10.1021/ja995689q

Fieser's Reagents for Organic Synthesis, Volume 18. By Tse-Lok Ho (National Chiao Tung University). John Wiley & Sons, Inc.: New York. 1999. xii + 504 pp. $79.95. ISBN 0-471-24477-5.

This book, the eighteenth volume of its kind, is a valuable addition to the classic series that adorns the shelves of most organic chemists today. Professor Ho has beautifully continued the tradition gallantly held up by the late Mary Fieser for so many years. Particularly welcome is the highly informative, yet brief, descriptions of the relevant papers. The needed information can be found easily enough through the use of well-documented indexes. It is the hope of this reader that Professor Ho will continue this valued tradition in organic synthesis for many more years to come.

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JA995703Z

10.1021/ja995703z

Protein Phosphorylation: Selected Methods in Enzymology. Edited by B. M. Selfton, Tony Hunter. Academic Press: San Diego, CA. 1998. 598 pp. $59.95. ISBN 0-12-634490-6.

Protein phosphosphorylation impinges on a great many aspects of biology. So much so that it is probably impossible to study a biological process without referring to a method that is covered in this excellent volume. *Protein Phosphorylation* contains articles selected from two volumes of *Methods in Enzymology*, Volumes 200 and 201. Two renowned experts in the field of protein phosphorylation, Bartholomew M. Selfton and Tony Hunter of the Salk Institute have carefully chosen the articles which are of most relevance and use to scientists new to the rapidly expanding field of protein phosphorylation. Although the articles are now several years old, a large number of methods are presented that cover a wide variety of techniques that are still used today. The following sections are covered: (1) the classification of protein kinases and phosphatases, (2) assays of protein kinases and protein phosphorylation, (3) purification and cloning of protein kinases and phosphatases, and (4) the use of inhibitors of protein kinases and phosphatases. Progress in understanding protein phosphorylation events in cells is occurring at an ever increasing rate. New discoveries are being reported in the literature constantly. The fundamental philosophy behind this volume stems from the fact that many of the currently used methods have evolved from methods presented in this volume. A researcher new to the field could do a lot worse than check through this volume first before embarking on a protocol described more recently. In some cases the attention to detail are unsurpassed. By noting these details many a researcher, young or old, should be able to avoid the many practical pitfalls that exist in this particularly demanding field.

For the price this is a real bargain. This book should be present in any laboratory that studies protein phosphorylation.

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JA9856856

10.1021/ja9856856

Humic Substances: Structures, Properties and Uses. Edited by G. Davies and E. A. Ghabbour (Northeastern University). Royal Society of Chemistry: Cambridge, UK. 1998. 241 pp. $119.00. ISBN 0-85404-704-2.

This book is comprised of a collection of symposium papers from the Humic Substances Seminar II, held in March 1998. As is common with books prepared by compilation of symposia presentations, it is difficult to find a common thread that weaves through this book, as each chapter is written as a "stand alone" document. Some chapters cover subjects, such as "Humic Substances for Enhancing Turfgrass Growth", that are too applied to be of interest to most chemists. However, chemists with an interest in the characterization or chemical reactivity of humic substances will find that sections of this book can provide valuable insights.

The book begins with a chapter describing the history, methods of isolation, and role of humic substances in the environment, providing a good background for the novice reader. The rest of this chapter describes the use of 2D 600 MHz NMR experiments to achieve partial functional group assignments for a humic acid. This theme of providing molecular-level characterization, even for these complex mixtures, reappears periodically throughout the text and is paramount for understanding the chemistry of humic substances.

The process of humification during decomposition of leaf litter is discussed in three chapters by comparison of the solid-state ^{13}C NMR and FTIR spectra of senescent and nonsenescent leaves and the leachates of these leaves derived during composting. The ^{13}C NMR and IR spectra of these samples reveal mechanistic insights into the chemical reactions occurring in the degradation process. Not surprisingly, simpler, better resolved spectra are obtained for humic and fulvic acids isolated from senescent leaves compared with those of soil humic substances. This combination of ^{13}C CPMAS NMR spectroscopy and FTIR was further applied, in a subsequent chapter, to the analysis of humic and fulvic acids isolated from the products of a wastewater treatment plant.

The application of other analytical methods, including mass spectrometry, capillary electrophoresis (CE), and fluorescence spectroscopy, for the characterization of humic substances is also described in separate chapters. Laser desorption (LD) and fast atom bombardment (FAB) are compared as sample volatilization/ionization methods for the mass spectrometric analysis of humic substances. Because of the complex and polydisperse nature of humic substances, LD-MS is superior because of the large matrix background encountered in FAB. A short but useful chapter is devoted to the CE analysis of humic substances using capillaries filled with PEG gel. The gel results in a fractional "sieving" based on size and charge. Unfortunately, the reported CE results are not placed into a more general context, and it would be interesting to compare the electrophoretic apparent molecular weights with those obtained by other methods, such as flow field-flow fractionation. Steady-state fluorescence measurements are often used to characterize humic substances. A chapter describing time-resolved fluorescence spectroscopy provides additional information about the polydispersity of humic samples.

In soils, humic substances coat mineral particles; therefore, characterizing the interactions of humics with mineral surfaces is central to defining their behavior. One chapter provides a thorough study of the adsorption of a soil-derived humic acid on high surface area particles of kaolinite. For the chemist who is unsatisfied by the lack of a molecular-level understanding of humic substances, another chapter is devoted to modeling the interactions of humic substances with mineral surfaces. The pictures generated in this chapter were truly "worth a thousand words" in aiding my conceptualization of the molecular-level processes that govern these interactions. Unfortunately, no connection is made in this book between the experimental and computational chapters devoted to humic−mineral interactions.

In addition to characterizing humic structures and interactions with mineral surfaces, the book delves into their chemistry, through the complexation of metal ions and solubilization of hydrophobic organic

compounds. Two chapters are devoted to the study of humate−metal complexes through voltammetric measurements and through size-exclusion chromatography−ICP-MS. The latter method can investigate the metal binding properties of different molecular weight fractions. For example, although Zn^{2+} and Cu^{2+} were found to be strongly bound to all humic fractions, Pb^{2+} was bound exclusively by the intermediate weight fraction of the humic acid sample. A chapter is devoted to competitive sorption of hydrophobic organic compounds to humics. Again, a weakness in this monograph is the absence of linkages between chapters. For example, one of the compounds for which sorption isotherms are measured is atrazine. An earlier chapter modeled interactions of this herbicide with organic matter−mineral aggregates, and a subsequent chapter examined the effect of dissolved organic matter on the transport of atrazine through the soil column. Although these chapters individually provide a snapshot of the interactions of atrazine with organic matter, a unified approach could have provided a more detailed molecular-level description of these interactions that could have set this work apart from similar reports.

One of the more interesting chapters, from a chemical perspective, describes the photochemical generation of free radicals by humic acid. Although catecholic and quinoid radicals were found to result from moderate UV exposure, the more reactive hydroxyl radical was also produced through Fenton chemistry resulting from minor metal-containing impurities. Another chapter described the alkylation reaction of plant and lignin-derived humic acid with ^{13}C-labeled methyl iodide and the characterization of the reaction products by NMR. Methylation greatly reduced the solubility of humics in aqueous and alcoholic media over the pH range 1−10, indicating that these materials may be useful scavengers for alkylating agents in waste treatment or remediation applications.

For individuals currently investigating the chemistry of humic substances, this book will be of value because it touches upon recent developments in a number of diverse areas. However, the book is probably not a good choice for the novice reader, in large part due to the lack of continuity of topics.

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JA995692+

10.1021/ja995692+

Electronic Materials: The Oligomer Approach. Edited by K. Mullen and G. Wegner. Wiley: Weinheim. 1998. 599 pp. $145.00. ISBN 3-527-29438-4.

This book is an excellent and interesting treatment of the subject. The book includes reviews of the different aspects of conjugated oligomers and their role as electronic materials in a detailed and extensive manner. The book is organized in the following manner: a preface entitled, "Introduction: What can Material Science Learn from Conjugated Oligomers?", 11 chapters, each written by different authors, and an index. The authors of individual chapters are selected from an international team of experts who represent inorganic, organic, physical, theoretical, industrial, and polymer chemistry and physics as well as material science.

The introduction is written by K. Muller and G. Wegner from Germany and first gives some general aspects of the chemistry and physics of oligomers, followed by discussion of the role of π-conjugation in oligomers, and concludes with a description of the function of oligomers in material science, for instance, as active components of electronic devices. The first four chapters describe synthesis, characterization, and physical and chemical properties of major groups of oligomers, such as, Chapter 1, "Hydrocarbon Oligomers" by Y. Geerts, G. Klarner, and K. Mullen from Germany; Chapter 2, "Sulfur-Containing Oligomers", part 2.1 "Oligothiophenes" by P. Bauerle from Germany and part 2.2 "Oligotetrathiafulvalenes" by J. Becher, J. Lau, and P. Mork from Denmark; Chapter 3, "Nitrogen-Containing Oligomers" by L. Groenedaal, E.-W. Meijer, and J. A. J. M. Vekemans from The Netherlands; and Chapter 4, "Oligomeric Metal Complexes" by E. W. Constable from Switzerland. Chapter 5, "Crystal Structure" with part 5.1 "Oligomers as Structural Models for Polymers" by V. Enkelman from Germany, discusses the crystal structures of various models of oligomers and polymers, and part 5.2 "Packing Calculations Based on Empirical Force Fields" by R. Hentschke from Germany reviews molecular mechanics and dynamic methods with special emphasis on molecular crystal packing calculations, whereas Chapter 6, "Structure and Optical Properties of Conjugated Oligomers from Their Vibrational Spectra" by G. Zerbi, C. Castiglioni, and M. Del Zoppo from Italy, deals in detail with the IR and Raman spectra of oligomers and polymers with delocalized π-electrons. Chapter 7, "Electronic Excitation" with part 7.1 "Electronic Excitations of Conjugated Oligomers" by H. Bassler from Germany, and part 7.2 "A Quantum Chemical Approach to Conjugated Oligomers: The Case of Oligothiophenes" by J. Cornil, D. Beljonne, and J. L. Bredas from Belgium, collects and reviews spectroscopic information such as optical absorption and fluorescence spectra and investigates the evolution of the geometric and electronic structure and optical properties of neutral and charged molecules with chain lengthening, respectively. Chapter 8, "Nonlinear Optical Properties of Oligomers" by C. Bubeck from Germany, considers third-order nonlinearities in oligomers. Chapter 9, "Electrochemical Properties" by J. Heinze and P. Tschuncky from Germany, deals with redox properties of conjugative oligomeric π-systems, whereas Chapter 10, "Optical Applications" by M. G. Harrison and R. H. Friend from the United Kingdom, discusses optical and optoelectronic device applications such as light-emitting diodes (LEDs), photovoltaic and photoconductive devices, and field-effect optical modulator devices, as well as all-optical modulator devices. Finally, Chapter 11, "Field-Effect Transistors Based on Conjugated Materials" by F. Garnier from France, describes in detail the area of field-effect transistors (FETs) based on organic materials. The entire text is completed with an excellent subject index.

A substantial portion of each of the first four chapters is devoted to a discussion of the preparation and synthetic modification of various classes of oligomers and is illustrated with numerous synthetic schemes, drawings, etc. In addition, where applicable, each remaining chapter gives a complete review of its topic: an introduction or overview with historical background, basic theory including energy level diagrams, chemical and physical properties, applications, and detailed descriptions of examples of applications. There are numerous figures, schemes, diagrams, and tables, and each chapter ends with a conclusion or summary. The extensive research published in this area over the past several years and covering the literature up to 1998 is clearly reviewed by experts in the field and is provided at the end of each chapter.

Altogether, the present book is well-written, has excellent coverage, and emphasizes the practical problems that the synthetic oligomer scientist needs to bear in mind in order to prepare an oligomer for any particular final use. I agree with the editors that the book complements the current literature rather than competes with it. I also concur that such an oligomeric approach will contribute to a better understanding of electronic materials, will provide better access for researchers who plan to enter the field, and will definitely encourage prolific interdisciplinary research. This book is strongly recommended to anyone contemplating or engaged in research involving polymers and oligomers as electronic materials. I also believe this book to be an important and highly recommended addition to any library collection in material science.

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JA985753O

10.1021/ja985753o