Additions and Corrections

Primary Vinyl Cations in Solution: Kinetics and Products of β,β-Disubstituted Alkenyl(aryl)iodonium Triflate Fragmentations [*J. Am. Chem. Soc.* **1999**, *121*, 7437−7438]. ROBERT J. HINKLE,* ANNE J. MCNEIL, QUINN A. THOMAS, AND MARIE N. ANDREWS

Page 7438: Although we correctly plotted and interpreted the data as first order, the units for the rate constants in Table 1 are labeled as second order rather than first order. The units should be "sec^{-1}" rather than "mol/L·sec".

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Evolution and Study of Polymer-Supported Metal Catalysts for Oxygen Atom Transfer: Oxidation of Alkanes and Alkenes by Diamide Manganese Complexes [*J. Am. Chem. Soc.* **1999**, *121*, 8965−8966]. MIROSLAV HAVRANEK, ARUN SINGH, AND DALIBOR SAMES*

The Supporting Information deposited here replaces that deposited with the communication.

Supporting Information Available: Experimental protocol for preparation of solid-bound ligands and complexes, results of all tested libraries (Library 1-4), and crystallography data for **10** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Book Reviews

Advances in Nitrogen Heterocycles, Vol. 3. Edited by Christopher J. Moody (University of Exeter). JAI Press: Stanford, CT. 1998. x + 224 pp. $109.50. ISBN 0-7623-0209-7.

Volume 3 of *Advances in Nitrogen Heterocycles* updates the reader on synthesis and application of pyrroles, pyrrole-type analogues, and indoles and, in addition, includes a most interesting chapter on nitrogen ylide cyclizations. Chapter 1, by L. W. Hodges and W. N. Harman, focuses on pyrrole complexes, while Chapter 2, by E. D. Edstrom, considers the chemistry of annelated pyrroles. D. StClair Black, in Chapter 3, addresses iminium ion chemistry and its role in the preparation of functionalized indoles. Chapter 4, by L. S. Beall and A. Padwa, covers nitrogen ylide cyclizations as stepping stones to a number of unique heterocycles, and this Volume concludes with Chapter 5, by M. E. Wood and A. M. Fryer, on the synthesis of kainoids.

Harman and Hodges present their work (Chapter 1), as well as that of other contributors, on pyrrole complexes. Substituted pyrroles are most desirable heterocycles due to their multifaceted roles in natural products, e.g., porphyrins and antibiotics. New synthetic methods leading to their preparation are continually sought. This chapter provides some of the recent work on pyrrole η^2 complexes and demonstrates their synthetic utility in providing a variety of pyrroles, including those which are highly substituted. A list of abbreviations used in the chapter precedes the reference section.

In Chapter 2, Edstrom covers the synthesis of [*b*]-annelated pyrroles using the acylative pyrrole annulated approach. Having been involved in the preparation of pyrrolo[2,3-*d*]pyrimidines and several other closely related systems, I found this chapter most enjoyable. Edstrom starts with his synthesis of rigidin, a novel pyrrolo[2,3-*d*]pyrimidine alkaloid. This is followed by studies on nucleoside Q (queuosine) and other nucleosides containing the pyrrolo[2,3-*d*]pyrimidine moiety. Other bicylic systems are considered, and the chapter ends with the synthetic methodology leading to 7-aminoaziridinomitosenes.

Chapter 3 by Black continues the theme on pyrrole chemistry. It focuses on the use of the Vilsmeier reaction with activated indoles. Under Vilsmeier conditions, 4,6-dimethoxyindoles activate the C-7 position to provide the iminium salt, which undergoes electrophilic substitution. A variety of products resulting from formylation, acylation, and imines are depicted. The application of triflic anhydride is also explored. Black points out that this reagent led to better yields and cleaner products, and the iminium triflic salt generated precipitates out and can be purified prior to basification.

The following chapter by Beall and Padwa centers on the application of nitrogen ylide cyclizations and their synthetic utility. A brief history of the scope and mechanism of the Sommelet−Hauser rearrangement is provided and directs the reader to earlier reviews. The chapter outlines the versatility of the three classes, i.e., ammonium, azomethine, and nitrile, of ylides and illustrates their involvement in synthetic strategies. It is well-written with ample references and is a definite source for new ideas.

Chapter 5 by Wood and Fryer reviews kainoid chemistry. A large portion of the chapter is devoted to naturally occurring and unnatural acromelic acids. A short, cost-effective pathway to these compounds employs the readily available *trans*-4-hydroxy-L-proline as starting material. The functional groups residing at C-2 and C-4 make feasible stereoselective functionalization at all other ring positions. The chapter also contains an interesting section on palladium(0)-catalyzed cross-

coupling reactions. The methodology covered in this chapter is current and, as pointed out by the authors, should be readily applicable to other kainoids.

This series is invaluable. The present edition brings together unique topics on nitrogen heterocycles and new synthetic techniques for preparative strategies. Volume 3, like the first two, is well-illustrated and contains current references on each topic. Once again, I highly recommend this series for inclusion in your private collection.

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Lysosomal Cysteine Proteinases. By Heidrun Kirschke (Martin-Luther-Universitat Halle-Wittenberg, Germany), Alan J. Barrett (The Babraham Institute, United Kingdom), and Neil D. Rawlings (The Babraham Institute, United Kingdom). Oxford University Press: Oxford, New York, and Tokyo. 1998. xiii+ 131 pp. $45.00. ISBN 0-19-850249-4.

The Protein Profile series aims to provide a current review of a specific protein family. This second edition of *Lysosomal Cysteine Proteinases* focuses primarily on enzymes of vertebrate animals, covering not only the ubiquitous proteases cathepsins B, H, and L and dipeptidyl peptidase but also the enzymes of restricted tissue expression, cathepsins S and K. The less well-characterized cysteine proteases mammalian legumain and cathepsins T, N, and O are also briefly discussed.

Each chapter presents extensive characterization data but in a condensed format, due to a limited discussion and to an extensive use of tables and figures. Following a brief introduction, the gene structure and chromosomal location, domain structure, precursors, purification, activation and inhibition, and hydrolysis of synthetic substrates, polypeptides, and proteins is summarized for each protein. Extensive referencing makes it easy to locate original sources for the data presented. A figure relates gene, mRNA, and protein structure when known, while tables compare rate constants with different substrates and list functions ascribed to each particular protein, along with the appropriate reference. This makes the book an excellent source to locate facts quickly, and thus a valuable resource.

A full half of the book is references, 1830 summarizing the literature through 1996. The publication of full titles as well as the organization by topic makes this section interesting to peruse and not just a list of supporting material for the chapters. The references for the first and second editions are separated, however, thus requiring paging between the two lists to acquire the full picture. The additional references for the second edition obviously present the more recent work, but they also incorporate older references one might have expected in the first edition. Sections include reviews, catalytic properties, determination and purification, reaction with inhibitors, expression of enzymes in cancer and in pancreatitis, expression of the enzymes in normal tissues and disorders, processing, gene structure, nucleotide and amino acid sequences, and structure−function relationship.

The potentially interesting section entitled Physiological Functions is merely a list of diseases with references, ending with the conclusion that the contribution of each enzyme is not clear. Space limitations have prevented more than cursory mention of extracellular functions of cysteine proteinases, although data increasingly suggest participation in normal physiological functions such as spermatogenesis. Similarly, discussions of potential roles in endosomes, antigen processing, and viral uncoating are omitted.

The most thought-provoking chapter is probably that entitled Structures and Evolution, which compares the structures known for mammalian family members. The presentation of each structure in a similar orientation, coupled with the indication of sites that show sequence variation with species, makes this section interesting reading.

The book is paperback, reducing cost and increasing portability. An online version is planned but not yet available, although the book can be ordered online (http://www.oup.co.uk/protein_profile). The easy accessibility of facts about lysosomal cysteine proteinase family members, coupled with the extensive bibliography, makes this volume a worthy addition to one's personal library.

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Molecular Symmetry and Spectroscopy, 2nd Edition. By P. R. Bunker (National Research Council, Canada) and P. Jensen (Bergische Universität−Gesamthochschule Wuppertal). NRC Press: Ottawa, Canada. 1998. xix + 747 pp. $64.00. ISBN 0-660-17519-3.

This book is a much-expanded version of the first edition, published in 1979. The authors' stated intention is to instruct the reader in the *application* of modern group theoretical methods to problems in molecular spectroscopy. The book is written at a high level and is intended for scientists principally involved with high-resolution, gas-phase, molecular spectroscopy. The book is suitable for graduate students or researchers active in this field. However, it is not particularly suitable for synthetic chemists interested in chemical applications of group theory, for which other well-known texts would be more appropriate.

The new edition has much of the original material of the first edition, but it is enriched with many essentially new sections. In addition, the older material is enhanced with many references to very recent work in the field, as well as experimental spectra, illustrating real molecular examples of the topics being discussed. Chapters on nonrigid molecules and weakly bound cluster molecules provide introductions to these important areas of modern molecular spectroscopy research, which are not found in older, more traditional spectroscopy texts.

I believe the main value of the book is in the authors' clear presentation of the material. The prose is crisp and clear with numerous worked examples sprinkled liberally throughout the text. These examples do much to demystify the mechanics of the application of the ideas discussed to real molecular problems.

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Advances in DNA Sequence Specific Agents, Volume 3. Series edited by Graham B. Jones (Clemson University). Volume Edited by Manlio Palumbo (University of Padova). JAI Press Inc.: Greenwich, CT. 1998. ix + 283 pp. $109.50. ISBN 0-7623-0203-8.

This book is the third volume in a series titled *Advances in DNA Sequence Specific Agents*. The previous two volumes contained reviews of important classes of DNA-interactive agents along with chapters devoted to discussion of methods for the analysis of DNA−drug interactions. The current volume is dedicated exclusively to DNA-interactive agents and does not contain any chapters concerning analytical methods. The book begins with a short chapter by the volume editor which provides an overview of the potential impact that understanding, characterizing, and harnessing sequence-specific drug−DNA interactions might have on the future of cancer chemotherapy. The introduction is followed by chapters concerning DNA topoisomerase II and topoisomerase I inhibitors. Chapters 4 and 5 are devoted to minor groove-binding bis-benzimidazoles and polypyrrole-related agents (e.g., netropsin and distamycin), respectively. Chapter 6 provides an interesting survey of recent approaches for directing the alkylating power of nitrogen mustards selectively toward DNA and tumor cells, and Chapter 7 examines the DNA chemistry, biochemistry, and biological activity of nonclassical platinum-based antitumor agents. The eighth chapter provides a review of kedarcidin and maduropeptin, two relatively new and intriguing enediyne−protein complexes with potent biological activity. The final two chapters cover antisense and antigene therapeutic approaches that utilize sequence-specific binding by oligonucleotides and peptide nucleic acids (PNAs).

To its credit, the focus of this book (and the series in general) is somewhat broader than the "...Sequence Specific..." title might imply. For example, there are several excellent chapters devoted to important classes of agents where the roles of sequence-specific DNA interactions, while undoubtedly important, are not well characterized at the present time (e.g., topoisomerase inhibitors). While many of the chapters do, in fact, emphasize discussions of sequence-specific DNA−ligand

interactions, each chapter also provides useful information regarding the chemical mechanisms, biological properties, and medicinal potential of the compounds that are discussed. Thus, the true value of this book may be that the chapters serve as state-of-the-art overviews of important classes of DNA-interactive agents. All the authors are well-qualified experts in the field, and the chapters are clearly written. In general, the book contains a good number of high-quality schemes and figures depicting the chemical structures of the subject molecules. However, for a book dedicated to a "structural topic" such as sequence-specific DNA interactions, there is a surprising dearth of figures depicting X-ray, NMR, or computer-modeled DNA−ligand structures (there are approximately two such figures in the book). There are no color diagrams, and the one space-filling depiction of a DNA−ligand complex is poorly rendered by the printing process. This is a problem that the publisher should remedy in future volumes of the series. The volume contains a reasonable, though not extensive, index which is probably appropriate, given that the book is not intended as a reference text. Overall, this is a high-quality book that contains up-to-date, well-written overviews of nine important classes of DNA-interactive agents. Priced slightly over $100, it is a book that some nucleic acid researchers may wish to purchase for their personal collections, and it is certainly a worthwhile addition to institutional library collections

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Tartaric and Malic Acids in Synthesis: A Source Book of Building Blocks, Ligands, Auxiliaries, and Resolving Agents. By Jacek Gawroński and Krystyna Gawrońska (Adam Mickiewicz University, Poznań, Poland). Wiley: New York and Toronto. 1999. xxii + 591 pp. $149.00. ISBN 0-471-24451-1.

A byproduct of the wine industry, tartaric acid is available in high enantiomeric purity and at nominal cost, two features that surely contributed to the interest in this and related molecules as starting materials for chemical research. The successful utilization of tartaric and malic acid derivatives in endeavors including natural product syntheses, asymmetric catalysis, resolutions, and syntheses of crown ethers, boronate esters, and other stoichiometric reagents testifies to their versatility. Although each of these topics has been the subject of independent reviews, the book provides a unique perspective on these disparate topics by association from their tartaric or malic acid progeny.

The book is divided into 20 chapters, with the first 14 being dedicated to tartaric acid and the remainder to malic acid. The chapters are arranged according to oxidation state, beginning with the diacids and ending with threitol and 1,2,4-butanetriol. This organizational scheme makes finding most entries straightforward. Textual indexes on desymmetrization, resolutions, ligands, synthesis, and general subjects together with over 70 well-referenced tables make finding entries on a particular structure uncomplicated, despite no graphical indexes. The tables provide a preview of each chapter and quick reference to the primary literature. As would be expected for a mature field, the book includes a few references from the early 1900s, and the majority of the references date from the 1970s and 1980s. However, for the more descriptive chapter subdivisions describing special topics, such as protecting groups, TADDOL's, or asymmetric catalysis, the references appear thorough and up-to-date.

The authors tackled the extraordinarily vast subject of enantiomerically pure four-carbon derivatives of tartaric and malonic acids, and the product of their effort is a comprehensive reference book that is easy to navigate. The structures are well drawn, and the layout is easy on the eye. Whether in academia or industry, the book will likely be appreciated by chemists requiring a handy summary of optically active four-carbon synthons.

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Highly Excited Atoms. By Jean-Patrick Connerade (Imperial College). Cambridge University Press: New York. 1998. xxiii + 501 pp. $110.00. ISBN 0-521-43232-4.

Molecules are made of atoms. From our perspective at the end of the twentieth century, this statement seems rather prosaic, and perhaps even self-evident. It was not always so, however; acceptance of the atomic theory in many ways marked the birth of chemistry as an exact science and ultimately paved the way for today's increasingly detailed investigations of chemical behavior at the molecular and submolecular levels.

But are atoms of interest to chemists beyond their role as molecular "building blocks"? More precisely, can modern-day chemists profit from a closer look at the physics of isolated atoms? The answer to these questions is most certainly, "yes". Our everyday concepts of chemical valence are based on gas-phase atomic electronic configurations described by an independent-electron model. When correlations between electrons become important, this approximate model breaks down, leading to irregularities in the Aufbau sequence and reminding us, as quantum chemists know all too well, that much of chemistry is controlled by correlation energy.

In this monograph, Connerade surveys the relatively young field of highly excited many-electron atoms; these are systems in which electron correlation and many-body effects play a central role. He begins with a brief review of self-consistent field theory as applied to closed-shell atoms and then immediately launches into a discussion of Rydberg states of atoms and small molecules. He analyzes these states within the context of quantum defect theory and describes the variations in absorption intensity along a Rydberg series.

This phenomenological introduction to highly excited states of atoms is followed by an elegant treatment of centrifugal barrier effects in the d and f periods of the Periodic Table. Connerade then turns his attention more fully to the correlated motions of electrons in excited atoms, discussing autoionization, excitation of inner-shell electrons, and doubly excited states of atoms (including hollow atoms) within this context.

The central chapter of the book (Chapter 8) presents an exposition of scattering theory as applied to autoionizing resonances of highly excited atoms. This chapter is impressive in its scope and depth but is probably the chapter of least interest to chemists. The next two chapters, however, treat topics of considerable current interest in the chemical physics community: the behavior of atoms in intense laser fields and the possibility that such atoms could exhibit remnants of chaotic dynamics.

The text concludes with two brief chapters discussing atomic electronic structure in solids and the geometric and electronic structure of metal atom clusters. These chapters are serviceable introductions to their respective subjects; however, readers seeking in-depth or up-to-date treatments of these topics are best advised to turn elsewhere.

The main text of the book is attractively typeset, with few typographical errors, and incorporates an impressive array of cleanly reproduced figures from the research literature. The book contains an adequate index and an extensive list of over 700 references. Roughly two-thirds of these references are to the "modern" atomic physics literature (1980 and later); however, Connerade is mindful that present-day work in this area owes a great deal to earlier studies, and it is a pleasure to find among the references a number of seminal experimental and theoretical papers from the early days of quantum mechanics.

As the author acknowledges in his preface, this book is not a textbook. Nevertheless, the chapters on atomic and molecular Rydberg states and on quantum defect theory would make very nice reading for graduate students learning quantum mechanics. Similarly, Connerade's discussion of double-excitation spectra, atomic autoionization, and atoms in strong laser fields would be welcome additions to a graduate-level spectroscopy course.

Because Connerade's perspective is unmistakably that of a physicist, his book is likely to appeal to a relatively narrow segment of the chemical community. However, practitioners of atomic spectroscopy, and theoreticians seeking an entrée into the field of highly excited atoms, will find it useful and surprisingly accessible.

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