

Additions and Corrections

Total Synthesis of Novel Subclass of Glyco-amino Acid Structure Motif; C²- α -D-C-Mannosyl-L-Tryptophan [*J. Am. Chem. Soc.* **1999**, *121*, 9754–9755]. SHINO MANABE AND YAKISHIGE ITO*

The configuration of the mannosyl residue was erroneously described as L throughout the publication.

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Real-Time Probing of a Three-Electron Bonded Radical: Ultrafast One-Electron Reduction of a Disulfide Biomolecule [*J. Am. Chem. Soc.* **2000**, *122*, 5082–5091]. Y. GAUDUEL,* H. GELABERT, AND F. GUILLOUD

Equation 14 should read:

$$\frac{S^{1.72\text{eV}}[e^-S]_{\text{RSSR}}(\tau)}{S^{1.72\text{eV}}[e^-S]_{\text{NaCl}}(\tau)} = \exp^{-[\text{RSSR}]/C_{37}(\tau)}$$

$$\Rightarrow C_{37}(\tau) = \frac{0.5}{\ln\left(\frac{S^{1.72\text{eV}}[e^-S]_{\text{NaCl}}(\tau)}{S^{1.72\text{eV}}[e^-S]_{\text{RSSR}}(\tau)}\right)} \quad (14)$$

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Book Reviews

Advances in Cycloaddition. Volume 6. Edited by Michael Harmata (University of Missouri-Columbia). JAI Press: Stamford, CT. 1999. x + 250 pp. \$115.00. ISBN 0-7623-0531-2.

This volume in this continuing series contains six chapters covering a variety of cycloaddition reactions. Three chapters deal with transition-metal-mediated cycloaddition reactions, two others cover aspects of Diels–Alder chemistry, and one addresses [5 + 2] cycloaddition chemistry. All but one of the six chapters contain a number of references to work through 1998 and 1999.

The volume begins with a chapter by Mascarenas on the [5 + 2] cycloaddition chemistry of β -alkoxy- γ -pyrones. He presents a good discussion of his own group's work in the area beginning with their first attempts at thermal intermolecular reactions with alkenes. Sequential O-methylation/O-desilylation of hydroxypyrones as a highly effective route to 4-methoxy-3-oxopyrylium ylides and their subsequent cycloaddition chemistry are presented in detail. Acid catalysis of [5 + 2] cycloadditions of β -hydroxy- γ -pyrones completes the general discussion of [5 + 2] cycloaddition chemistry. The chapter concludes with further discussion of synthetic elaborations of the [5 + 2] cycloadducts, tandem [5 + 2], [4 + 2] cycloadditions of pyrones, and attempts at asymmetric [5 + 2] cycloadditions.

Chapter two is a review of metallocarbenoid-induced cyclizations of acetylenic carbonyl compounds, by Padwa and Straub. After a brief introduction, this chapter provides a discussion of possible mechanisms for these cyclizations, focusing on work from the groups of Hoye and Padwa. The scope and limitations of these reactions when the substrates contain diazo acyl and alkynyl groups that are ortho to one another on an aromatic ring are discussed, and other Rh(II)-catalyzed cyclizations of α -diazo carbonyl compounds with alkynes are covered.

The third chapter, by Rigby, is on recent applications of Cr(0)-mediated higher-order cycloaddition reactions. Stoichiometric and catalytic versions of the Cr(0)-mediated [6 + 4] cycloaddition are discussed. The resolution and enantioselective cyclizations of Cr(CO)₃ complexes with cycloheptatriene and its heterocyclic analogues are presented here. This [6 + 4] section concludes with a discussion of post-cycloaddition synthetic manipulations that can be performed on the bicyclo[4.4.1]undecane core. The last section of this chapter briefly presents Cr(0)-mediated thermal and photochemical [6 + 2] cycloadditions of cycloheptatriene and cyclooctatriene complexes with alkenes and alkynes, including diynes.

The fourth chapter, by Lee and Snyder, discusses indole as a dienophile in inverse electron-demand Diels–Alder and related cycloadditions. Inverse electron-demand Diels–Alder reactions of indole with 1,2,4,5-tetrazines and 1,2,4-triazines leading to carbazoles and β - or γ -carbolines, respectively, are outlined. This azadiene discussion is then followed by a presentation of Diels–Alder reactions of indoles with other electron-deficient 1,3-dienes. A survey of 1,3-dipolar cycloadditions of indole with a number of 1,3-dipoles, such as nitrilimines, nitrile *N*-oxides, nitrones, and munchnones, completes the chapter.

Key and Hunt, in chapter five, present aspects of the intramolecular Diels–Alder reaction of a furan diene (IMDAF) leading to the formation of 1,4-epoxydecalin systems. Details of their work on the catalysis of IMDAF reactions of these substrates are the focus of this chapter. They provide a detailed account of their discovery that MeAlCl₂ may be used as a catalytic Lewis acid for IMDAF reactions with enones, but that a stoichiometric amount is required for ynones. The authors also provide an overview of their use of IMDAF reactions as key elements

in the synthesis of 1,4-epoxycadinane and the C-15 to C-23 segment of venturicidins A, B, and X.

The volume concludes with a review of metal-mediated allenic [2 + 2 + 1] cycloadditions, written by Brummond. She first describes her group's finding that intramolecular Pauson–Khand (P–K) reactions of allene–alkyne substrates are effected by both Mo(CO)₆ alone and in situ-generated zirconocene in the presence of CO; the traditional P–K initiator, Co₂(CO)₈, is less effective in such cases. The next section of this chapter is a nice overview of cobalt- and iron-mediated intermolecular [2 + 2 + 1] cycloadditions of alkynes and allenes. The scope and limitations of these reactions are presented along with a mechanistic rationale for observed regio- and stereochemical outcomes of these cycloadditions. Discussion here concludes with the use of the intramolecular allene–alkyne [2 + 2 + 1] cycloaddition in the syntheses of hydroxymethylacylfulvene and suberosenone.

Overall, this is a nice collection of reviews that will be of interest to synthetic chemists, in general, and to those working in the area of cycloaddition reactions, in particular.

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Perspectives on Bioinorganic Chemistry. Volume 4. Edited by Robert W. Hay (University of St. Andrews), Jon R. Dilworth (University of Essex), and Kevin B. Nolan (Royal College of Surgeons in Ireland). JAI Press: Stamford, CT. 1999. xvi + 246. \$109.50. ISBN 0-7623-0352-2.

This is the fourth volume of the series. It contains six well-written and authoritative reviews covering a wide range of current bioinorganic topics. The first article, "Lithium in Biology" (J. Bramham), is a survey of the various roles the nonessential element plays in biological processes. The organization and prose are sound and make for a good read even if one has research interests unrelated to lithium chemistry. The goal of the author was to collate the considerable amount of data on the biochemistry of the lithium cation, and in this she was largely successful. Unfortunately, while the referencing was comprehensive with over 250 citations(!), only four or five were given to articles post 1994.

The second article (P. Lindley et al.) focuses on the copper-containing enzyme ceruloplasmin. It summarizes the salient spectroscopic, structural, and biochemical studies on the protein and discusses its potential function(s) largely on the basis of structural results that were first reported in 1996 by these authors and a slightly improved structure (3.0 Å resolution) of human ceruloplasmin reported here. This is a particularly timely article due to considerable recent interest in the family of multi-copper oxidases as a whole. The authors do a terrific job in painting a clear picture of the current view of this protein while noting gaps in knowledge with respect to both structure and function. As such, this article is rich in both data and ideas.

The third topic, "The Chemistry of Rhenium in Nuclear Medicine" (P. Blower and S. Prakash), summarizes the current status of rhenium radiopharmaceuticals. The article is exhaustive in its treatment of the material, concentrating on applied medicinal chemistry and both the inorganic and radiochemistry of rhenium-186 and rhenium-188. Considering that some rhenium radiopharmaceuticals have advanced recently to clinical trials and, in at least one case, the market, the subject matter is certainly noteworthy.

The fourth article, "Macrocyclic Polyamines and Their Metal Complexes: A Novel Type of Anti-HIV Agent" (E. Kimura, T. Koike, and Y. Inouye), reviews the current state of development of primarily bis(tetraazamacrocycles) as a new class of anti-HIV agents. The remarkable discovery that tetraazamacrocycles, bis(tetraazamacrocycles), and some of their metal complexes inhibit replication of HIV-I and HIV-II was made in 1992. Since then, the topic has drawn the attention of many, with more recent bis(macrocyclic) zinc complexes shown to be quite potent and selective. This review successfully draws upon recent advances to provide not only a survey of structures that exhibit potent anti-HIV activity but also the current view as to their mode of action.

The fifth article, "Chemistry of Platinum Anticancer Drugs" (J. Arpalahiti), examines a well-studied and historically significant class of coordination compounds. This well-written review covers the

chemistry of platinum compound (both Pt(II) and Pt(IV))–discrete nucleic acid interactions with a concentration on kinetic and mechanistic details. In addition, platinum binding to DNA and defined oligonucleotides is discussed thoroughly. Despite the tremendous amount of work done in this field, the author clearly shows the need and provides direction for future kinetic studies.

The final article, "Functional Model Complexes For Dinuclear Phosphoesterase Enzymes" (R. Krämer and T. Gajda), concentrates on low-molecular-weight dinuclear metal complexes capable of hydrolyzing phosphate ester bonds while briefly surveying di- and trinuclear phosphoesterases as a whole. A number of model systems are discussed, in particular with regard to kinetics. The authors clearly describe model complexes that have mechanistic features similar to those proposed for specific phosphoesterases. This area has been quite topical for some time, and it is to the authors' credit that their referencing is as current as possible for a book.

Finally, it should be noted that this volume contains a tribute by Dr. David Richens to the late Professor Robert W. Hay, senior editor of the series. As I look at my bookshelf and see a worn copy of Professor Hay's 1984 paperback titled simply *Bio-Inorganic Chemistry*, I am reminded of how many scientists were both directly and indirectly influenced by his work.

In short, this volume is a fine addition to the series and, in particular, will be of considerable value to those with specific interests in the six topics covered. I look forward to volume 5.

John W. Sibert, East Carolina University

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Heterogeneous Catalysis in Organic Chemistry. By Gerard V. Smith (Southern Illinois University) and Ferenc Notheisz (József Attila University, Szeged, Hungary). Academic Press: San Diego, CA. 1999. xvi + 346 pp. \$89.95. ISBN 0-12-651645-6.

The aim of this book is to act as a primer for experimental organic chemists in the art and science of heterogeneous catalysis. The basic thesis of this monograph is that graduate students in organic chemistry are not educated in methods that use heterogeneous catalysts, in particular, in the basics of surface chemistry as applied to organic transformations under heterogeneous conditions. In fact, the authors make it very clear that this is an area that is considered "black magic" by practicing organic chemists, and so their goal is to provide the underpinning to remove the mystique.

The book is organized around seven chapters and an appendix. Chapter 1, entitled "Introduction to Catalysis", provides the novice with the basics of what a catalyst is, how heterogeneous catalysts are prepared and characterized, and a number of other fundamental topics. The section on "The Chameleonic Surface" was particularly interesting; the authors point out that part of the misunderstanding of how heterogeneous catalysts operate stems from the different points of view that different researchers have about mechanisms and the surface of the catalyst. This chapter sets the stage for the rest of the book.

Chapters 2–6 deal with examples of different kinds of reactions catalyzed by heterogeneous catalysts: "Hydrogenations" (Chapter 2), "Enantioselective Hydrogenations" (Chapter 3), "Hydrogenolysis" (Chapter 4), "Bond Breaking Reactions" (Chapter 5), and "Oxidations" (Chapter 6). The final chapter is entitled "Immobilized Homogeneous Catalysts" (Chapter 7), and it bridges the homogeneous and heterogeneous approaches. Each of the chapters is evenly illustrated with graphics; references are found at the end of each chapter with citations up to 1997, and even the odd reference to work published in 1998. There is an author index as well as a subject index; the Appendix is entitled "Some Basic Assumptions About Heterogeneous Catalytic Hydrogenation".

This book is a valuable resource for synthetic organic chemists. It should be on the shelf of or at least accessible to academic organic laboratories as well as industrial synthetic labs, simply because it

concentrates much of this literature and provides real examples of useful transformations.

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Advances in Molecular Structure Research. Volume 5. Edited by Magdolna Hargittai and István Hargittai (Hungarian Academy of Sciences). JAI Press: Stamford, CT. 1999. x + 390 pp. \$115. ISBN 0-7623-0555-X.

This volume, like its predecessors, presents a diverse group of reviews dealing mainly with experimental methods for studying molecular structure. Both the topics and the authors reflect a wide range of interests, making it useful to readers desiring an overall view of a variety of topics in this area. A novel feature in this volume is the first chapter, which consists of reminiscences by Lawrence S. Bartell about his career. Bartell is one of the second generation of workers in the field of gas-phase electron diffraction and an important contributor to its development into a powerful structural tool. This chapter emphasizes the author's work rather than attempting to give a general history of the field. Although certain events and personalities tend to be remembered somewhat differently by different observers, the chapter presents a valuable first-hand account from a central figure in the history of structural studies.

One general comment can be made about most of the remaining chapters in the book. They all give a thorough historical background of the areas with which they are concerned and are written to serve the needs of a reader unfamiliar with the topic rather than provide an update for experienced workers. Thus, the volume can be recommended to round out the understanding of a scientist interested in the wide range of methods for studying molecular structure; it is less useful as an aid to bring the expert up-to-date. It certainly has a place in university libraries for student use and makes interesting reading for more advanced workers wishing to obtain a general knowledge of a field.

Marvin Charton offers a chapter on "The Quantification of Structural Effects in Stereochemistry by Correlation Analysis". Fully half the references are to his own work and only a half dozen references are to work published during the past decade. The chapter is thus best suited as an introduction to the field rather than as an update for fellow workers. However, it is comprehensive in its coverage and clear in its explanations.

The next chapter, by Robert Glaser and Dror Shifan, on "The Stereochemistry and Interconversion of Nine-Membered Rings Containing One Strong Torsional Constraint", presents an excellent overview of the complexities in the conformational behavior of this family of medium-sized rings. The literature is surveyed up to about five years ago and the coverage is comprehensive. This chapter is worthwhile reading for a newcomer to the field.

The remaining chapters are more brief than the first two. The exciting new field of "Porphyrin-Containing Catenanes and Rotaxanes" is summarized by James J. Bruce and Jean-Pierre Sauvage. D. B. Chesnut and L. D. Quin write on "The Theoretical Determination of Phosphorus NMR Chemical Shielding". A chapter on "Symmetry-Broken Inversion Structures for Group 15 EX₃ Halides", by Peter Schwerdtfeger and Patricia Hunt, follows.

The next chapter, "Vibrational Effects in Diffraction and Microwave Experiments: A Start on the Problem", by Victor A. Sipachev, is primarily a presentation of new work rather than a survey of the field, unlike the other chapters in the book. However, calling it "A Start on the Problem" plays down a large amount of work by others over a period of many years.

Károly Süvegh, Attila Vértes, and Toshio Hyodo write on "Positronium as a Sensitive Detector of Changes in Molecular Structure". After a summary of the basic physics of positronium, this very interesting chapter presents studies of polymer structure, nuclear spin states, and structural changes in aqueous solution using positron lifetime spec-

troscopy as the working tool. Finally, there is a brief chapter by Joel F. Liebman and Suzanne W. Slayden on "Some Relationships between Molecular Structure and Thermochemistry: Part 3", the earlier parts having appeared in Volume 4 of the present series.

This book is not the place to turn for a review of current work in the fields covered as the series title, "Advances in...", might suggest. It is rare to find references dated as late as 1996. Rather, the articles present thorough overviews of their research areas, didactic in approach, and well suited to casual or introductory reading. There is a somewhat brief index. The binding of the volume does not suggest that it will hold up well to rough handling.

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Molecular and Supramolecular Photochemistry. Volume 4. Multimetallic and Macromolecular Inorganic Photochemistry. By V. Ramamurthy (Tulane University) and Kirk S. Schanze (University of Florida). Marcel Dekker: New York. 1999. xii + 345 pp. \$175.00. ISBN 0-8247-7392-6.

The editors of Volume 4 of *Molecular and Supramolecular Photochemistry* have maintained the same high standards of quality as seen in the previous numbers of this series. It provides concise, well-referenced, and self-contained surveys of areas of photochemistry that are of current interest to a large number of scientists. The contributors to the volume's six chapters are all active researchers who have made abundant contributions to the surveyed areas. Although Volume 4 has been reduced to half the number of chapters in Volume 1, the length of the chapters has not decreased and the quality of graphs, structures, and schemes is very high. The style of the monographs prevent them from being easily read material, but they are nevertheless potent tools for readers wanting to venture into the various areas of multimetallic and macromolecular inorganic photochemistry. In more general terms, Volume 4 also makes an excellent source for consultation.

The book begins with a chapter dedicated to inorganic polymers (W. E. Jones, Jr., L. Hermans, and B. Jiang) and incorporates information about the preparative routes and photophysical properties of the polymers. Two chapters review the photophysical properties of polynuclear complexes of Cu(I), Ag(I), and Au(I) (V. W.-W. Yam, and K. K.-W. Lo) and metallo-1,2-enedithiolates (R. S. Pilato and K. A. VanHouten). Although the technical quality of the latter is unquestionable, it is weakly related to areas of multimetallic and macromolecular inorganic photochemistry. The photophysical properties, photoinduced electron transfer, and thermal redox reactions of polymetallic complexes with tridentate bridging ligands (S. W. Jones, M. R. Jordan, and K. J. Brewer) and polypeptides and de novo-designed proteins (M. V. Ogawa) are reviewed in two other chapters. A useful description of the experimental methods available for the investigation of the kinetics of electron transfer processes is made in the latter. In the last chapter (S. Takagi and H. Inoue), considerable space is dedicated to reviewing the photochemistry of molecular and supramolecular porphyrins and metalloporphyrins. An introduction to the basic principles governing the kinetics of photochemical and photophysical processes and a good description of the porphyrins' molecular photochemistry are provided in the first part of the chapter. These complement the review of the supramolecular photochemistry of porphyrins in the last part of the chapter very well.

The book provides an excellent review of multimetallic and macromolecular photochemistry and will generally serve as a useful reference, particularly to photochemists. It is recommended as a valuable resource in a private or institutional library.

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