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BOOK REVIEWS

Characterization of Compounds in Solution: Theory and Practice. By William H. Streng (Quintiles, Inc., Kansas City, MO). Kluwer Academic/Plenum Publishers: New York. 2001. xv + 273 pp. $65.00. ISBN: 0-306-46595-7.

The book provides a very brief review of select thermodynamic and kinetic methods that are currently used to characterize compounds in solution. Spectroscopic methods are for the most part ignored, except when the method is used to determine equilibrium concentrations, equilibrium constants, and partition coefficients. The book is loosely divided into eight chapters in which the fundamental principles of each process are discussed, with the final chapters devoted to instrumentation, experimental procedures, and specific applications.

The book begins with a short chapter explaining the importance of why compounds should be characterized and is followed by two chapters in which basic thermodynamic principles and chemical kinetics are discussed. The latter two chapters are written at the level typically found in an undergraduate physical chemistry textbook. Topics in the chapter on thermodynamics include chemical potential, partial molal quantities, ideal solutions, activity coefficients, and standard states. The notation is outdated in that internal energy is denoted as *E* (rather than *U*) and Gibbs free energy (rather than Gibbs energy) is used throughout the discussion. In the chapter on chemical kinetics, rate and order of chemical reactions, reversible and nonreversible reactions, and the Arrhenius equation are discussed. Chapter 4 is devoted to thermodynamic principles governing equilibrium, again written at the level of an undergraduate physical chemistry textbook, and the determination of equilibrium constants using pH titration, spectrophotometric, calorimetric, and chromatographic methods. Specific examples that illustrate the various methods appear in the last two chapters of the book.

There are several serious omissions in the text. For example, in the discussion of activity coefficients, the discussion is limited to ionic compounds. It is not until Chapter 6 in the section dealing with the solubility of crystalline compounds that activity coefficients of nonelectrolyte compounds are mentioned in reference to the Hildebrand solubility parameter approach. Discussions pertaining to the spectroscopic, calorimetric, and chromatographic determination of equilibrium constants are incomplete, to the point that I seriously doubt if readers will learn how to measure equilibrium constants solely on the basis of the discussion in Chapter 4 and the specific examples in the last two chapters. A much better discussion of the determination of equilibrium constants appears in the book *Binding Constants: The Measurement of Molecular Complex Stability* by K. A. Conners (Wiley-Interscience: New York, 1987). Similar deficiencies are noted in the chapters on partition coefficients, solubility, aqueous solubility of weak acids and bases, and solution stability. The text is extremely abbreviated, and there are insufficient references at the end of the chapters for readers to learn more about the topics. Each chapter lists fewer than 10 references, and many of the papers cited pertain to the author's earlier work. In Chapter 9, there is a brief discussion of pH and conductivity meters, high performance liquid chromatographs, UV/vis spectrophotometers, and calorimeters at the level typically found in an undergraduate quantitative analysis textbook. The text is dated and does not really discuss modern instrumentation. For example, the author states that the detector for UV/vis radiation is a phototube or photomultiplier tube. No mention is made of photodiode arrays (in commercial instruments since the 1980s) or charge-transfer devices.

I found the book to be written at an extremely elementary level with very few references. I cannot recommend purchasing the book. There are far better books on both solution chemistry and instrumental methods for studying compounds dissolved in fluid solution.

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Organic Conformational Analysis and Stereochemistry from Circular Dichroism Spectroscopy. by David A. Lightner (University of Nevada) and Jerome E. Gurst (University of West Florida). Wiley-VCH: New York. 2000. xvi + 488 pp. $94.95. ISBN: 0-471-35405-8.

Although the spine of this book clearly shows its complete title, the front cover tends to obscure the main thrust of this monograph by showing the words *Organic Conformational Analysis* in feeble gold on a white background, as if those words were only fit to be whispered. The artistic style for the title is somewhat misleading because the work is, in fact, much more narrowly targeted than the more visible second half of the title would suggest, offering nothing to biochemists or inorganic chemists who would use circular dichroism (CD) spectroscopy in their stereochemical studies. Indeed, it concentrates heavily on one class of organic compound: chiral nonracemic cyclic ketones, although giving some space to unsaturates and aromatics toward the end.

Nonetheless, such tight focusing is, in this reviewer's opinion, all to the good, for it permits a thorough review of a large body of literature and a scholarly consideration of the implications of fine points that would be glossed over in a broader treatment. The keto group is one of the most commonly occurring functional groups, with its n-π^* transition occurring in the middle of the near UV. The transition is weak because it is "electric dipole forbidden", which could hinder chiroptical measurements; such absorption as does occur is "magnetic dipole allowed" and potentially is capable of differentiating right- and left-circular polarized light. "Background" chiroptical effects (seen in optical rotation measurements) do not appear in CD so that it becomes possible to zero in on structural elements causing chiral perturbations of the transition per se.

It should be stressed that this is not yet a technique generally useful for determining conformational compositions, energies, or equilibrium constants. Employed with NMR and molecular mechanics modeling, however, it can provide insights into subtle details of conformational structure not accessible in any other way. The key to that application is the Octant Rule, the mother of all sector rules, which is applied throughout. Its origin and the developing and changing interpretation of its physical basis are carefully considered here. Special attention is paid to attempts to make the rule quantitative and to the problem of the shape, location, and the significance of the "third plane", the construct normal to the carbon−oxygen bond that converts quadrants to octants.

Perhaps of most value to the practicing organic chemist is the assembly in this monograph of widely scattered data and the generous provision of actual spectra. These could well prove useful from time to time for anyone working in the currently important fields of asymmetric synthesis and enantiomerically enriched pharmaceuticals. Accordingly, this book is strongly recommended for research libraries serving organic and pharmaceutical chemists and, perhaps, to some individuals working those areas. Its price, however, would probably rule it out for the more general organic chemist.

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Kinetics of Homogeneous Multistep Reactors. Comprehensive Chemical Kinetics. Volume 38. By F. G. Helfferich (Pennsylvania State University). Elsevier: Amsterdam and New York. 2001. xv + 410 pp. $244.00. ISBN: 0-444-82606-8.

This book is part of the series *Comprehensive Chemical Kinetics*, edited by R. G. Compton and G. Hancock, which addresses modern methods, theory, and data in the field. This book provides a wealth of knowledge beyond modern textbooks on kinetics about the practical application of reaction kinetics. In this vein, the book is not focused too much on the science behind the kinetics, but rather takes the reader through the rudiments of developing kinetic models and their applications to laboratory and industrial chemical kinetic problems. The real strength of the textbook is that it gives good advice in the application of kinetics to problems and processes that would typically be encountered in the chemical industry. As such, the book should have enormous appeal to the chemical engineer needing a good resource on how to handle an array of kinetic problems commonly encountered in the chemical industry. Chemists will also find the book useful in the array of chemical examples that are used to illustrate the application of various approaches to developing models and of kinetic strategies to industrial and laboratory problems.

The book consists of 12 chapters, which can be divided into four major sections. The first (Chapters 1 and 2) covers fundamental concepts of kinetics by introducing basic definitions and conventions as defined by the author. The conventions used are not ones normally followed in standard kinetics textbooks, but with some careful attention to the details, the reader with a previous basic course in kinetics can adapt to the formalism introduced in this text. In the second section (Chapters 4−7), the author introduces tools that can be used to solve various kinetic systems, including tools for solving reaction processes that are limited by irreversible and reversible steps and those that are in quasi-equilibrium. Standard kinetic textbook cases, such as the solution to reversible, parallel, and competing steps, are covered. Chapter 7 provides very interesting coverage of how to deduce mechanistic steps in complex reactions that consist of a large network of reaction steps. This chapter should be of most interest to the industrial chemist, but some of the ideas and methodology could be used by those researchers studying combustion and complex biochemical processes. The third section (Chapters 8−10) covers three major applications: homogeneous catalysis, chain reactions, and polymerization reactions. The last two chapters of the book are dedicated to the application of kinetic approaches to developing complex kinetic models for chemical plant processes as well as to the analysis and consideration of thermal and major-transfer effects in such processes.

The odd chapter in the organization of the book is Chapter 3, which consists of an overview of experimental kinetic reaction systems and how these systems can be used to measure reaction rates. Batch, continuous stirred-tank, tubular, and differential reactors are mainly covered, systems that may be more suited for the chemical engineer.

Overall, this book is a useful contribution to the series and provides the practitioner with good, useful approaches and strategies for eliciting complex chemical mechanisms. Those researchers involved in the analysis of atmospheric, biochemical, and combustion processes may find the book of practical value.

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Glycochemistry: Principles, Synthesis and Applications. Edited by Peng George Wang (Wayne State University) and Carolyn R. Bertozzi (Howard Hughes Medical Institute and University of California, Berkeley). Marcel Dekker, Inc. New York, Basel. 2001. xvi + 682 pp. $195.00. ISBN: 0-8247-0538-6.

The recent realization that saccharides and glycoconjugates are involved in a wide range of biological processes has transformed carbohydrate chemistry into a multidisciplinary subject area in which synthetic and structural chemistry are often intertwined with biological studies. The book, edited by Wang and Bertozzi, captures these recent developments and provides a fresh perspective on chemical and biochemical aspects of bioactive oligosaccharides and glycoconjugates. It is organized according to three topics, namely, synthesis, biological principles, and applications. Some chapters are focused on broad subject areas, whereas others are rather specialized. In these cases, the coverage includes relatively detailed experimental procedures.

The first seven chapters are focused on oligosaccharide synthesis and cover recently developed methods as well as target synthesis. The following subjects are reviewed: solid-phase oligosaccharide synthesis, dehydrative glycosylation with

1-hydroxy donors, synthesis of β-mannopyranosides using glycosyl triflates, C-glycoside synthesis, synthesis and conformational studies of arabinofuranosides from mycobacteria, chemical synthesis of bioactive steroidal saponins, and glycosylations with sialic acid. Although each chapter is written by an expert in the field and provides an up-to-date description of the topic area, some chapters are rather narrowly focused and mainly describe contributions by the author. This feature probably precluded a more comprehensive coverage of recent advances in glycoconjugate synthesis.

The next six chapters have a more biological focus. In them, fundamental principles related to oligosaccharide and glycoconjugate biology and cover several important classes of saccharide-containing biomolecules are explored. Two complementary chapters deal with carbohydrate−protein interactions and are focused primarily on multivalent interactions to increase binding affinities. Different concepts of multivalency, methodologies for determining binding affinities, and approaches for the preparation of glycoclusters and glycopolymers are covered. In the two subsequent chapters, a comprehensive review of the chemistry and biochemistry of aminoglycoside antibiotics is provided. These compounds bind with high selectivity to RNA to block protein biosynthesis. A detailed knowledge of their mode of binding will assist synthetic chemists to design new and more selective antibiotics. This is an important area because of the emergence of many resistant pathogenic bacteria. The next chapter covers chemical methods for preparing glycosyl amino glycosides (GAGs), such as hyaluronan, chondroitin sulfate, dermatan sulfate keratin sulfate, and heparin and heparin sulfate. It is now well-established that these structurally diverse polysaccharides are involved in many biological processes, and organic synthesis will provide an important tool to determine the ligand requirement for a particular GAG-binding protein. A chapter authored by Jacquelyn Gervay-Hague covers sugar amino acids and focuses on the preparation of an unnatural class of saccharides that are linked by amide bonds. Researchers in this relatively new area of chemistry hope to use these oligomers as new materials with defined secondary structures.

The last four chapters deal with chemoenzymatic approaches for oligosaccharide assembly and cover the application of biotransformations for the modification of polysaccharides, enzymatic synthesis and biological aspects of a carbohydrate epitope that complicate xenotransplantations, and the use of bacterial glycosyl transferases that are involved in the assembly of bacterial cell wall components. The final chapter reviews an imaginative new approach to remodel oligosaccharides on cell surfaces by employing chemically modified donor substrates. This method provides a new means to study the functions of cell-surface oligosaccharides and may lead to new ways to fight diseases, such as cancer. Although every chapter indicates potential uses of oligosaccharides, the last four chapters are aimed at highlighting recent developments that may lead to commercial applications.

This book, which is well referenced, provides a good introduction for those chemists who are interested in bioactive oligosaccharides and glycoconjugates and nicely shows the enormous diversity of contemporary glycochemistry. It has a relatively large synthetic component and demonstrates how synthetic chemists can play key roles in the emerging field of glycobiology.

Glycochemistry is now such a wide field of research that it is impossible to cover all of its aspects in a single volume. The editors, however, have managed to recruit a distinguished group of relatively young investigators who have managed to capture many important developments in this field. In particular, this book reviews the chemistry of many important classes of oligosaccharides and glycoconjugates. The only distraction is that some chapters are rather specialized and are mainly of interest to those active in the field.

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Palladium in Heterocyclic Chemistry. A Guide for the Synthetic Chemist. Tetrahedron Organic Chemistry Series, Volume 20. By Jie Jack Li (Pfizer Global Research and Development) and Gordon W. Gribble (Dartmouth College). Pergamon (An Imprint of Elsevier): Amsterdam and New York. 2000. xviii + 413 pp. $52.50 Paperback. ISBN: 0-08-043704-4.

This volume is the latest contribution from the well-regarded Tetrahedron Organic Chemistry Series, and it continues the tradition of this series for providing practicing organic chemists with timely, well-written, and well-researched overviews of topics of contemporary interest. The current volume collects together numerous examples of the burgeoning and often diverse field of heterocyclic synthesis via organopalladium chemistry.

The book is organized according to the principal heterocycle that is either prepared by or participates in a palladium-mediated reaction, and typical chapter headings include Chapter 3, Indoles; Chapter 5, Thiophenes and Benzo[*b*]thiophenes; and Chapter 10, Pyrazines and Quinoxalines. Within each of these chapters are further subdivisions that are delineated by the particular type of organopalladium reaction that is employed for the heterocycle under consideration. For example, included among the sections within the indole chapter are two entitled “Stille Coupling” and “The Larock Indole Synthesis”, each of which is replete with numerous well-chosen examples that nicely illustrate the chemistry being discussed. This organizational scheme is user-friendly and would seem to fit well with the way most synthetic chemists think about their problems.

In the book’s first chapter, a brief but quite useful overview of the basics of organopalladium chemistry is presented. There is a short (perhaps too short) discussion of the mechanism of cross-coupling reactions mediated by palladium as well as short descriptions of the most often used “named” organopalladium reactions. These include such well-known carbon−carbon bond-forming processes as the Negishi coupling, the Stille coupling, and the Hiyama coupling. The growing importance of carbon−heteroatom bond formation promoted by palladium is acknowledged in a short section devoted to the powerful Buchwald−Hartwig C−N and C−O bond-forming technology. On the other hand, the section on “Jeffery’s ligand-free conditions” did not effectively convey some of the unique attributes of this often overlooked variation on the Heck reaction. The book, published in 2000, is well-written, and the references selected for inclusion are, by and large, of a relatively recent vintage, including a

reasonable number from 2000. As is often the case with works of this type, the index was somewhat sparse and not particularly thorough. Efforts to check the utility of the index revealed, for example, that the entry for "Amaryllidaceae Alkaloids" in the subject index had only one page number listed, but visual inspection of the text revealed a number of other pages in which these alkaloids were involved.

All in all, this is a fine addition to the Tetrahedron Organic Chemistry Series and would be a valuable addition to the library of practicing organic chemists in both academe and the pharmaceutical industry.

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Organobismuth Chemistry. Edited by Hitomi Suzuki (Kwansei Gakuin University) and Yoshihiro Matano (Kyoto University). Elsevier: Amsterdam. 2001. xvi + 620 pp. $147.00. ISBN: 0-444-20528-4.

This is an outstanding and comprehensive compilation of the chemistry of bismuth compounds involving carbon. The title understates the breadth of coverage, because the presentation includes compounds without carbon−bismuth bonds and excludes only entirely inorganic bismuth compounds. The relevant literature is listed up to the end of 1999, with a few examples of results reported in 2000. Six authors−Hitomi Suzuki, Takuji Ogawa, Naoki Komatsu, Yoshihiro Matano, Toshihiro Murafuji, and Tohru Ikegami−have collaborated on this accurate and detailed reference text, which is edited by two of the authorities in the area of organobismuth chemistry. The six chapters include a general introduction followed by compilations describing compounds containing carbon−bismuth(III) bonds, carbon−bismuth(V) bonds, and bismuth-containing heterocyclic compounds. In each case, specific examples of synthetic procedures are presented in detail, and all known examples of compounds are superbly tabulated, together with listings of the types of available characterization data and the specific references. Appropriate inclusion of certain compounds in more than one chapter makes for informative cross-referencing for the reader.

Chapter 5 is a discussion of the involvement of bismuth compounds in organic transformations with useful lists of synthesis reaction schemes and tables of substrates, conditions, and products. Summaries of the reactivity for key compounds are presented in pinwheel schemes. The categorization of transformations in terms of oxidation, reduction, and carbon−element bond formation is again convenient for the reader. The final chapter is a discussion of the structural aspects of bismuth chemistry and contains a tabulation of all structurally characterized examples of organobismuth compounds, including structural views and selected bond lengths and angles for each compound. The order of presentation of the facts is easy to follow, the discussion is concise, and the attention to detail is outstanding. The table of contents provides a facile search mechanism and complements the brief subject index. The authors have not taken full advantage of the opportunity to comment in a general or concluding fashion, but this is an excellent reference text that is essential for all bismuth chemists and scientists interested in the chemistry of the heavy elements.

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Solid Support Oligosaccharide Synthesis and Combinatorial Carbohydrate Libraries. Edited by Peter H. Seeberger (Massachusetts Institute of Technology). Wiley-Interscience: New York. 2001. xii + 308 pp. $100. ISBN 0-471-37828-3.

Developments in glycosylation methods over the past two decades revived interest in solid-phase oligosaccharide synthesis in an attempt to facilitate product isolation, which is a major problem in solution glycosylations, and simultaneously, to decrease the time between successive glycosylation steps. This book is a collection of state-of-the-art reviews on the subject written by experts in their respective fields of oligosaccharide and glycopeptide synthesis.

The book begins with an excellent historical overview of early work in the field, written in a style that makes it suitable to be integrated into academic courses on carbohydrates. Each of the subsequent 13 chapters, ranging from 10 to 32 pages, offers detailed descriptions of all major areas of the subject. Solid-phase-supported enzymatic oligosaccharide synthesis, however, is not covered, except for a selective paragraph in the chapter on the soluble polymer-supported techniques. In addition to the introduction, two more chapters are written by the editor, whereas the rest are written by others.

The first half of the book is organized according to the various glycosylation methods. In addition to the established glycal, sulfoxide, trichloroacetimidate, and the thioglycoside-based glycosylations, a separate chapter covers the glycosyl phosphate method in solution and its application for solid-phase glycosylations. One chapter provides a discussion of stereoselective β-mannosylation on solid support. A timely chapter gives an overview of the "on-bead" monitoring of the reaction progress using IR and NMR spectroscopic methods. One chapter gives a lucid review of the development of soluble poly(ethylene glycol)-based syntheses and catalogs potential problems associated with oligosaccharide synthesis on resins. References to the limitations of the solid-phase approach can also be found in chapters on the glycal- and the thioglycoside-based glycosylations. The synthesis of carbohydrate libraries using bidirectional strategies, programmable one-pot syntheses, and random glycosylations are reviewed in separate chapters. The final two chapters give extensive surveys of solid-phase-based synthesis of glycopeptides and glycopeptide libraries. A selective review of this subject can also be found in the chapter on the glycal method.

The timeliness of the more than 900 references ranges widely. Almost 90% of the references in the chapter on the thioglycoside-based carbohydrate libraries are more than 5 years old. In two chapters (glycal method and the random glycosylation), ~75% of the references are more than 5 years old. On the brighter side, 50−65% of the references are less than 5 years old in four chapters (sulfoxide method, glycosyl phosphate

method, poly(ethylene glycol)-supported syntheses, and glycopeptide libraries) and more than 80% of the references in the chapters on the trichloroacetimidate method and "on-bead" monitoring are less than 5 years old.

The conceptual difference between solution and solid-phase-based oligosaccharide synthesis is the use of a linker unit connecting the growing saccharide chain to the polymeric support. Although this question is dealt with in several of the reviews, the chapters on the trichloroacetimidate method and the poly(ethylene glycol)-supported methods stand out in their breadth of coverage and organization. Supports and linkers for solid-phase-based glycopeptide synthesis are covered in detail in the final two chapters, which also include numerous protecting group technologies particularly developed for glycopeptide synthesis.

As is the case with other edited, multiauthored books, some overlap in coverage could not be avoided, most notably on the use of thioglycosides as glycosyl donors. The reviews on the sulfoxide method, the glycosyl phosphate approach, and β-mannosylation are somewhat disproportionate in their coverage of solution-phase applications; this is, after all, a book on solid-phase synthesis. What I missed most was a concluding editorial chapter that matter-of-factly summarized the current state of polymer-supported oligosaccharide synthesis and discussed not just the scope but also the limitations of these methods that, despite major advances, continue to prevent their applicability for the synthesis of many biologically important oligosaccharides.

Solid-phase oligosaccharide synthesis is likely to be a developing area. This book successfully integrates early achievements with the most recent results and can serve as an important reference until early 2000. Overall, this book is a welcome addition to the fast-growing library of the books on carbohydrates and deserves its place on the shelves of the libraries of organic chemists who have particular interests in oligosaccharide synthesis.

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