Additions and Corrections

Catalytic Asymmetric Syntheses of Antifungal Sphingofungins and Their Biological Activity as Potent Inhibitors of Serine Palmitoyltransferase (SPT) [*J. Am. Chem. Soc.* **1998**, *120*, 908−919]. SHŪ KOBAYASHI,* TAKAYUKI FURUTA, TAKAOMI HAYASHI, MASAHIRO NISHIJIMA, AND KENTARO HANADA

Page 919: The following mp and IR data should be added.

(2S,3R,4R,5S)-2-Amino-2-methyl-3,4,5-trihydroxy-14-oxoeicos-6-enoic acid (sphingofungin F) (8): Mp 142−144 °C. IR (KBr) 3399, 2927, 2855, 1710, 1638 cm^{-1}.

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Book Reviews

Chirality in Industry II: Developments in the Manufacture and Applications of Optically Active Compounds. Edited by A. N. Colins (Zeneca Specialties, Manchester, U.K.), G. N. Sheldrake (The Queen's University of Belfast, U.K.), and J. Crosby (Zeneca Pharmaceuticals, Macclesfield, U.K.). Wiley: New York. 1995. xiv + 411 pp. $215.00. ISBN 0-471-96680-0.

This book, the second volume with this title, is devoted to individual case histories of the application of asymmetric synthesis for industrial products. As the contributors to this volume are different from those of Volume I, the editors have provided variety to the readers.

Due to the importance of asymmetric synthesis, several single and series volumes of books have appeared in the past 15 years. Many of these books contained chapters contributed by chemists in academia. An average academic chemist is unaware of the developmental problems in the industry and the industrial chemist's perspectives on several of these reactions and reagents. Accordingly, the volumes edited by Collins, Sheldrake, and Crosby should be well received.

This book contains 20 chapters with an introductory chapter by Crosby (much shorter than the one in Volume I), followed by chapters on the regulatory aspects of chiral drugs, production methods for chiral nonsteroidal antiinflammatory Profen drugs, and synthesis of enantiomerically pure nucleosides. Subsequent chapters are organized under three sections: (I) Physical methods and classical resolution (Chapters 5−8), (II) Biological methods and chiral pool syntheses (Chapters 9−14), and (III) Asymmetric synthesis by chemical methods (Chapters 15−20).

Chapters 5 and 6 transmit the message that although organic chemists have been trying to develop efficient methods for asymmetric syntheses, classical resolution methods have retained their importance and are still viable alternatives. In Chapter 7 crystal science techniques in the manufacture of chiral compounds are presented. Chapter 8 deals with membrane separation for optically pure compounds. However, this methodology is still in its infancy and has potential to develop in the future. Chapter 9 is an extensive treatise of four case studies in the development of biotransformation-based processes. While Chapter 10 discusses the bioprocess involved in the industrial synthesis of (*S*)-chloropropionic acid, Chapter 14 describes the biotransformation in the production of L-carnitine. Chapter 11 reveals four processes for the synthesis of a chiral pyrrolidine starting with (*S*)-proline. Chapter 12 illustrates the development of an intermediate for an anti-glaucoma drug, and in Chapter 13, the properties and preparation of chiral liquid crystals are reported. The rest of the book (Chapters 15−20) elucidates the industrial applications of asymmetric synthetic methods (that any graduate student should be aware of) for the production of useful materials, including fragrances.

The chapters are sufficiently long and do not distract the reader. Since each chapter is the illustration of one methodology or product, they stand apart. All of the chapters do not possess the same standard. Some provide details and enlighten the reader while some are very shallow. For example, the authors of Chapter 6 present a strong case that the classical resolution method is still alive, whereas those of Chapter 20, entitled asymmetric reduction of prochiral ketones, do not discuss any process development in their affiliated industry (SIPSY, France). They merely cover some reactions that are already known in the literature. The references quoted of Professor Brown's post-1985 contributions to asymmetric reduction are wrong (1975). Midland's Alpine-Borane has been attributed to Brown, and the commercial source of chlorodiisopinocampheylborane has been mentioned as Callery Chemical, although Aldrich Chemical Co. initially made this reagent commercially available and owns a patent for the reduction applications of this reagent. At the very least industrial chemists should be aware of these matters.

Overall the editors have done good to asymmetric synthesis. This book presents an understanding of the intricacies involved in the application of laboratory-scale reactions to plant-scale and would be ideal for a course on "industrial organic chemistry", although only affluent students can afford the price.

P. V. Ramachandran, *Purdue University*

JA975603Y

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Time-of-Flight Mass Spectrometry: Instrumentation and Applications in Biological Research. By Robert J. Cotter (The Johns Hopkins University). ACS: Washington, DC. 1997. xvi + 326 pp. $119.95. ISBN 0-8412-3474-4.

The stated purpose of this book is to present "the basic principles of time-of-flight mass spectrometry with a strong emphasis on applications in biological research", and the book is remarkably successful in achieving this goal. Coverage of topics is thorough, presenting both historically important contributions and relevant recent experimental results. The author has drawn generously from important studies performed in both his own and other laboratories to provide concrete examples of the maturation of time-of-flight mass spectrometry (TOFMS), the development of biological analyte ionization methods, and current/evolving applications of TOFMS to biological research. The topics are presented in an extremely readable format with ample figures to reinforce the textual descriptions. Each chapter is well referenced, and a detailed index is provided at the end of the text.

The book is divided into 12 chapters which cover a range of topics from fundamental principles to applications of TOFMS. Chapter 1 provides a thorough survey of the historical development of TOFMS, emphasizing the close linkage of these developments to improvements in ionization methods and detection/recording electronics. Chapters 2 and 3 cover the basic physical principles of both linear and reflectron TOFMS. In these chapters the author implements a valuable device which should make this text of interest to both novices and specialists. As various important equations related to TOFMS are discussed, separate boxed and highlighted sections are included which show the derivation of the equations. The text is written in such a way that a novice can readily skip these derivations and still gain a thorough appreciation of the fundamental relationships of importance. On the other hand, the inclusion of this information certainly enhances the long-term value of the book since these derivations can subsequently be referred to when greater insight into a particular relationship is desired.

Chapters 4−6 cover the basic principles, relevant fundamental studies, and important applications of the major desorption/ionization methods for biological mass spectrometry. The decision by the author to include chapters on plasma desorption mass spectrometry (Chapter 4) and secondary ion mass spectrometry (Chapter 5) is admirable since these techniques are often overshadowed by the present research emphasis on matrix-assisted laser desorption/ionization (MALDI) TOFMS. The book highlights both the valuable historical contributions that these techniques have made and the important current research efforts in these areas. In Chapter 6 equal treatment is given to a discussion of the development and application of laser ionization, laser desorption/ionization, and MALDI. In addition, a brief discussion of the important studies of the mechanism of laser desorption/ionization is presented. This topic is treated somewhat superficially and will leave the specialist in the area dissatisfied, but the depth of the treatment is consistent with the stated goal of the book. Furthermore, adequate references are provided for the interested reader to begin a more thorough exploration of the important mechanistic studies.

Chapters 7−9 cover important instrumental developments in the areas of both coupling continuous ionization sources with TOFMS and performing product ion analysis using delayed extraction and tandem TOFMS techniques. In the area of coupling continuous ionization sources with TOFMS, particular emphasis is given to orthogonal extraction and ion storage techniques. This latter topic is expanded to cover the opportunities for obtaining product ion mass spectra from undifferentiated parent ions by allowing fragmentation to occur in the ion storage device or during a delayed extraction event. The possibilities for obtaining parent ion selected product ion mass spectra are explored further in subsequent discussions of post source decay/scanned reflectron techniques and tandem TOFMS techniques.

Finally, Chapters 10 and 11 focus on the application of TOFMS to the analysis of proteins and oligonucleotides. Here the author is necessarily limited to providing only a sampling of the range of current applications of TOFMS to biological research due to the explosive growth of this field in recent years. Despite this challenge the author has done an outstanding job, not only of providing examples of the wide variety of applications of TOFMS, but also of emphasizing the useful interplay between TOFMS and conventional bioanalytical techniques. Both practicing mass spectrometrists and novices to the field will appreciate the concisely collected descriptions of various conventional bioanalytical methodologies as a starting point for designing solutions to challenging bioanalytical problems. Furthermore, the numerous examples of successful TOFMS applications to biological research, both independent of and in concert with conventional bioanalytical procedures, clearly illustrate the powerful role that TOFMS has come to play in biological research.

Overall, the emphasis on fundamental principles and the broad introduction to various applications of TOFMS to biological research should make this book particularly valuable as a starting point for newcomers to the field. There is also ample in-depth coverage of numerous topics to justify a position for this book in the library of practicing mass spectrometrists who already have a solid foundation in TOFMS.

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Experimental Innovations in Surface Science: A Guide to Practical Laboratory Methods and Instruments. By John T. Yates, Jr. (University of Pittsburgh). Springer: Newark. 1997. $89.95. xv + 904 pp. ISBN 0-387-98332-5.

Assembled by one of the premier surface scientists in the world, this book of 904 pages is an extraordinarily valuable contribution to those of us who do experimental surface science. The text amounts to a compilation of “tricks of the trade” which seldom, if ever, get described and discussed in the literature. As such, all who are in or are getting into the field of ultrahigh vacuum surface science (chemistry, physics, and engineering) will find this book to be of immense value. The text is organized into nine major sections, each of which deals with an experimental aspect of surface science. For example, the first section deals with vacuum science technology and comprises 176 pages of discussion organized into 56 separate topics, each of which describes, in 2−4 pages, some experimental device or application that is useful experimentally. This strategy continues throughout on topics that include mechanical fabrication techniques, measurement methods, thermal control, delivery of adsorbates to surfaces, ultrahigh vacuum windows, surface preparation methods, high area solids, and safety. In all, there are 239 short presentations of the type described above. There are also two appendices. The first lists useful experimental surface science books, and the more valuable second lists manufacturers worldwide of various experimental components. Of particular note, the illustrations are superb. This “handbook” will be highly valued on the shelf of every surface scientist.

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Heterocyclic Chemistry. Third Edition. By Thomas L. Gilchrist (University of Liverpool). Addison Wesley Longman: Essex. 1997. xvii + 414 pp. £22.99. ISBN 0-582-27843-0.

As true for the earlier editions of Gilchrist’s *Heterocyclic Chemistry*, this new edition provides an excellent introduction to this very large and vitally important field. The approach is that of a textbook, and this book is written in an attractive style and at a level that makes it useful for advanced undergraduates and graduate students. Frequent mention of medicinal compounds helps to emphasize the contemporary importance of this old field. The new edition has exactly the same format as the Second Edition, and indeed the tables of contents are almost identical. The first four chapters serve as a general introduction to the field, stressing the subjects of aromaticity, nonaromatic systems, and general methods of ring construction. The next six chapters treat particular ring systems, in adequate depth as to provide an excellent background for the student. These ring systems (and some of their fused derivatives) include the five- and six-membered rings, each with one heteroatom, and then with two heteroatoms, three- and four-membered rings, and seven-membered rings.

A valuable feature of the new edition is the inclusion of more references to review articles, as well as to the more recent literature. Users of the Second Edition will find the changes in the text to be rather limited, and indeed the editions are identical in many places. The summaries of each chapter, given in both editions, are an extremely useful feature, and these too are identical for many chapters. The limited amount of new material, aside from references, is mostly concerned with new reactions of heterocycles or synthetic methods. The problems at the end of each chapter of the Second Edition are retained largely intact in the new edition, but in some chapters one or two new problems are added.

In a book surveying such a large field, it is inevitable that some important matter could not be included. So it is here with the extremely important application of NMR spectroscopic techniques in the study of heterocyclic systems. Someone desiring data or information on NMR properties of the major ring systems will not find very much in this book. A few applications of ^{1}H NMR, with little data, are included, but there is no mention of ^{13}C or ^{14}N NMR shifts, and only one of ^{15}N. Also, this book, as regrettably true for other texts on heterocyclic chemistry, ignores the very large field of heterocyclic systems based on atoms other than N, O, and S. Students deserve to receive some exposure to this important and growing area. Phosphorus especially has achieved prominence in heterocyclic chemistry, and is accorded extensive coverage in the Second Edition (1996) of *Comprehensive Heterocyclic Chemistry* by A. R. Katritzky, C. W. Rees, and E. F. V. Scriven (Pergamon Press). There are only two occasions where phosphorus rings are mentioned in Gilchrist’s new *Heterocyclic Chemistry*, one simply showing a structure for phosphabenzene (phosphinine) in a table of six-membered aromatic rings, the other stating that five-membered rings based on the heavier atoms of Groups

15 and 16 (Groups V and VI) resemble those with N or S, respectively, in the participation of the lone pair in an aromatic sextet. This statement, without qualification, is in fact incorrect for P and As.

This book can be strongly recommended for use as a text in a course on heterocyclic chemistry; it is also a convenient source of general information on this field, and the references are well chosen to guide the reader to more complete coverage.

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Thermodynamics of Molecular Species. By Ernest Grunwald (Brandeis University, Massachusetts). John Wiley: New York. 1997. xx + 323 pp. $64.95. ISBN 0-471-01254-B.

It is difficult to do justice to this book in a short review, because every chapter is packed with chemical observations, calculations, and conjectures, each of which could itself be the legitimate subject of a separate review. Despite a wide scope, which includes topics from thermodynamics as well as kinetics, Grunwald's book has a simple purpose, and that is to explore the consequences of adding chemical species to the set of thermodynamic variables, which in the case of solutions, consists ordinarily of temperature, pressure, and the mole fractions of chemical components. In quantum mechanical terms, a *species* can be described by the configuration coordinates of a local minimum of the potential energy surface. By contrast, a *component*, as defined by Gibbs, is a substance that can be independently isolated and purified. This definition leaves out, for example, H_3O^+ and OH^-, produced by the spontaneous ionization of water. Nonetheless, many such ionization products, oligomers, isomers, etc., can be detected in liquid solutions by modern spectroscopic methods. Rigorously, the effects of species on reactions should be taken into account by statistical thermodynamics. There are formidable mathematical difficulties in such a program, however, and Grunwald's book explores to what extent these can be circumvented by applying thermodynamics.

On the face of it, the extension of thermodynamics to cover species should lead to an uncontrollable increase in the number of thermodynamic variables. However, because of the existence of chemical equilibria linking the concentrations of components and their descendent species, the consideration of species introduces no new *independent* variables and consequently does not come into conflict with the Gibbs phase rule. Moreover, selection of species need not proceed ad hoc, but as shown by Grunwald, their practical existence is limited by an energy-concentration criterion, which he calls the *stability theorem*.

In the case of two-component solutions, the production of species is logically restricted to solvent−solvent interactions, solvent−solute interactions, and solute−solute interactions. As concrete examples of these three cases, the book analyzes the isosbestic point in the Raman spectrum of liquid water, the effect of aprotic solutes on the dielectric constant of liquid carboxylic acid solvents, and the dimerization of acetic acid in liquid benzene, respectively.

In addition to the *stability theorem*, the basic concepts and results of the book are codified in more than a dozen other simply stated and clearly derived theorems. Some of these are obviously general and profound. One is called the *tolerance theorem*. This theorem depends on the concept of molar strain, which refers to the extent of reaction, and the concept of molar stress, which refers to the derivative of the total free energy with respect to the strain. Inter alia, one is reminded that in chemical kinetics the law of mass action is an expression relating the strain rate to the stress (Castellan, G. W. *Ber. Bunsen-Ges.* **1963**, *67*, 898. Haase, R. *Z. Phys. Chem. (NF)* **1987**, *153*, 217). Since the free energy has a minimum at equilibrium, the energy effects of strain errors associated with any given model show up only in second order. After reminding us that one of the connections between kinetics and thermodynamics is transition state theory, Grunwald suggests that the tolerance theorem is behind the surprising effectiveness of empirical reactivity correlations such as Hammett plots and the Brønsted catalysis law.

Although not a textbook (there are no homework problems, for example), Grunwald's monograph can be easily read by anyone having a firm foundation in undergraduate physical chemistry. Certain terminology is particularly efficacious in this regard. For example, elementary textbooks often refer to partial derivatives such as $(\partial f/\partial x)_y$ as the "partial derivative of f with respect to x with y constant". Taken literally, this implies that when $(\partial f/\partial x)_y$ is subsequently differentiated with respect to y, the resulting second partial derivative $(\partial^2 f/\partial y \partial x)$ should be zero. Grunwald neatly avoids this confusion by declaring that, in $(\partial f/\partial x)_y$, x is the "active" variable, while y is the "inactive" variable. The implications of such thermodynamic derivatives are investigated rather thoroughly in the book. Indeed, several chapters consider the difference between thermodynamic derivatives calculated with molar strain inactive as opposed to molar stress inactive. The difference terms, called "molar shifts" are often small, but can be important in special cases.

Although not comprehensive of all of chemical thermodynamics, this book is a *must* for chemists interested in solution phase molecular interactions. The latter chapters concentrate on analyzing, for example, hard sphere and potential energy solvent cages, environmental isomers, solvation in dilute solutions, and the thermodynamics of ions in aqueous solutions. Beyond its emphasis on the solution phase, however, Grunwald's book describes a general system of thermodynamics, which should make it of interest to all chemists. If the book goes through subsequent editions, it may well become a classic of the chemical literature.

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Ion Properties. By Yizhak Marcus (Hebrew University of Jerusalem). Marcel Dekker: New York, Basel, Hong Kong. 1997. iv + 259 pp. $135.00. ISBN 0-8247-0011-2.

The book *Ion Properties* by Yizhak Marcus is a thorough compilation of numerical data on ion properties. The breadth of the data assures that this book will be of significant interest to biologists, chemists, and physicists alike. This reviewer found the book much more complete and easier to use than, for example, the *CRC Handbook of Chemistry*. A particular strong point of the book is that it comes with a computer disk for even easier access to the researcher's data of interest (the database is created by Microsoft Access Version 2.0 for Windows). Furthermore, the data in the book is timely, the result of a "systematic" literature search through the end of 1994, but there are many references with later dates also. The author also clearly summarizes the methods and equations utilized to obtain the particular quantities of interest in each subject area before he begins to tabulate data. Finally, the author thoughtfully includes the CAS number, the Chemical Abstract name, a general name (if different from the Chemical Abstract name), and the formula for each ion.

The data is grouped by a general subject heading into eighteen chapters. Just a few of the subject areas that are covered include ionization potentials, electron affinities, ion radii, magnetic susceptibility, polarizability, electrode potentials, ion transport, hydration numbers, coordination properties, and ion−solvent properties. A particularly complete subject area that is covered is the thermodynamic properties of both isolated and hydrated ions, with data tabulated for heat capacities, enthalpies, Gibbs free energies, and entropies.

A word of warning to specialists is that the book is focused primarily on solution chemistry. Therefore, although there is still an impressive amount of data on ions in gas and solid phases, experts in these areas will find that coverage is less complete. Also, the book is more complete for aqueous data than for nonaqueous solvents. Most researchers, however, will find this book a very useful place to begin a literature search for ion properties.

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