# *Additions and Corrections*

**Zirconocene Complexes of Imines: General Synthesis, Structure, Reactivity, and in Situ Generation To Prepare Geometrically Pure Allylic Amines** [*J. Am. Chem. Soc.* **1989**, *111*, 4486–4494]. STEPHEN L. BUCHWALD,* BRETT T. WATSON, M. WOODS WANNAMAKER, AND JOHN C. DEWAN

Page 4490: In the experimental procedure given for the preparation of **2c**, the second and third sentences should be deleted. There is no need for the addition of chlorotrimethylsilane or for the addition of a second equivalent of *n*-butyllithium. We thank Daniel A. Gately (Colorado State University) for pointing out this error.

**Practical, High-Yield, Regioselective, Rhodium-Catalyzed Hydroformylation of Functionalized $\alpha$-Olefins** [*J. Am. Chem. Soc.* **1993**, *115*, 2066–2068]. GREGORY D. CUNY AND STEPHEN L. BUCHWALD*

Page 2067: The n:iso ratio given for entry 15 in Table I should be (n:iso = 2.8:1). We thank Professor W. R. Jackson (Monash University) for pointing out this error.

# *Book Reviews*

**Electrochemical and Electrocatalytic Reduction of Carbon Dioxide.** Editor-in-Chief, B. P. Sullivan (University of Wyoming); Associate Editors, K. Krist (Gas Research Institute) and H. E. Guard (Office of Naval Research). Elsevier: Amsterdam, The Netherlands. 1993. xiii + 299 pp. $212.50. ISBN 0-444-88316-9.

There has been a considerable amount of recent work focused on the problem of $CO_2$ reduction. One difficulty with this area is that much of the work has been done by electrochemists, photochemists, and inorganic and organometallic chemists with their results being reported in a wide variety of journals. The wide spread of different journals covering this area makes it difficult to follow the progress and direction of the field. This volume does a nice job of bringing together many diverse approaches to the reduction of this important molecule.

The first short chapter by F. Richard Keene sets the thermodynamic foundation for any proposed $CO_2$ reduction scheme. This chapter is followed by an excellent comprehensive review by Carol Creutz of the binding of $CO_2$ to transition metal centers. In his introduction to the third chapter, Peter Ford admits that a chapter on the catalysis of the water gas shift reaction may be out of place in a book about $CO_2$ reduction. However he then points out that this reaction, when run in reverse, is simply the hydrogen reduction of $CO_2$ to CO and water. In his contribution he emphasizes the mechanisms of homogeneous catalysis of the water gas shift reaction. A chapter by Dan Dubois and the group at the National Renewable Energy Laboratory discusses the electrochemical concentration of $CO_2$ via redox active $CO_2$ carriers. Concentration of atmospheric $CO_2$ is necessary to prevent additional $CO_2$ from being added to the atmosphere, which would result if carbonate minerals or natural $CO_2$ reservoirs were used as $CO_2$ sources for the production of fuels. Although artificial systems easily outstrip the efficiency of green plants in converting solar energy to electricity or chemical fuels, we will have difficulty in competing with their ability to produce complex molecules from such a dilute source of $CO_2$.

In Chapter 6, B. Patrick Sullivan and F. Richard Keene discuss the mechanistic aspects of transition metal catalyzed $CO_2$ reduction, specifically C–H bond-making and C–O bond breaking steps. A similar and very detailed discussion by Karl Freese, Jr., of Interfacial Sciences, Inc., focuses on the mechanisms and product formation in the electrochemical reduction of $CO_2$ at metal electrodes. Next, Anthony F. Sammells and Ronald L. Cook review work, much of it their own, using high current–high overpotential systems for $CO_2$ reduction using metal and perovskite electrodes. The last chapter by Nathan Lewis and Gary Shreve reviews the progress in photochemical and photoelectrochemical $CO_2$ reduction. These authors cover reduction by homogeneous photocatalysts, particulate semiconductor systems, and semiconductor electrodes both as catalysts and coupled to solution catalysts.

The editors have done a good job of organizing this topic so as to avoid overlapping discussion in the various chapters, which often occurs in a volume of this type. An additional chapter on coupling electrochemical energy directly into biological $CO_2$ reduction pathways would have been appropriate, since there is significant literature in this area. I am hesitant to suggest that every researcher interested in $CO_2$ reduction buy this book, since its cover price is rather high for a 299 page book. However it will be a valuable reference work, and perhaps a nearby library would have the budget to obtain this volume.

**Bruce Parkinson,** *Colorado State University*

**Organic Reactions. Volume 41.** Edited by Leo A. Paquette. John Wiley & Sons: New York. 1992. xvii + 645 pp. $90.00. ISBN 0-471-54409-4.

*Organic Reactions* has been published since 1942, and more than forty volumes have now appeared. These volumes contain authoritative reviews of preparatively important organic reactions. They are designed to provide chemists with valuable practical information about the reaction, including its scope, limitations, and the selection of specific experimental conditions. Because *Organic Reactions* serves a useful purpose and has maintained a tradition of excellence, it is acquired almost automatically by most chemistry libraries and by many individual chemists.

Volume 41 is a particularly important addition to the series. It consists of a shorter chapter on the divinylcyclopropane–cycloheptadiene rearrangement, written by Tomáš Hudlicky and coworkers, and a longer chapter on organocopper reagents, written by Bruce Lipshutz and Saumitra Sengupta. Each chapter will be widely consulted, and each will simultaneously serve as a valuable source of references and as a stimulus for future research.

The chapter on the divinylcyclopropane–cycloheptadiene rearrangement highlights a reaction that is both theoretically interesting and preparatively valuable. The review is thorough, and more than 80 pages of tables listing specific examples and reaction conditions are included as well as several pages of representative experimental procedures. Moreover, simple heterocyclic permutations of the basic rearrangement are discussed. In addition, it is up-to-date (the literature is covered through December 1990, and much unpublished information is provided), and it is written by a team intimately familiar with practical aspects of the subject. Unfortunately, the chapter contains annoying minor errors, including incorrect structures and phrases such as "...with some degree of stereospecificity". In addition, the authors occasionally create confusion by using a single, stereochemically defined structure to represent other stereoisomers in subsequent discussion. Finally, conclusions are not always presented as clearly and concisely as possible. Nevertheless, the chapter is unquestionably valuable.

The chapter on organocopper reagents reviews a subject of major importance in organic chemistry. It updates earlier reviews of Posner in *Organic Reactions* (**1972**, *19*, 1; **1975**, *22*, 253) by broadly surveying substitutions, conjugate additions, carbocuprations, metallocuprations, and other reactions characteristic of organocopper reagents. All types of organocopper species are discussed, including those derived from Grignard reagents using both catalytic and stoichiometric amounts of copper, lower-order and higher-order lithiocuprates, and simple neutral organocopper reagents. Special attention is given to newer developments such as the use of organocopper complexes activated by the addition of Lewis acids. A measure of the importance of the subject and the thoroughness of the review is the length of the reaction tables (more than 300 pages) and the large number of representative experimental procedures (more than 30) and references (almost 1700, including some from 1991).

The chapter on organocopper reagents is exceptionally well written: The development of ideas is logical, the prose is graceful, and the exposition is unusually clear. Only two very minor improvements could be made. One would be to indicate even more clearly that the structure of higher-order cyanocuprates is still a controversial subject and that the formula $R_2Cu(CN)Li_2$ implies, perhaps erroneously, that cyanide is directly coordinated to copper. A second improvement would be to make the chapter even more useful to the practicing chemist by providing very explicit references to recommended procedures for the purification of key reagents such as copper halides and their complexes. Nevertheless, the chapter is an outstanding model for contributions to *Organic Reactions*. It is an extremely valuable addition to the literature of organic chemistry, and it helps make Volume 41 of *Organic Reactions* an essential acquisition for all chemistry libraries and for the collections of many individual chemists.

**James D. Wuest,** *Université de Montréal*

**Gas-Liquid-Solid Chromatography**. By V. G. Berezkin (A. V. Topchiev Institute of Petrochemical Sciences, Academy of Sciences of the USSR). Marcel Dekker: New York. 1991. x + 232 pp. $99.75. ISBN 0-444-88316-9.

This monograph is Volume 56 of the Chromatographic Science Series published by Marcel Dekker. This series has a long history of covering general and highly specialized topics related to all aspects of chromatographic practice. The present volume clearly falls into the latter group in addressing a specialized niche within the general field of chromatography. The overriding focus of this book is telegraphed by the title. Specifically, while gas-liquid chromatography is typically envisioned as the partitioning of a volatile solute between a mobile gas phase and supported stationary liquid phase, the underlying support matrix (be it a porous solid support or the wall of a narrow capillary) and interface of the supported liquid do not always play passive roles in the separation. Adsorption of solute at the liquid stationary phase/solid support and liquid stationary phase/gas interfaces may significantly contribute to the observed overall retention. This phenomena impacts a number of practical areas of chromatographic practice which are examined in this book.

Chapter 1 provides a brief historical introduction to gas-liquid chromatography and sets the stage for the perspective advocated by the author throughout the remainder of the book. The author notes that neglect of solute adsorption at the stationary phase/solid support and stationary phase/gas interfaces has a number of practical consequences, including lowered interlaboratory reproducibility in the determination of chromatographic retention indices, complications if retention indices are used for qualitative identification purposes, and systematic errors in the determination of solution thermodynamic quantities by gas chromatography. Although representative examples are largely drawn from chromatographic data acquiried using packed column technology, evidence is presented that while these effects are diminished by the use of fused silica capillaries, they are not eliminated.

Chapter 2 (Absolute Retention of Analyzed Compounds) contains the fundamental theoretical motivation of the author's perspective. The author develops a general model for retention in which the discrete components of the observed retention are assumed to combine in an additive fashion and presents retention equations in which the interfacial contributions to solute retention are explicitly incorporated.

Chapters 3–9 cover the practical consequences of interfacial absorption in gas chromatographic separations. Retention indices are commonly considered to quantify the relative gas → liquid stationary phase transfer free energy. According to studies by the author and others, a major cause of interlaboratory variability in the determination of retention indices is the neglected contribution of interfacial adsorption to chromatographic retention. Chapter 3 examines the contribution of the solid support matrix on calculated retention indices and presents a number of schemes to calculate relative retention indices from which the contribution due to adsorption has been removed. The impact of interfacial sorption on separation efficiency is examined in Chapter 4.

Naturally, in chromatographic systems in which interfacial adsorption and partitioning both occur, the relative contribution of partitioning and adsorption to the net observed retention is a function of the phase ratio employed. This topic is examined in Chapter 5. In particular, the author examines the impact of phase ratio on the selectivity of a separation (a feature which is not considered in ideal GLC).

Interfacial adsorption certainly perturbs the development of a chromatographic separation. In extreme cases, one can observe irreversible loss of solute to the stationary phase and/or on-column reaction of analyte. Chapter 6 is dedicated to a discussion of these effects in the chromatographic analysis of a wide range of solutes.

Chapters 7 and 8 provide a very brief treatment of the use of gas chromatography as an experimental tool for characterizing the thermodynamics of the separation process. In Chapter 7, the major emphasis is on isolation of the component of the observed net retention due to solute partitioning into the stationary liquid phase from that due to interfacial adsorption of the solute. Naturally, good correspondence between partition coefficients determined by gas chromatography and static methods implicitly relies on the successful removal of the component due to interfacial adsorption from the chromatographic data. Chapter 8 focuses on the other facet of the separation, interfacial adsorption, and how this component to the observed net retention can be reliably estimated.

The final chapter considers the fate of chromatographic supports over time and how aging changes the chromatographic support (both the solid support and supported liquid stationary phase).

Overall, this book is a reasonable exposition of the impact of adsorption effects on gas-liquid chromatographic separations. The author provides an excellent summary of the Russian literature on this topic; however the related Western literature is not neglected. For this highly specialized topic, the author provides good coverage.

On the negative side, the presentation is marred by a large number of typographical, grammatical, and editing errors. These errors include simple misspellings, unlisted references, listed references which are never cited in the text, and awkward literal transition of the original text. The frequency of errors is high for a book of this price and roughens the flow of the presentation. However, the errors do not irretrievably compromise the content of the book. A cautious reader will be able to negotiate the text without significant problems. In addition, in part due to the poor coverage of the Russian literature by Western workers, the author uses this book as a platform to claim priority on some specific developments (see, e.g., footnote on p 40). This is an inappropriate exercise in editorial license which only serves to distract from the immediate focus of the book.

This book has a number of potential audiences. For the practicing chromatographer, this book treats specialized topics that are usually developed in a cursory fashion in other monographs. While the author provides some examples of analytical consequence, the issues treated in this book primarily impact applications which employ gas chromatography for the measurement of parameters related to solution and adsorption thermodynamics. Workers in this narrow domain of gas chromatography would benefit from this volume. This book also provides an accessible summary of the pertinent Russian literature that is not readily available elsewhere. In addition to the practicing chromatographer, this book should also be of interest to chemometricians involved in the development of quantitative structure/retention relationships (QSRR). The book examines phenomena which can serve as uncontrolled (and typically, undiscussed) factors which contribute to the observed retention data used in QSRR's. Finally, while the book has a rather general title, it should not be mistaken as an overview treatment of either the fundamental or practical aspects of gas chromatography. Students and practicing chromatographers looking for a general text on gas chromatography should go elsewhere; chromatographers struggling with the analysis and interpretation of retention data adulterated by adsorption phenomena should benefit from this book.

**James E. Brady,** *Hercules Incorporated*

**Radiochemistry and Nuclear Methods of Analysis**. By William D. Ehmann and Diane E. Vance. J. Wiley and Sons: New York. 1991. $95.00. ISBN 0-471-60076-8.

*Radiochemistry and Nuclear Methods of Analysis* is a nicely organized presentation on radiochemistry and related subjects, obviously drawn from the author's lecture notes and from many years of experience in teaching the subject. The book overtly addresses itself to an undergraduate level audience with a variety of background and interest; in this respect, the material is presented clearly and at a level requiring a minimum of mathematical background. Also, there is the right amount of emphasis on concepts with which undergraduate students invariably have the most trouble, like the mass–energy relationship or the various mechanisms of interaction of radiation with matter. The set of exercises offered at the end of each chapter is in general well chosen to illustrate the material covered; again, the right emphasis seems to have been put on practical challenge to students, like the gymnastics of using formulas with the proper units. The main criticism of this book aims at its very purpose, which is to stay at an introductory level. Overall, the presentation looks too much like a set of lecture notes. One would like a book to provide extra details of what was offered during the lecture and also a chapter in which the authors would dwell on their particular interests such that the book could be a reference for this subject. Finally, the price of the book appears much too high, considering that it is not aimed at specialists but rather to a general audience of undergraduate students.

**Jean-Claude Brodovitch,** *Simon Fraser University*

**Inorganic Synthesis. Volume 29.** Edited by Russell N. Grimes. Wiley Interscience: New York, Chichester, Bisbane, Toronto, and Singapore. 1992. xxii + 427 pp. $54.95. ISBN 0-471-54470-1.

Volume 29 is the latest in this long-running series, whose stated purpose is "to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds". Of course it is difficult to decide just what compounds are "important and timely"; nevertheless, the series continues to meet its goals. A glance at the table of contents reveals the breadth of modern inorganic chemistry covered: (1) main-group compounds—general, (2) boron compounds, (3) transition metal coordination compounds, (4) transition metal organometallics and ligands, and (5) cluster and cage compounds containing transition metals. While there is no "theme" evident in Volume 29, a few syntheses caught this reviewer's eye. They include the syntheses of the following compounds: superconducting synthetic metals; a large-scale and economical synthesis (likely to be widely used) of that useful organometallic ligand, pentamethylcyclopentadiene; and new preparations of useful transition metal starting materials such as the anhydrous metal halides and "weak" ligand complexes. Finally there is reported a resolution of the dodecaammine hexa-$\mu$-hydroxo-tetracobalt(III) ion, a classic compound used by Werner to prove that the origins of optical activity did not reside in the nature of carbon. Although it is certainly not a book for casual browsing, the formula index allows relatively easy access to the compounds to be found in the series. The technical aspects of the book remain excellent, and it certainly belongs on the shelf of most libraries.

**Carl J. Carrano,** *Southwest Texas State University*

**Chirality. From Weak Bosons to $\alpha$-Helix.** Edited by Rudolf Janoschek (Karl-Franzenz-Universität Graz). Springer-Verlag: New York, Berlin, and Heidelberg. 1991. xi + 246 pp. $124.00. ISBN-0-387-53920-4.

The origin of chiral homogeneity in the essential biological macromolecules has long been (and still remains) a matter of speculation and controversy, and this interesting collective book has apparently been designed to support the now widely publicized opinion that *all is written* in the fundamental properties of elementary particles and forces. This opinion takes a particularly romantic and enthusiastic form in the last chapter by S. Hoffmann (Chapter 10), where it is lyrically depicted how the "chiral message," carried by the electroweak interaction, predetermined the "grand process" so as to allow (in short) the development of the nucleoproteinic systems that are responsible for the existence of life. In this context, it would perhaps have been appropriate to quote the recent review by Bonner (*Top. Stereochem.* **1988**, *18*, 1–96), a unique, exhaustive and critical source of information on the theories and experiments in this area. Nevertheless, one should credit R. Janoschek for the last statement of his own contribution (Chapter 2), "that any hypothesis on long time processes such as homochirality evolution will most probably remain unproven forever."

The other chapters treat various aspects of chirality in a more technical fashion. According to the logics of the story—from bosons to life—Chapter 1 by H. Latal is devoted to a discussion of Parity Violation in Atomic Physics, which should normally allow the nonspecialist to understand, if not the details, at least the spirit.

Chapter 3 by G. Derflinger, Chirality and Group Theory, summarizes earlier and more recent works on the mathematical description of chiral systems, a topic that should be of general interest to a broad range of scientists. All chemists who have known the late G. Snatzke will certainly recognize in his contribution (Chapter 4, Helicity of Molecules) the lucid and pictorial description he used to give of the circular dichroism of chiral molecules. A special mention has to be given to Chapter 5, in which the rather mysterious yet important phenomenon of the anomalous dispersion of Xrays, and its application to the determination of the absolute handedness of molecules, is explained to nonspecialists by C. Kratky.

Chapters 6 and 7 are devoted to the preparation of pure enantiomers by biocatalysis (Faber and Griengl) and by various kinds of enantioselective syntheses (E. Winterfeld). We note that, in this last chapter, following a recent and regrettable usage, the term "homochiral" has been used in a systematic way to mean "enantiomerically pure." Moreover, there is almost nothing about the strategies based on crystallization, which still represent the most widely used methods, particularly for large scale applications. Finally, Chapter 8 (Chirality in Transition Metal Chemistry, by H. Brunner) and Chapter 9 (Liquid Chromatographic Resolution of Enantiomers) represent excellent short reviews in their respective fields.

In summary, although the scope of this book is somewhat more narrow than it is claimed, it may be useful to those wishing to gain basic information on subjects related to chirality that they are not used to dealing with.

**André Collet,** *Ecole Normale Supérieure de Lyon*

**Tandem Organic Reactions.** By Tse-Lok Ho (National Taiwan University). Wiley-Interscience: New York. 1992. x + 502 pp. $79.95. ISBN 0-471-57022-2.

The goal of this book is to familiarize readers with important classes of tandem reactions so that they might incorporate such transformations into synthesis planning. "Tandem" is defined in a very broad way, so the potential scope of the book is enormous. The author then narrows the scope by choosing classes of reactions that he feels are most important. What remains is still a very broad swath of modern synthesis, and this is an ambitious book that, by and large, meets its goal. However, a good knowledge of synthetic organic reactions is needed to profit from the book.

Tandem reactions are classed by the final key reaction in the sequence, and each selected reaction receives a (beautifully drawn and reproduced) scheme and a short vignette (two or three sentences) summarizing the transformation. The book probably summarizes more than a thousand transformations in areas ranging from carbonyl addition and condensation reactions to pericyclic reactions to radical reactions. Examples are drawn in a balanced fashion from synthesis of natural and non-natural (structurally interesting) products and from synthetic methods. There are probably about 1500 references that range from the 1950s up to 1991; there is heavy emphasis on recent work.

The trade off for this broad scope of the book is of course detail. There is little discussion of synthetic strategy or scope and limitations of reactions. Schemes sometimes show intermediates or mechanisms; often they do not. Students of synthesis may enjoy deducing the sequences of reactions that occur in some of the schemes. There is little or no historical discussion, so the reader does not get a good perspective of what the important early contributions were in a given area and who made them. Most of the chapters present exactly the kinds of information that the reader will expect, but a few are handicapped by the broad definition of "tandem". Every reversible reaction is considered tandem, as is every reaction in which a reactive intermediate is generated prior to a key reaction. Such a definition includes much of organic chemistry. For example, nitrile oxide/alkene dipole cycloadditions (and virtually all 3 + 2 dipolar cycloadditions for that matter) are considered tandem because the dipole is generated in situ prior to the cycloaddition. But the treatment of this huge area is (of necessity) so cursory that the book is not especially useful compared to existing sources.

The book is a fantastic source of references, but the presentation of the references is less than ideal because the book lacks an author index. It is thus impossible to search the 1500 or so references by author. To find a reference, one needs to know the first author. Once found, the reference is of limited use, since there is no indication of what page of the book it appears on. The standard index is good, and that, along with the chapter titles and subtitles, helps make it possible to locate information.

This timely book does a good job of providing an overview of a huge, diverse field. It is a great source of references, and it is also fun to browse. The elegance and efficiency of many of the examples cited in *Tandem Organic Reactions* show the imagination of the organic chemist at his or her best. As you page through this book, you will be impressed and inspired by the work of your predecessors and contemporaries.

**Dennis P. Curran,** *University of Pittsburgh*

**Methods in Computational Chemistry. Volume 4. Molecular Vibrations.** Edited by Stephen Wilson (Rutherford Appleton Laboratory). Plenum: New York and London. 1992. xiii + 239 pp. $69.50. ISBN 0-306-44168-3.

The Born–Oppenheimer approximation, which separates electronic and nuclear motions, is fundamental to most studies of molecular structure and dynamics: the electrons, being much lighter and therefore faster than the nuclei, are assumed to adjust "instantaneously" to nuclear positions, providing an electronic potential energy surface on which the nuclei move. Nuclear motion is often further separated into translational, rotational, and vibrational motion. Molecular vibration is thus a rather large topic encompassing many currently active research areas, progress in many of which has profited greatly from recent advances in computational abilities. Thus, a volume entitled *Molecular Vibrations* in a series *Methods in Computational Chemistry* might include a number of timely topics. Unfortunately, the four chapters presented here address a rather small sampling of the currently exciting work in this field.

The first chapter is an introductory "overview of the 'traditional' approach to the problem of describing vibrational motion" written by the series editor. It is at the level of an undergraduate text, covering several topics reasonably well, but omitting others. For example much is said about Dunham expansions for the potential energy function of diatomic molecules, including different choices for the radial coordinate, but the venerable RKR method, which is a numerical alternative for the same problem, is not mentioned.

The second chapter, by Sutcliffe, is a rather thorough discussion of the Born–Oppenheimer approximation itself. Despite its rather universal use, the question of the applicability of this method is far from trivial, and the excellent, if somewhat technical, treatment given here provides the required background for such practical matters as choosing coordinate systems. Good discussions are given of the best choice for internal coordinates for the electronic potential energy function and of permutational symmetry, points on which there is not yet universal agreement. The presentation is purely formal, however. Those interested in actual applications must wait until the next chapter.

Written by Tennyson, a long-time collaborator of Sutcliffe, and colleagues, the third chapter provides a good example of what one might hope to find in this volume. It discusses application of the formal theory to triatomic molecules. The last two decades have seen much progress in calculating accurate electronic potential energy surfaces for such systems, and recent work has used these potentials to calculate vibrational energy levels with some success. A detailed account is given here of current computational methods, including a description of how these are implemented in the authors' computer programs. A good review of recent results is also provided.

The final chapter discusses an innovative approach to obtaining vibrational energies directly from ab initio electronic structure calculations, i.e., without first calculating and fitting points on the electronic potential surface. In addition to the usual electronic creation and annihilation operators, it introduces vibrational operators into the second quantized form of the Hamiltonian. The presentation here relies heavily on the use of diagrammatic perturbation theory, which may not be universally familiar (it is not to this reviewer). This approach appears to be related to other methods under active development which use analytic derivatives of the ab initio electronic energy to infer vibrational information. But I must confess that after reading this chapter I did not have a clear understanding of the methods being used.

**Sheldon Green,** *NASA/Goddard Institute for Space Studies*

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**Organic Superconductors (Including Fullerenes). Synthesis, Structure, Properties, and Theory.** By J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini (Argonne National Laboratory), and M.-H. Whangbo (North Carolina State University). Prentice Hall: Englewood Cliffs, NJ. 1992. xv + 400 pp. $66.00. ISBN 0-13-640566-5.

This book succeeds in its stated aim, which is to discuss the *chemical* aspects of organic superconductors, especially the ET [bis(ethylenedithio)tetrathiafulvalene] salts and related materials. As noted by the authors, there is a companion volume with the same title which covers the *physical* aspects of the topic [T. Ishiguro, K. Yamaji, Springer-Verlag (1990)]. Taken together, these two monographs provide an excellent introduction to the subject. While the present text contains a six-page appendix on the superconducting alkali metal-doped $C_{60}$ compounds and also includes references from 1990, the subject has shown remarkable development in the past two years.

The first three chapters of the book—Introduction, Synthesis, and Structure—are excellent and reflect the experience of the authors, many of whom have made important contributions to these aspects of the subject. The next chapter—Superconducting Properties—suffers from the very recent advances in the field and does not capture the current turmoil in the subject. The nature of the superconductivity in the ET and TMTSF compounds is currently of intense controversy.

When a material becomes superconducting, an energy gap is normally opened by the Bose condensation of the conduction electrons. In most compounds this energy gap is finite over the whole Fermi surface. It is theoretically possible in the case of a complex superconducting wave function ("non-s-wave") for the energy gap to vanish at certain points or lines on the Fermi surface, and this has important consequences for the properties, since it is one of the most fundamental properties of a superconductor. One way to measure this property is through the decay of the muon spin rotation as these particles are deposited in the superconductor. The same superconductor, $\kappa$-$(ET)_2Cu(NCS)_2$, has been measured on the same accelerator in this way by two different groups with diametrically opposite conclusions. Other measurements of the symmetry of the superconducting wave function have also come down on different sides of this question. The role of flux pinning, the upper critical magnetic field, and the behavior of the NMR relaxation times below $T_c$ are further unresolved questions regarding this material. The nature of the vibrations which are responsible for coupling the conduction electrons into Cooper pairs in superconducting ET salts has recently resurfaced as a subject of discussion in the literature.

The last chapter, entitled Electronic and Structural Properties of Organic Superconductors, is the best in the book. This is not surprising because Whangbo (together with Mori of the Institute for Molecular Science in Japan) has carried out the majority of the electronic structure calculations on the ET salts which are now in the literature. These calculations employ extended Huckel band structure programs developed in the Hoffmann group and have proved to be surprisingly effective in providing a semiquantitative account of the electronic structure of these complex materials. By combining the band structures with an in-depth analysis of the structures, the authors lay out their model for the mechanism of superconductivity in the ET salts. In the fullerene superconductors, the degree of overlap between the $C_{60}$ molecules seems to control $T_c$, whereas the intramolecular vibrations provide the necessary electron–phonon coupling. The authors argue against this mechanism for the ET salts, which show an inverse isotope effect. They propose that lattice vibrations are the source of electron pairing and that differences in the lattice softness, particularly as it affects the C–H groups of the ET molecule, are primarily responsible for the variations in $T_c$. Although alternatives have been suggested, the lattice softness model is clearly the leading contender at this time.

The classic motivation for the study of organics as active electronic materials has been that they allow for the possibility of "tuning" materials properties through the well-known versatility of organic synthesis. Reference to the contents of this book will quickly persuade the reader otherwise. The book is almost solely devoted to one organic molecule: ET. The only other organic superconductor of comparable reputation is tetramethyltetrasenafulvalene (TMTSF). So why are there so many organic superconductors? The superconductors are charge transfer salts in which the organic radical cation must be paired with a counter anion. All of the "molecular engineering" has come through modification of the (inorganic) counterion, and many papers in this area are published in *Inorganic Chemistry*. In fact, substitution of S by Se in ET or Se by S in TMTSF destroys the superconductivity in the compounds which have been examined to date. Unfortunately much the same situation seems to prevail with the fullerene superconductors, but in an opposite sense. The variations in materials properties are achieved through manipulation of the cationic counterion, and $C_{60}$, but not $C_{70}$, produces metals and superconductors.

So why has the field shown such remarkable development? It is now being broadly recognized in the materials science and solid state physics community that many organic conductors are clean materials. Clean in the sense that resistivity ratios of $10^2$ between 10 K and room temperature are readily achieved in carefully grown crystals (the fullerides are an exception in this regard). Furthermore it is also being recognized that the main subjects of this book, the ET salts, are highly two-dimensional materials with strong similarities to the cuprate superconductors, although the superconducting transition temperatures ($T_c$) are only comparable on the logarithmic scale usually adopted by practitioners of the subject (final page of this book). Nevertheless there are now experiments being published on organic superconductors such as $\kappa$-$(ET)_2Cu(NCS)_2$ which have not been possible for other superconductors. The most encouraging outcome would be that organic superconductors will be accepted into the fold of other electronic materials without the perennial title of "exotic." Until we start to treat the study of superconducting materials as a unified subject, organics will remain as materials to be avoided at all costs by those interested in applications.

The book contains compendia of organic superconductors, their structures and properties, and researchers active in the field. A previous review of the book has appeared: Little, W. A. *Science* **1992**, *258*, 1384.

**R. C. Haddon,** *AT&T Bell Laboratories*

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**Studies in Organic Chemistry. 46. Biocatalysts in Organic Synthesis.** By J. Halgaš (Comenius University, Bratislava, Czechoslovakia). Elsevier: Amsterdam, London, New York, and Tokyo. 1992. xiii + 334 pp. $180.00. ISBN 0-444-98698-7.

This is the 46th volume in the continuing series of *Studies in Organic Chemistry*. The book is broken up into nine chapters, all dealing with some aspect of biocatalysis within the realm of organic synthesis.

The first three chapters contain an overview of enzyme kinetics (aqueous and nonaqueous systems), unimmobilized and immobilized enzymes, and the selectivity (substrate stereochemical differentiation) of various biocatalytic reactions. The majority of discussion found in these chapters is very basic; however, there is an ample supply of references for the more interested reader.

Chapters 4–9 deal with enzyme catalyzed reactions from an organic chemist's viewpoint. The author has chosen to document the following reactions: substitution, elimination, addition, acyl transfer, oxidation, and reduction. By far the most comprehensive treatment of these enzymatic reactions concerns that of the acyl transfer reactions. Numerous examples are provided for both aqueous and anhydrous conditions, in addition to enzyme chemo- and regioselective preferences, and the power of enzymatic kinetic resolution is examined.

The entire book is well referenced (>900), the majority of these citations being relatively up-to-date (latest 1990). The volume also contains a list of recommended literature for further reading; a rather nice touch, although its use is somewhat limited by the fact that article titles are not provided. Most of the chapters are well written and easily readable; however, it should be noted that only the basic characteristics of each of these biocatalysts are reported. The main thrust of this book is to introduce the reader to the use of enzymes in organic synthesis, rather than an all encompassing treatise on this subject. Keeping these thoughts in mind, this volume will serve to educate and entice newcomers to begin to participate in this exciting area of research.

**Kim D. Janda**, *The Scripps Research Institute*

**Organic Peroxides**. Edited by W. Ando (University of Tsukuba, Japan). John Wiley and Sons: New York. 1992. xvi + 645 pp. $330.00. ISBN 0-471-93438-0 (cloth).

Peroxides as sources of "active oxygen" are among the most useful and versatile reagents in organic chemistry. This important subject has been reviewed extensively—most recently in the three-volume treatise *Organic Peroxides* edited by D. Swern (1970) and in the Patai's functional group series *The Chemistry of Peroxides* (1983). This 15-chapter sequel presents a potpourri of selected current topics in peroxide chemistry, some by experts in this subfield. Especially topical are authoritative accounts of alkyl hydroperoxides by N. A. Porter, dioxiranes from ketones and dioxetanes from alkenes by W. Adam, et al., endoperoxides from dienes by E. L. Clennan and C. S. Foote, and sulfur/phosphorus peroxides by Y. H. Kim. An interesting version of polyoxides (tri and tetra analogues) is given by B. Plesnicar as an update to his 1983 review in Patai. A provocative (theoretical) chapter on peroxide bonding and structure in relationship to heterolytic and homolytic reactivity is given by K. Yamaguchi, K. Mizuno, and collaborators. Other topics dealing with dialkyl peroxides, peroxy acids and esters, and diacyl peroxides are standard accounts brought up-to-date with limited development from earlier reviews. Chapters on metal peroxides and peroxometal complexes as well as catalytic oxidation are (inorganic) add-ons to the principal theme. The coverages of organic peroxides from ozonation and superoxide and in biological systems duplicate, to a certain extent, the chapters by Porter, Adam, et al. The literature is more or less covered through 1990 (with some 1991 entries). Since organic peroxides constitute a rather slow-moving field of research, this update offers only incremental changes from the earlier monographs. As such, it is mainly desirable for library collections, and it may be useful to those individuals who require the latest in (organic) peroxide fundamentals.

**Jay K. Kochi**, *University of Houston*

**The Design and Analysis of Research Studies**. By Bryan F. J. Manly (University of Otago). Cambridge University Press: Cambridge, U.K. 1992. xvi + 353 pp. $37.95. ISBN 0-521-41453-9.

The universal use of personal computers, whose speed and memory capacity increase as rapidly as their prices fall, now puts tremendous powers of statistical calculation at the disposal of every experimental scientist. Extensive suites of programs allow the application of a huge range of statistical tests to any set of data. These are perhaps mixed blessings. All too often results are evaluated using inappropriate methods, and false conclusions are thus drawn. Even more dangerous is the tendency to apply statistical thinking only after the experimental data have been obtained: in reality, quantitative experiments must be designed and planned with care if the maximum information is to be derived from the inevitably limited number of replicates, specimens, etc. Professor Manly's clear and well-written book encourages scientists to plan their experiments logically and interpret the results critically. Successive chapters deal with sample surveys and other sampling issues; with the principles of simple and multiple linear regression; with a range of elementary and more advanced experimental designs; and with methods of handling data with non-normally distributed errors such as count data, proportions, log–linear models, survival data, etc. An excellent chapter on "computer intensive statistics" emphasises the value of randomization, robust, and simulation methods, which are not really practicable without the iterative power of a PC, but which are as a result rapidly increasing in popularity. An unusual chapter covers ethical considerations in experimental work, and the last chapter provides an overview of the text as a whole.

The general level of the book is suitable for a graduate student: the principles of basic statistics such as significance testing are largely taken for granted. For workers in chemistry and related areas, the book's principal drawback is that it is mainly aimed at a biomedical readership. Of the many interesting examples (including some deliberately chosen to demonstrate pitfalls), only a very few are explicitly chemical, and some come straight from the social sciences. The presentation and layout of the book may seem a little old-fashioned to American readers, and I was surprised to find that the pages in my copy were already going slightly yellow at the edges—poor quality paper. Despite these reservations, the clear and stimulating ways in which the book addresses its main themes make it highly recommendable to any graduate scientist with some basic statistical knowledge.

**James N. Miller**, *Loughborough University of Technology*

**Handbook of Organophosphorus Chemistry**. Edited by Robert Engel. Marcel Dekker: New York. 1992. x + 900 pp. $199.00. ISBN 0-8247-8733-1.

This is a major work that covers a wide spectrum of topics in organophosphorus chemistry, including current developments in new synthetic methodology and reactivity, analytical and experimental procedures, and applications of organophosphorus compounds. The following subjects are covered in 16 chapters, each written by a distinguished, internationally recognized scientist: (1) Optically Active Phosphorus Compounds (T. Imamoto, 53 pp, 227 refs); (2) Developments in the Preparation and Use of Silicon-Containing Organophosphorus Compounds (J. Thottathil, 59 pp, 237 refs); (3) The Perkow and Related Reactions (G. Borowitz and I. J. Borowitz, 57 pp, 108 refs); (4) Nonhydrolytic Cleavage of Phosphorus Esters (R. Engel, 20 pp, 106 refs); (5) The Reduction of Quinquevalent Phosphorus to the Trivalent State (R. Engel, 47 pp, 199 refs); (6) Phosphorus-Containing *Umpolung* Reagents (A. Amer and H. Zimmer, 36 pp, 133 refs); (7) $\alpha$-Substituted Phosphonates (P. Mastalerz, 99 pp, 380 refs); (8) Some Aspects of H-Phosphonate Chemistry (J. Stawinski, 57 pp, 189 refs); (9) Advances in $^{13}$P NMR (D. Gorenstein, 47 pp, 140 refs); (10) Phospholes and Related Compounds (A. Hughes, 75 pp, 210 refs); (11) The Use of Carbon-Phosphorus Analogue Compounds in the Regulation of Biological Processes (R. Engel, 42 pp, 242 refs); (12) Glycerophospholipids: Some Reliable and Recent Syntheses (L. Vargas, 53 pp, 297 refs); (13) The Application of Phosphinyl-Stabilized Ylides and Carbanions in the Synthesis of Phosphonates and Phosphinates of Biological Interest (R. W. McClard and J. F. Witte, 28 pp, 58 refs); (14) Phosphorus-Based Flame Retardants (E. D. Weil, 56 pp, 239 refs); (15) Aliphatic Carbon-Phosphorus Compounds as Herbicides (J. A. Sikorski and E. W. Logusch, 67 pp, 228 refs); (16) Phosphorus-Containing Insecticides (M. Eto, 67 pp, 238 refs). A 25-page subject index of several hundred specific compounds and reaction types is included.

Rather than attempting to be all-inclusive, the individual chapters each summarize the development of the discipline and then present the current state with ample and usually up-to-date references. The book succeeds fairly well in addressing its two targeted audiences. First, to those active in the field of organophosphorus chemistry, it will be useful as a new general reference source. Second, and more importantly, it will be useful to many scientists who need to use organophosphorus compounds and reactions, but who are not specialists in the field. The inclusion of detailed experimental procedures for representative reactions, etc. in most chapters along with the strong emphasis on applications in some chapters should make it a valuable resource to both groups of investigators.

**Robert H. Neilson**, *Texas Christian University*

**Toxic Metal Chemistry in Marine Environments. Environmental Science and Pollution Series. Volume 1.** By Muhammad Sadiq (King Fahd University). Marcel Dekker: New York. 1992. vii + 390 pp. $115.00. ISBN 0-8247-8647-5.

This is a very dangerous book. It is filled with errors which could seriously mislead readers not knowledgeable in marine geochemistry. The book might have some value to the professional marine chemist, who can ignore the glaring errors, because it does have many up-to-date literature references and many tables of data and equilibrium constants. The professional marine chemist would not, however, take the calculations made throughout the book using this data very seriously, since he would know that most processes in the ocean are controlled by kinetics, not thermodynamics.

Almost every paragraph in the book contains errors and misleading statements. A few examples of these will be given later, but first some conceptual errors which permeate the book will be mentioned. The first of these has been alluded to above, namely the emphasis on thermodynamic equilibrium when kinetic factors are so important in marine processes. As just one example of this, it can be pointed out that the dissolved nitrate in the ocean is 10 orders of magnitude lower than that in equilibrium with atmospheric nitrogen! Biological activity determines the concentration and distribution of many minor elements in the sea, as the book correctly points out, but biological activity is not an equilibrium process.

The author tries to evoke equilibrium to explain the well-known "nutrient-like" distribution of cadmium dissolved in seawater, saying perhaps it precipitates with carbonate at the sea surface and is released at depth when the carbonate dissolves. Cadmium, however, correlates closely with phosphorus in the water column, which is released at shallow depths as organic matter decays, not at the deeper depths where carbonate dissolution is important. Cadmium is taken up actively by organisms, not passively by inorganic precipitation.

The main point of the book seems to be to calculate the distribution of various possible species of a few trace elements in seawater (As, Cd, Cr, Cu, Hg, and Pb). A full chapter is devoted to each element. It is claimed that this is necessary because no techniques are available for direct measurements. This is only partially true, and the book does a disservice by ignoring the work that has been done. In order to make calculations the author has to make assumptions. Some of these are listed at the beginning of the calculations for arsenic, the first element discussed. Essentially every listed assumption is wrong, so how valid can the calculations be? He assumes, for example, that Mg is controlled by equilibrium with dolomite, but every marine chemist knows this is not true. Likewise, it is unlikely that the chosen solid phases control Fe and Mn, and it is certain that gibbsite, which is chosen to control Al, does not do so. Assumptions made regarding activities of dissolved species such as oxygen, bicarbonate, sulfate, sulfide, etc. can also be questioned, and in any case, these change rapidly with depth in the sediment pore water, requiring a kinetic modeling approach. In his defense, the author does urge caution in using his models, but such caution may not be exercised by the novice marine chemist. The printed page often assumes an unwarranted validity.

A second major conceptual misunderstanding the author apparently has regards steady-state and geochemical cycling. Even though most of us do not believe the ocean to be in equilibrium for most constituents, we do think it is in steady state. That is, the dissolved concentrations are not changing (or are changing very slowly) with time. Inputs are balanced with removals to a first approximation. Thus it is surprising to see the author, in the third sentence of his preface and repeatedly throughout the book, refer to metals as "...continuously accumulating in marine environments...." Such a statement might, in fact, be hard to disprove for trace metals, on the basis of our present poor knowledge of their behavior, but certainly not for sodium. Yet on page 31 of the book, we are told, "For all practical purposes, whatever Na reaches the ocean remains in seawater." If this were the case, we could calculate the age of the ocean from its Na content and the input rate from rivers. It was pointed out at least 40 years ago that this is not possible.

One further general comment is that no attempt is made in the book to judge any of the literature data presented. Thus, we are told repeatedly that the concentrations of each trace metal discussed vary widely in every media (water, sediment, and organisms), and we are given data to illustrate this fact. Again, there is some truth to this assertion, but there is also no doubt that much of the data presented, especially the older data, is simply wrong, often by orders of magnitude. The reader should be warned of the unreliability of trace metal data. The reader should also be told that trace metal concentrations in sediments vary with mineralogy. A sediment with 100 ppm Zn is quite normal, if it is clay mineral-rich; however, it is contaminated if it is mostly quartz or carbonate. This is not explained in the book.

As promised, only a few of the many factual errors in the book will be pointed out. We can start with the most basic concepts in marine chemistry, those of chlorinity and salinity, both of which are defined incorrectly on page 9 of the book. On page 8 is a table giving element ratios of chlorinity and salinity. The salinity column is wrong, because it multiplies by 1.80655 instead of dividing, resulting in a Na ratio greater than 1; a part that is greater than the whole! On page 12, we find an equation for converting molality to molarity that only works for pure water, not for seawater with its specific gravity of about 1.026. On page 20, we are told "an anoxic regime is characterized by the absence of oxidizable species in any appreciable amounts." In fact, anoxic regimes almost always have more oxidizable material, organic matter for example, than oxic regimes. If the book meant to say reducible species, this is also wrong because sulfate ion concentration is about 28 000 $\mu$M in seawater, and it will be used by bacteria to oxidize organic matter after the approximately 200 $\mu$M molecular oxygen is depleted (the book gives an oxygen concentration 10× too high, but this does not affect this argument). On page 12, we are told that it is common in the marine literature to express concentration as mg/L. It isn't. Real marine chemists express things on a per kg basis, a small distinction perhaps, but one that illustrates how out of touch with real marine chemists this author is. I hope no non-marine chemist reads this book and takes it as the state-of-the-art in our business. It isn't.

**Bob Presley**, *Texas A&M University*

**Chromatography Today**. By C. F. Poole and S. K. Poole. Elsevier: Amsterdam, The Netherlands. 1991. 1096 pp. $75.00. ISBN 0-444-89161-7.

This work by C. F. Poole and S. K. Poole presents an overview of the field of chromatography as it exists in the early 1990s. In nine chapters and approximately a thousand pages of text, the reader is taken from a summary of fundamental chromatographic principles (Chapter 1) to the use of chromatography in hyphenated analytical methods (Chapter 9). In between are Chapters 2 and 3, which focus on gas chromatography, and Chapters 4 and 5, which examine liquid chromatography. In Chapter 6 the authors introduce the subject of supercritical fluid chromatography. Chapter 7 deals with the subject of thin-layer chromatography, and Chapter 8 highlights some modern approaches to sample work-up procedures, appropriate for chromatographic analysis. This book is written clearly, is adequately illustrated, and contains an extensive list of contemporary references. This book's usefulness as a reference text for the practicing chromatographer is its major strength.

The authors' modular approach to the organization of this book does not produce, as the authors' desired, a suitable text for a graduate-level separation science class. While this text would be useful to the instructor in preparation for such a class, it is less desirable as a required textbook for the students. The modular approach as presented does not allow the authors to develop the subject matter in a logical fashion, i.e., from a review of basic chromatographic theory and traditional GC and LC topics to the related, but technically more advanced, field of microseparations (microcolumn LC techniques and SFC).

The book presents an excellent balance between chromatographic principles and practical chromatographic considerations that a chromatographer should be aware of. For example, discussion of retention mechanisms in GC has been balanced well with the discussion of practical aspects of column preparation and evaluation. Similarly, the discussion on column evaluation and test methods for LC columns is as valuable to a chromatographer as the discussion on the LC retention mechanisms. The book provides good practical information on LC instruments, e.g. high-pressure vs low-pressure mixing for gradient generation. However, the authors lost an opportunity to inform the readers on how to use this information for selection of an instrument to suit their specific needs. Similarly, the information on LC detectors is valuable, but a selection guide could have been provided to help the readers in making an informed selection of detectors.

The chapter on sample preparation makes this book a particularly valuable reference book in chromatography. The information on sample preparation techniques, sampling techniques, derivatization techniques for LC and GC samples, visualization techniques, and microreaction techniques for GC samples is extremely valuable to a chromatographer. While this information is available from a variety of sources, rarely has such information been integrated into a book on chromatography which deals with separation principles, techniques, and instruments. The only criticism for this chapter is that the information on stereoisomer separation should have been presented as a separate chapter and not as a part of the sample preparation chapter.

**Dhiren R. Thakker and Robert L. St. Claire**, *Glaxo Inc.*