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 α-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