

Additions and Corrections

Fluorine-Substituted Ferracyclopentadiene Complexes with an Unprecedented Fluorine Bridge between Boron and Carbon [*J. Am. Chem. Soc.* **1990**, *112*, 461]. CHAD A. MIRKIN, KUANG-LIEH LU, GREGORY L. GEOFFROY,* and ARNOLD L. RHEINGOLD

The formulation of compounds **2a,b** as fluorine-substituted ferracyclopentadienes with fluorine atoms bridging between boron and carbon atoms is incorrect. Instead of fluorine, the molecules have hydroxy substituents on the ferracyclopentadiene rings that are coordinated by the Lewis acid BF_3 and hydrogen bonded to the nitrogen atoms of the imine substituents. The initial conclusion of fluorine bridges was based on the crystal structures of the two molecules and was consistent with the preliminary spectroscopic data. However, it is well-known that X-ray crystallography does not distinguish well between fluorine and oxygen atoms because of similar scattering factors, although initially we had no reason to suspect the presence of a hydroxy group. Subsequent detailed spectroscopic analysis revealed inconsistencies with the initially proposed structure and instead led to the correct formulation of the compounds as hydroxy-substituted ferracyclopentadienes. Complete details will be reported in a full paper.

Structure and Basicity of Silyl Ethers: A Crystallographic and ab Initio Inquiry into the Nature of Silicon-Oxygen Interactions [*J. Am. Chem. Soc.* **1990**, *112*, 697-703]. SOROOSH SHAMBAYATI, JAMES F. BLAKE, SCOTT G. WIERSCHKE, WILLIAM L. JORGENSEN,* and STUART L. SCHREIBER*

Page 698: Figures 2 and 3 are mislabeled. The figure captions reading Figure 2 and Figure 3 should be interchanged.

Page 699: Entry 3 in Table I should read $\text{H}_3\text{SiOSiH}_3$ instead of H_3SiSiH_3 .

Book Reviews

NMR: Principles and Applications to Biomedical Research. Edited by Jay W. Pettegrew (University of Pittsburgh School of Medicine). Springer-Verlag: New York. 1990. xvi + 618 pp. \$69.00. ISBN 0-387-97094-0.

This book is somewhat schizophrenic in its attempt to, as the editor states in the preface, "...review the fundamental theory and principles needed to understand selected aspects of NMR and then demonstrate the application of these principles to important unsolved biomedical research questions". Undoubtedly a split personality is a problem for any book that endeavors to cover basic principles and medical applications in a single volume, because the field is simply too vast for such a treatment.

The first four chapters are dedicated to basic principles, relaxation theory, 2D, NMR, and solids. Each of these chapters is independently well written. In an excellent first chapter (Principles of Pulse NMR Spectroscopy), Professor Farrar describes the classical picture of NMR using both the Bloch and Bloembergen points of view. Basic concepts of the rotating frame, relaxation, and several fundamental pulse experiments are covered. This is a good, understandable introduction for a medical worker with limited background. However, it does not cover coupled spin systems in the rotating frame, and this topic is not explained in any of the other chapters, but is assumed knowledge for the purposes of Professor Bothner-By's excellent chapter introducing 2D NMR. Bothner-By's presentation is exceptionally lucid and immensely appropriate for the less well-versed medical researcher. His chapter is the most understandable description of 2D NMR for beginners that I have yet encountered. Dr. Woessner's chapter on relaxation is particularly appropriate in that it stresses water and aqueous sodium ions as examples of systems undergoing primarily dipolar and quadrupolar relaxation,

respectively. These subjects both are important to later chapters on imaging and ion transport. Dr. Frye's chapter on solids NMR is well written and an excellent introduction to the principles and methods of solids NMR that is necessary for understanding later chapters involving work on membranes and metal accumulation in the brain. This chapter is also particularly appropriate since I anticipate that we shall witness an explosion in the use of solids NMR techniques for studying larger biomolecules in the coming years.

A chapter is dedicated to artificial intelligence techniques used in 2D experiments, which is primarily a description of the PROTEAN program developed at Stanford. In that chapter, NMR determination of the structure of a small cytochrome (b_{562}) is described. The organization of this book is such that the two chapters describing 2D spectroscopy, one a simplified discussion of the underlying principles (by Bothner-By) and the other a simple application (Jardetzky et al.), stand out somewhat like unwanted stepchildren. Although well written and informative in their own right, they seem, in this context, to be unrelated to the more medical subjects that are the apparent primary concern of this book.

In my opinion the value of this book for readers of *J. Am. Chem. Soc.* lies in the remainder of the chapters presented here. What I mean by this statement is that this book will probably be of most value for NMR-familiar people who wish illustrations of selected applications, problems, and procedures involving studies of clinical importance. (Good introductions to NMR theory and practice can be found in many places where more justice is done to them than here.) Those remaining spectroscopy chapters provide reasonably current descriptions of NMR spectroscopy uses in the context of clinically relevant themes. An introduction to surface coils is provided as well as chapters that include ^{31}P

NMR in eye research; ^{31}P and ^{27}Al NMR work on brains with a focus on Alzheimer's Disease; ^{31}P , ^1H , and ^{13}C NMR studies of tumors and their responses to therapy; separate chapters dedicated to proton and phosphorus spectroscopy of human and animal brains; cation NMR relative to transport and psychiatric diseases; and finally, a treatment of brain and cell pH and its regulation studied by ^{31}P NMR. I found the emphasis on brain research in these applications chapters interesting.

The remainder of the book is devoted to imaging and related topics. Two chapters describe the background and methods. The chapter Introduction to NMR Imaging by Dr. Lowe is a nicely written simple introduction for the uninitiated. The topics covered in the remaining three chapters are a somewhat limited sampling of the many clinical uses of MRI, but include chapters on contrast enhancement agents, the brain (again), and psychiatry.

There are a number of spelling errors and confusion of terms (such as T_2 instead of t_2) that should not occur in this day of electronic spelling and grammar checkers.

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Collision Theory for Atoms and Molecules. NATO ASI Series B: Physics Volume 196. Edited by F. A. Gianturco (University of Rome). Plenum: New York and London. 1989. viii + 532 pp. \$110.00. ISBN 0-306-43202-1.

This book is the proceedings of a NATO Advanced Study Institute held in Cortona, Italy, in 1987. The stated aim of the book, which comprises three sections and 13 chapters, is to "provide a broad audience of researchers ... with individual and self-consistent treatments for a wide variety of phenomena which entail collisional events between atoms, molecules and electrons, photons or ions".

The first section, Scattering Processes with Photons and Electrons as Projectiles, has seven contributors. The first three chapters discuss dynamical theories and include a chapter on molecular targets by P. G. Burke and one on atomic targets by C. J. Joachain. M. Gavrila introduces the complications of an external radiation field to atomic targets in the third chapter. The next three chapters concern experiment and include work on correlation experiments by G. Stefani, Experiments with Polarised Electrons by J. Kessler, and Low Energy Electron-Molecule Collision Experiments by M. Tronc. The section ends with a contribution by R. Schinke on theoretical treatments of the dynamics of diatomic and polyatomic photodissociation.

Section two, Non-Adiabatic Scattering Processes, has four chapters. The first two are theoretical treatments devoted to atom-atom collisions by B. H. Bransden and molecular collisions by V. Sidis. Two experimental chapters follow. One, by M. Noll and J. P. Toennies, details studies of proton-molecule charge-transfer reactions. The second, by B. Brunetti and F. Vecchiocattivi, examines ionization processes in collisions of excited rare gas atoms.

Section three, Adiabatic Processes in Molecular Scattering, includes two chapters. The first chapter, by F. A. Gianturco, is a theoretical treatment of rotationally inelastic collisions between atoms and molecules at thermal energies. The final chapter, Chaos and Collisions: Introductory Concepts by W. P. Reinhardt, is again theoretical and has a distinct pedagogical orientation.

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Organic Photochemistry. Volume 10. Edited by Albert Padwa (Emory University). Marcel Dekker: New York. 1989. xiv + 485 pp. \$135.00. ISBN 0-8247-7920-7.

Volume 10 is a collection of two reviews concerning applications of photochemical cycloaddition reactions for natural product syntheses, with separate reviews on aryl olefin cyclizations and the photochemistry of reactive intermediates sandwiched in between. As in previous volumes of the series, each chapter is camera-ready copy prepared by the authors themselves. Nonetheless, strict editorial policies maintain a semblance of uniformity which makes for an attractive volume. Each chapter is extensively illustrated, and the volume has good subject and author indices.

Chapter 1, by Dan Becker and Nizar Haddad, provides numerous illustrations of the use of intramolecular 2+2 photocycloadditions of alkenones bearing pendant olefinic groups as a methodology for the total synthesis of primarily terpenoid systems. While the review succeeds in conveying the utility of the photochemical synthetic methodology in forming several stereogenic centers in one step, conceptual themes are elusive in the sections devoted to regio- and stereochemistry. The difficulty here is that minor changes in substitution often exert profound effects on regio- and stereochemical outcome. A contributing factor may

be that the mechanism is still not understood, as studies have appeared, recently, which undermine the exciplex mechanism for orientation in cyclic enone photocycloadditions. Of minor note, I found the use of carat signs to depict radical centers odd.

Chapter 2, by Wim Laarhoven, is an extensive review covering three decades of work in the area of photocyclization and photocycloaddition reactions of aryl- and polynuclear ethylenes, 1,3-dienes, and 1,3,5-hexatrienes. The author presents new material which does not overlap with his review of conjugated alkenes in Volume 9 of this series. Most of the examples are cyclizations which ultimately form polycyclic aromatic hydrocarbons via oxidation of the corresponding dihydro intermediates, whose properties are discussed whenever evidence is available. An in-depth mechanistic treatment of orientation in cyclization includes a discussion of the merits of various excited-state reactivity indices such as free valence numbers, localization energy, Mulliken overlap population, and ΔP (bond order). Additional embedded topics include photochromism, metacyclopentane photoreactivity, formation of helicenes and bridged annulenes, and control of product distributions by the principle of nonequilibration of excited-state conformers.

Sequential two-photon processes for the generation and photolysis of reactive intermediates is presented in Chapter 3 by J. C. Scaiano and L. Johnston. Most of the coverage is devoted to the photochemistry of free radicals and carbenes, whereas the treatment of biradicals, *ortho*-xylylenes and photoenols, and zwitterionic species is far more circumscribed. The carbene and radical sections include tabulated emission data and additionally, the few absorption spectra which are currently available.

Photochemical synthesis is again the subject in Chapter 4. Paul Wender, Lorenz Siggel, and John Nuss provide a well-integrated exposition of the use of the intramolecular photocycloaddition of arenes with alkenes as a methodology for the total synthesis of cedrene and polyquinanes such as hirsutene, coriolin, and (-)-retigeranic acid, to name a few. Electronic and steric factors controlling the regiochemistry and stereochemistry of cycloaddition are clearly illustrated. Quite a good mechanistic treatment is given of the *ortho*, *meta*, and *para* orientation for alkene additions to substituted benzenes, replete with an interesting historical perspective.

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The Problem Solvers. By E. J. Kahn, Jr. Little, Brown: New York. 1986. 234 pp. \$19.95. ISBN 0-316-48212-9.

An old adage describes the impossibility of creating a silk purse from a sow's ear. This aphorism so irritated Dr. Arthur D. Little that he set out deliberately to demonstrate that the task could, in fact, be accomplished. In the early 1920s researchers at the firm which bears his name extracted a viscous goo from 100 pounds of slaughtered sows' ears. From this material they succeeded in producing a synthetic thread which was converted into a pair of stylish purses. The solution to this problem is but one of many vignettes found in the aptly titled *The Problem Solvers*, an account of the first century of Arthur D. Little, Inc., one of the giants in the consulting industry it spawned.

The book was published in 1986 based on interviews conducted through 1984. Therefore, for today's reader much of the material, especially that pertaining to the revolution in electronic technology, will seem quaintly dated. Of special interest to the chemical community will be the descriptions of the early years of Arthur D. Little, Inc., which began as a two-person operation specializing in chemical analysis. From these humble origins the company has grown to thousands of employees worldwide with revenues in the hundreds of millions of dollars annually.

E. J. Kahn, Jr., is a staff writer for the *New Yorker* and the author of more than 20 books. His unexplained fascination with the endeavors of Arthur D. Little, Inc., apparently prompted an exploration of the company's inner workings. The outcome of this investigation is a set of loosely interrelated anecdotes about the firm and its employees. These tales were evidently culled from interviews with key company personnel, past and present. Often these reminiscences seem to have been thrown together randomly without any obvious interconnections. This makes for rather disjointed reading although the writing is light and breezy.

The Problem Solvers can hardly be characterized as the definitive oral history of the company. Will it be recognized as a major contribution to the history of science? Probably not, but that is not its intent. Rather, the book is a celebration of a great company on the occasion of the 100th anniversary of its founding. The result is a delectable smorgasbord of incidental information which provides a revealing glimpse into the changes in corporate America over the past century.

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