Book Reviews *

Reagents for Organic Synthesis. Volume 17. By Mary Fieser (Harvard University). Wiley-Interscience: New York. 1994. 443 pp. $54.95. ISBN 0471000744.

This book is the latest volume of a series which describes recent advances in organic synthesis by focusing on the reagent (or catalyst) used for a particular transformation. The chemistry using the reagent is usually dealt with, but in selected cases, reference is made to the preparation of the reagent (e.g., $RCrCl_2$). The presentation is usually brief and succinct and is excellent as a resource book. The organization follows that of previous volumes (i.e., reagents examined in alphabetical order, followed by author and subject indexes).

This reviewer not only uses this book, like others in the series, to obtain information on a specific reagent being considered for use in research but also enjoys scanning through the volume where useful information can be obtained for other applications. This book is reasonably priced and can be warmly recommended for purchase by chemists.

Howard Alper, *University of Ottawa*

JA945059I

Gaseous Molecular Ions: An Introduction to Elementary Processes Induced by Ionization. By E. Illenberger (Freie Universität Berlin) and J. Momigny (Université de Liège). Steinkopff Verlag: Darmstadt, Germany. 1992. 350 pp. $50.00. ISBN 3-7985-0870-4.

The book *Gaseous Molecular Ions* is by all appearances a very worthwhile addition to the mass spectrometric literature. In spite of its modest 330 pages, the table of contents shows that this book is very broad in scope, covering both negative and positive ions, theory as well as experiments. A unique aspect is that it deals primarily with the physical chemistry of molecular ions. At the same time, the authors have chosen to cover the various topics in a qualitative manner, giving only the important equations, without many of the derivations. It will thus be quite useful to many practitioners in the field of mass spectrometry who are interested in obtaining a general understanding of such topics as dispersive energy analyzers, photodetachment spectroscopy of negative ions, threshold laws in ionization, the kinetic shift, metastable peak shapes, RRKM theory, electron attachment processes, etc.

This book is divided into three parts, the middle section written by J. Momigny while the other two sections are written by E. Illenberger. Part I, dealing with instrumentation, is excellent. The various topics of PES, PIMS, PEPICO, VUV light sources, mass and energy analyzers, and ion and electron detectors are very well treated in the 75 pages allotted to this section. Just enough information is given to provide a physical understanding of the techniques. Many important equations are presented which will permit the reader to use this book to design, for instance, a TOF system with a reflectron.

Part II (150 pages) dealing with the theory of unimolecular decay is unfortunately, not up to the level of parts I and III. The use of English is cumbersome, so a number of points are not stated as clearly as they could be. Although many useful topics are discussed, the material tends to be rather dated. For instance, the Beyer and Swinehart (1973) method for calculating sums and densities of states by direct count is not mentioned, a serious oversight since this method is far simpler, faster, and more elegant than the brute force method suggested by the authors.

Part III (65 pages), dealing with negative ions and their formation, detection, and analysis, is very well written. It covers such topics as electron affinities, electron attachment spectroscopy, electron transmission and the formation of transient negative ions, and electron attachment to clusters and condensed phase molecules. This section is full of helpful examples and wonderful physical insights which help one understand some of the subtleties involved in the study of negative ions.

Tomas Baer, *University of North Carolina, Chapel Hill*

JA9448531

Electron Correlations in Molecules and Solids, 2nd Edition. Solid State Sciences. By Peter Fulde (Max Planck Institut, Stuttgart). Springer Verlag: New York. 1993. xiv + 422 pp. $52.00. ISBN 0-387-56376-8.

Electron correlation has historically been one of the thorniest and most contentious topics in quantum theory. The surest way I know to provoke a fistfight is to walk into a roomful of electronic structure theorists and make a statement (any statement) about correlation. Half the room will agree, half will object, and well over half will be confused. The discussion is certain to become heated, and if it continues more than half an hour, there is a serious risk of gunplay.

This problem is particularly acute in discussions between quantum chemists and solid-state physicists. Even the basic definition of correlation is different in the two fields. For the chemist, the self-consistent or mean-field interelectron repulsion is not a correlation effect; for the physicist, it is. The physicist tends to think of correlation in terms of on-site and intersite effects, which are inherently valence-bond concepts. Most recent quantum chemical research has been carried out using the complementary picture of delocalized, canonical orbitals. Even though members of the two research communities have begun to work on very similar problems in recent years, they remain separated by a broad gulf of culture and vocabulary.

Peter Fulde's stated goal in this monograph is "to present the problem of electron correlations in molecules and solids in a unified form." The book does not achieve that goal, but the task is a tremendously difficult one.

Fulde's book is generally well-written and clear, although its level is too advanced for a beginning student. Its greatest virtue is that it brings together in a single volume a large number of correlation topics which are usually studied separately, by narrow and disjoint subsets of the research community. However, the discussion of each topic is necessarily brief, probably too brief to be satisfying to an active researcher in the field.

The book is written primarily from the solid-state physicist's perspective. In the first half of the monograph, there are a number of nods toward quantum chemistry, but these sections suffer from many important omissions.

The most famous and influential correlation paper in the history of quantum chemistry was Löwdin's 1959 review article, which cut through the Gordian knot of fuzzy definitions of electron correlation that preceded it (Löwdin, P. O. *Adv. Chem. Phys.* **1959**, *2*, 207). This article appears nowhere in Fulde's text or bibliography. A brief discussion of the Thomas–Fermi method does not mention the fact that this approximation will not give interatomic bonding; from the chemist's point of view, this is its most important feature. Fulde's discussion of nonlocal gradient corrections in density-functional theory makes no reference to the work of Axel Becke, which is certainly the most important and interesting recent work on that topic. The section on the independent-electron approximation assumes implicitly that this approximation demands only a single Slater determinant, but it is well-known that, in many situations (e.g., open-shell singlets or systems of high symmetry), the Hartree–Fock wave function can require more than a single determinant in order to satisfy all the symmetries of the system.

The latter half of the book deals primarily with solid-state topics using solid-state formalisms, and here, the author is on firmer ground. These chapters include brief but clear treatments of such staples as the Fermi liquid, the Kondo effect, the Hubbard Hamiltonian, and heavy-fermion systems. The final sections, on high-T_c superconductors, are probably premature.

Fulde has made a worthwhile effort toward an important goal; although that goal is not achieved here, this book does serve as a useful topical collection on correlation problems. A definitive and unifying

*Unsigned book reviews are by the Book Review Editor.

monograph on correlation effects in molecules and solids is sorely needed, but it still remains to be written.

Michael Cook, *University of Massachusetts, Amherst*

JA934712J

Shape in Chemistry. An Introduction to Molecular Shape and Topology. By Paul G. Mezey (University of Saskatchewan). VCH: New York. 1993. xii + 224 pp. $75.00. ISBN 0-89573-727-2.

This book addresses the characterization and utilization of molecular "shape". Such shapes are presumed to be already given from (1) equidensity surfaces (of electron density), (2) superpositions of Van der Waals spheres about each atom, (3) equipotential surfaces (for molecular potential energy or more simply for just the nuclear potential energy), or (4) perhaps just the backbone curve of a polymer (such as a protein). Granted such molecular shapes' different "algebrazations" are considered, and since generally this leads to extensive condensation of the complete shape information, the focus devolves to the identification of what should be important numerical shape descriptors. To this end various fundamental mathematical ideas are utilized—say concerning differential-geometric characterisitics of surfaces, topological manifolds along with their homology groups and Betti numbers, or knot theory and Jones polynomial invariants. Such ideas to many chemists may be viewed as somewhat daunting—but the background in these areas seems to me to be relatively nicely developed by Mezey (avoiding some of the more extreme generalities, of which topologists seem often to be fond), and focus is directed to the aspects deemed useful for the molecular applications. Then, with this background, there are described several recently studied, seemingly very potent ways of numerically (or algebraically) characterizing shape, in terms of shape codes, shape matrices, etc., each such shape invariant being discussed to give a feel for the encoded shape information, and too there are illustrative (and illustrated) examples. Further, Mezey describes how these shape descriptors lead to measures of molecular similarity, molecular complentarity, molecular symmetry, and molecular chirality—again with examples. Indications are given of the utility in application to "quantitative shape−activity relations", to drug design, and in general to "molecular engineering".

Overall, Mezey has written an informative book about currently developing mathematically based shape-related ideas and techniques of much fundamental potential use for chemistry. It seems to me that the book should be of keen interest to researchers concerned rather generally with structure−property correlations. Though additional ideas will develop in this area, the fundamental background and the rationale in developing the various shape descriptors seem sound, and too, surely some of Mezey's emphasized invariants will survive as favored descriptors.

D. J. Klein, *Texas A & M University at Galveston*

JA944830M

Chemistry of Nucleosides and Nucleotides. Volume 3. Edited by Leroy B. Townsend (University of Michigan). Plenum Press: New York and London. 1994. xiii + 553 pp. $120.00. ISBN 0-306-44474-7.

This book is a timely addition to the previous two volumes of the series edited by Townsend. There are five chapters, each a comprehensive review of recent published research in the chemistry of nucleosides and nucleotides. A useful subject index is also included to facilitate searches of specific topics. Literature citations are extensive, and coverage up to 1993 is included in most cases.

The first chapter, written by M. N. Preobrazhenskaya and I. A. Korbukh of the Russian Academy of Sciences, reviews the synthesis and reactivity of pyrrole, pyrazole, triazole, indole, indazole, and benzotriazole nucleosides and nucleotides. This chapter is 105 pages long and has 317 references. Detailed syntheses of the nucleosides are presented, including methodologies for glycosylations. Chemical properties such as acid hydrolysis, isomerizations, transformations of the heterocyclic base, and transformations of the carbohydrate moiety are reviewed. There is a brief section on the use of NMR spectral data to examine the configuration and conformation of some of the molecules.

The second chapter is written by S. Chladek of the Michigan Cancer Foundation and covers the topic of peptidyl nucleosides and nucleotides, including aminoacyl nucleoside antibiotics. It is 37 pages long with 142 references. The chemical properties of the ester linkage of amino acids bonded to the 2′ or 3′ position of ribonucleosides or ribonucleotides are presented. The syntheses of 2′(3′)-*O*-aminoacyl nucleosides, nucleotides, and oligonucleotides are also reviewed.

This third chapter is written by W. Pfleiderer of the University of Konstanz and describes the synthesis and reactivity of nucleosides and nucleotides with various fused-ring bases. It is 117 pages long with 233 references. The chapter covers a variety of bicyclic heterocyclic nucleosides including benzo-fused six-membered ring nitrogen heterocyclic nucleosides, pyrido-fused five- and six-membered ring nitrogen heterocyclic nucleosides, pyrimido-fused five- and six-membered ring heterocyclic nucleosides, bicyclic sulfur-containing nitrogen heterocyclic nucleosides, and pteridine nucleosides. The phosphorylated derivatives make up a minor part of the chapter.

The fourth chapter, written by G. Shaw of the University of Bradford, covers the syntheses and reactivities of imidazole and benzimidazole nucleosides and nucleotides and is 158 pages long with 359 references. In the first part of this chapter, a discussion of the *de novo* biosyntheses of imidazole and benzimidazole nucleosides and nucleotides is presented. This is followed by a review of the various methods of synthesis of these molecules. Reactions such as the conversion to purine nucleosides, alkylations, ring openings, and phosphorylations are also reviewed. Some of the physical data for this class of compounds such as UV, optical rotation, and proton NMR are presented in tabular form in the chapter. Data on ionization constants and circular dichroism are also briefly discussed.

The fifth chapter is written by K. A. Watanabe of the Sloan-Kettering Institute for Cancer Research and reviews the chemistry of C-nucleosides. This chapter is 115 pages long with 373 references. It contains a compilation of C-nucleosides isolated from natural sources and the syntheses of C-nucleosides from carbohydrate as well as non-carbohydrate precursors. The reactivities of these molecules are presented in terms of modifications of the heterocyclic and carbohydrate moieties.

This book will be of most benefit to organic and medicinal chemists, although anyone with an interest in nucleosides and nucleotides, including biochemists, pharmacologists, virologists, and oncologists, will find it useful. With some exceptions, biological data, such as antiviral and anticancer activities, have not been included for the various classes of compounds. However, this volume on the chemistry of nucleosides and nucleotides, like its forerunners, provides an excellent reference source for scientists in both academia and industry.

Vasu Nair, *The University of Iowa*

JA945058Q

Organic Reactions. Volume 46. Edited by Leo A. Paquette (Ohio State University). Wiley & Sons: New York. 1994. xi + 393 pp. $89.95. ISBN 0-471-08619-3.

The volumes of *Organic Reactions* compile critical discussions of the more important reactions, with each chapter devoted to a single reaction or a definite phase of a reaction of wide applicability. Subjects are presented from the preparative viewpoint, and particular attention is given to limitations, interfering influences, effects of structure, and the selection of experimental techniques. Chapter headings include (1) Tin(II) Enolates in the Aldol, Michael and Related Reactions, (2) The [2,3]-Wittig reaction, and (3) Reductions with Samarium(II) Iodide. There are indexes of cumulative chapter titles, authors, and chapters and topics.

JA955127G

Molecular Structure and Statistical Thermodynamics: Selected Papers of Kenneth S. Pitzer. Edited by Kenneth S. Pitzer (University of California, Berkeley). World Scientific: Singapore. 1993. xvii + 517 pp. $65.00. ISBN 981-02-1439-1.

In the course of a distinguished 50-year career, Professor Pitzer pioneered research on molecules with internal rotation, the acentric factor theory for fluids, relativistic quantum chemistry for molecules with heavy atoms, and the Pitzer equations for complex aqueous solutions. Part I, Molecules, includes papers in three subject areas: Barriers to Internal Rotation, Ring Molecules, and Relativistic Effects on Molecular Properties. Part II, Dense Phases, covers Extended Corresponding States and the Acentric Factor, Spin Species Conversion in Methane, Semiempirical Equations for Aqueous Electrolytes, and Other Condensed-State Papers. The papers are updated with recent comments by the author.

JA955126O