

Book Reviews

Progress in the Chemistry of Organic Natural Products. Volume 62. Fortschritte der Chemie Organischer Naturstoffe. Edited by W. Herz (Florida State University), G. W. Kirby (The University, Glasgow, Scotland), R. E. Moore (University of Hawaii at Monoa), W. Steglich (Universität München), and Ch. Tamm (Universität Basel). Springer Verlag: Wien. 1993. viii + 330 pp. DM 280.00. ISBN 0-387-82401-2.

This is Volume 62 of the classic *Fortschritte der Chemie organischer Naturstoffe* reviews within the field of natural products chemistry. In this volume, two major reviews are featured: Forskolin and Congeners by Sujata V. Bhat and Steroidal Oligoglycosides and Polyhydroxysteroids from Echinoderms by L. Minale, R. Riccio and F. Zollo. Volume 62 is consistent with the generally high standards of past volumes within this series. The articles presented here are up-to-date analyses of developments within their respective fields and are thus important reference publications.

In the first part of Volume 62, Sujata V. Bhat provides a detailed overview of the history, botanical origin, ethnopharmacology, and chemical syntheses of diterpenoids of the Forskolin class. His review is particularly fascinating as it includes a historical account of the traditional uses of mint family plants in treating diseases involving cardiovascular, bronchopulmonary, and renal system dysfunctions. The chapter is inclusive in providing a complete account of the discovery of forskolin, in 1977, and the subsequent enormous scientific interest shown in this molecule. Sections on the isolation, structure determination, and chemistry of forskolin are followed by extensive discussions of numerous approaches to the syntheses of forskolin and its congeners. Also included are sections on the more recent pharmacology and structure-activity relationships within this class of compounds. Overall, this is a comprehensive, well-referenced, and timely review of an important class of bioactive natural products. It will serve as an important reference to those involved in terrestrial plant research.

The second half of Volume 62 is dedicated to an extensive analysis of the highly-oxygenated steroidal metabolites, both steroidal oligoglycosides and polyhydroxysteroids, produced by marine echinoderms. The review is focused on the chemistry of two echinoderm classes, the starfish (Asteroidea) and brittle stars (Ophiuroidea). The steroidal glycosides, well-known historically as fish toxins and defensive agents, were structurally unknown until the advent, in the 1980s, of appropriate HPLC separation methods, FAB mass spectrometry, and high-resolution NMR. Only during the past decade have the structural complexities of these molecules been defined. In constructing this review, Minale, Riccio, and Zollo should be credited for an exceptional job in organizing a massive data set comprising over 250 compounds and 190 references. The authors organize their chapter to include the novel methods required to isolate and purify these highly polar, often awkward, metabolites. Several tabulations of proton and carbon NMR data, which are particularly useful in differentiating between similar glycosides possessing different hexose isomers, are included. Additional spectroscopic information is presented with respect to studies of the absolute stereochemistry of substituents on the steroidal side chain. In total, the structures, occurrence, and physical and selected spectroscopic properties of 289 steroidal glycosides and polyhydroxysteroids are presented. At the end of the chapter, an alphabetical name index of the compounds, with molecular weights and formulas, is also provided. Overall, this is a superb reference for those wishing access to a comprehensive listing of these compounds. The added analyses of structures and attention to fine points of stereochemistry make this an excellent contribution and a valuable reference to these complex steroidal metabolites.

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JA934738A

Superacids and Acidic Melts as Inorganic Chemical Reaction Media. By Thomas A. O'Donnell (University of Melbourne). VCH: New York. 1993. xii + 244 pp. \$110.00. ISBN 1-56081-035-1.

Whereas most books on nonaqueous solvents tend to devote a separate chapter to each solvent or solvent class, this book is much

more solute-oriented. This is demonstrated by five (of the 10) chapters having the titles: Polyatomic Cations of Nonmetallic Elements, Homopolyatomic Cations of Metallic Elements, Transition Element Cations in "Normal" Oxidation States in Protonic Superacids and Acidic Melts, Cations of Transition Elements in Low Oxidation States, and Polyatomic Anions in Basic Media.

The material of the book is well-researched; the author knows the literature well and is not afraid to draw reasonable conclusions nor to criticize others for jumping to unreasonable ones. One major proposition put forward is that "despite differences in the chemical nature and temperature domains of various reaction media, elements will be expected to exist as cations under sufficiently acidic conditions and as anions in basic media." The author is careful to write "solvated cations" in some instances but too often leaves the notion that the cations are partially clad, if not "naked", while in fact there is always the next coordination sphere! There are a few specific places where I take issue with the author's comments, but I found few mistakes or typographical errors.

The one disappointing feature of the book is the absence of a formula index—in order to learn what is written about Se_8^{2+} , Sm^{2+} , or FeCl_2^{2+} , I must check all appropriate chapters; even a list of chapter subheadings would help. In conclusion, I enjoyed reading the book and recommend it to researchers and senior undergraduate and graduate students as a useful critique of the area.

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JA944895P

Phase Transfer Catalysis. Selected Problems and Applications. By Yuri Goldberg (Latvian Academy of Science). Gordon Breach Science Publishers: Philadelphia, PA. 1992. xvi + 456 pp. \$170.00. ISBN 2-88124-870-5.

Phase-transfer catalysis (PTC) is a general methodology widely used in organic synthesis research laboratory practice and in large-scale industrial processes. Practical attractiveness of this methodology, its application to a wide range of organic reactions, and many fascinating mechanistic problems result in continuous interest for research in this field and the flow of publications presenting new results and concepts.

Indeed, numerous review papers, chapters, and monographs describing these problems have been published. In spite of such rich literature dealing with this subject, some aspects of PTC are still not sufficiently understood and misleading opinions are alive. It is therefore appropriate and desirable that new texts are appearing which could further promote this methodology, bring up to date compilations of new results, and help to eliminate eventual misunderstandings. The monograph *Phase Transfer Catalysis* by E. V. Dehmlow (3rd ed., VCH Publishers: Weinheim, 1993) serves this purpose in a general way. The aim of this monograph is somewhat different than that of Dehmlow. As stated in the title, it presents Selected Problems and Applications of PTC, and these are discussed in a more detailed way than in general texts.

In Chapter 1, Basic Principles of Phase Transfer Catalysis, there is a short presentation of concepts, history, catalysts, conditions, and mechanisms of PTC. Although the milestones of these discoveries are properly presented, the references given to the original paper by C. M. Starks from 1971 and our review from 1975 (not our original papers from 1965–69) create an improper impression concerning priority. In Chapter 2, Phase-Transfer Catalysis in Chemistry of Nitrogen Containing Heterocycles, a variety of reactions such as alkylation, acylation, carbene reaction, etc., as well as ring closure under PTC conditions are presented. This chapter is the longest one and gives a lot of information. Reading it, I got the impression that the author's efforts to present the material in an orderly way were not always successful. Chapters 3 and 4, Phase Transfer Catalysis in Organometallic Chemistry and Metal Complex Catalysis, cover examples of the use of PTC in synthesis and transformations of organometallics, including organosilicon compounds, and the very interesting combinations of PTC and organometallic catalysis in such important reactions as carbonylation, reduction and oxidation, carbon-carbon coupling, etc. These chapters are of particular value because general texts treat the related problems separately. Chapter 5, Triphase Catalysis, presents possibilities con-

nected with the use of the polymer-bound catalysts such as tetraalkyl ammonium salts or macrocyclic polyethers in PTC reactions. There is a contradiction between highly-promoted advantages connected with the use of such catalysts and the information that in reality these catalysts can seldom be efficiently reused. In Chapter 6, Asymmetric Phase-Transfer Catalysis, the very important problem of enantioselective synthesis under an influence of a chiral PT catalyst is described. Although this problem is presented in detail, I could not find a generalization, nor the author's opinion concerning the future of this important field in which there are few successes. Finally, in Chapter 7, Nontypical Variants of Phase-Transfer Catalysis, a variety of interesting transformations catalyzed by transfer of active species between phases assisted by various transfer agents are presented.

These titles and short characteristics of the chapters define the scope of the book, which unquestionably addresses the most vital and actual problems of PTC and gives a wealth of information. This monograph is valuable reading for chemists interested in organic synthesis, organometallic chemistry, physical organic chemistry, and related topics working in academic and industrial laboratories.

I have, however, a few critical remarks and comments. First, in a monograph in which only selected problems of PTC are addressed, one could expect that the material be treated not only in a comprehensive but also in a critical way. Although the former expectation is nicely fulfilled, it is difficult to find a critical assessment of the results and concepts described in cited publications presented in the book. I am sorry to say that there are many spelling errors which are not necessarily due to the printing process. The unforgivable one is that Prof. E. J. Corey is spelled a few times as Cory (pp ix, 330). Minor spelling errors are very frequent.

The reaction schemes are well-designed and also give valuable information concerning the reaction conditions; there are, however, some errors in structural formulas (e.g. pp 103, 142, 238, 240, 241). Moreover, often different sizes of rings and font are used, even on the same page, so the aesthetic impressions are spoiled. There are also a few incorrect statements, e.g. that esters of phenylacetic acids cannot be alkylated under PTC conditions (p 165). In Subchapter 7.3, Interfacial Reactions Involving Neutral Molecules, the majority of reactions described do not proceed at the interface and with protonated molecules.

In my opinion, the book is a valuable source of information concerning selected topics of phase-transfer catalysis; however, due to the absence of a deeper critical discussion, many printing errors, etc., my overall impression is not very enthusiastic. I think that libraries should have a copy of this monograph, but taking into account its relatively high price, I do not expect that many individual researchers will decide to purchase a copy.

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JA934833J

The Chemistry of Organophosphorus Compounds. Volume 3. Phosphonium Salts, Ylides and Phosphoranes. Edited by Frank R. Hartley (Cranfield University). Wiley Interscience: New York, 1994. xvi + 442 pp. \$395.00. ISBN 0-471-93057-1.

This book is Volume 3 of a four-volume work dealing with the chemistry of organophosphorus compounds and is part of the well-known series of books *The Chemistry of Functional Groups*. This volume covers phosphonium salts, phosphonium ylides, and phosphoranes. (Volume 1 covers phosphines, polyphosphines, and phosphorus-containing heterocycles; Volume 2 covers phosphine oxides, sulfides,

selenides, and tellurides; Volume 4 is intended to cover phosphinous, phosphonous, phosphinic, and phosphonic acid compounds and halogen derivatives.) This work is an excellent reference in the tradition of *The Chemistry of Functional Group* series. It brings together material from current organophosphorus chemistry into one reference, referring, whenever appropriate, to leading or more detailed reviews.

There are seven chapters in Volume 3 of *The Chemistry of Organophosphorus Compounds*. Chapter 1 (D. G. Gilheany: 44 pages, 308 references) deals with structure and bonding of phosphonium ylides, salts, and phosphoranes, and it provides a very informative discussion of current theory concerning the involvement of d-orbitals in the bonding picture of these materials. This chapter includes many references to reviews and computational treatments of these systems. Chapter 2 (H.-J. Cristau and F. Plenat: 139 pages, 910 references) is a large and extensive review of the preparation, properties, and reactions of phosphonium salts, and it includes spectroscopic properties and modern applications of phosphonium salt chemistry (including polyphosphonium salts and polymer-supported phosphonium salts). Chapter 3 (R. Burgada and R. Setton: 88 pages, 363 references) covers preparation, properties, and reaction of phosphoranes, and it includes detailed descriptions of geometrical and stereochemical considerations. The discussion of trigonal bipyramidal vs tetragonal pyramidal geometries, apicophilicity, and pseudorotation vs turnstile isomerization complement the theoretical presentations in Chapter 1. Chapter 4 (S. M. Bachrach and C. I. Nitsche: 30 pages, 95 references) reviews the structure, bonding, and spectroscopic properties of phosphonium ylides. This chapter reiterates a number of concepts and structural examples brought out in chapter 1, but in generally greater and complementary detail. Nevertheless, a merger of these two chapters would have avoided unnecessary duplication and combined the information into one location. Chapter 5 (K. S. V. Santhanam: 21 pages, 58 references) provides a brief survey of the electrochemistry of ylides, phosphoranes, and phosphonium salts and includes synthetic aspects of electrochemical Wittig reactions, electrochemical reductive cleavage of phosphonium salts, generation of anion radicals, and conductivities of phosphoranes. Chapter 6 (M. Dankowski: 19 pages, 121 references) emphasizes the preparative aspects of the photochemistry of phosphonium salts, phosphoranes, and ylides. Chapter 7 (H. Feilchenfeld: 45 pages, 403 references), entitled Chemical Analysis of Organophosphorus Compounds, does not seem to fit in a book dealing with phosphonium salts, ylides, and phosphoranes. The chapter describes general techniques for analysis of phosphorus, decomposition of organophosphorus compounds, and oxidation to inorganic phosphate and various techniques for analysis of phosphate (gravimetric analysis, various titration techniques, etc.) as well as extraction, detection, and structure determination of organophosphorus compounds (useful in environmental and biochemical applications). Although perhaps out of place in a volume on functional groups, this review should nonetheless be useful.

The series, *The Chemistry of Organophosphorus Compounds*, is not intended to be an encyclopedia but rather refers to important reviews, monographs, textbooks, etc., and emphasizes recent material and/or subject matter not previously reviewed. Volume 3 of the series certainly fulfills these aims. The book is a modern, up-to-date, and advanced volume, not particularly suitable for an introduction to organophosphorus chemistry, but rather a reference source for researchers in the field. The book (and the series) would be an extremely welcome addition to a research library, but the cost (\$475 for Volumes 1 and 2; \$395 for Volume 3) makes it somewhat prohibitive for individuals.

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