Porphyrin Paradise!

The Porphyrin Handbook. Vols. 1–10. Edited by *Karl M. Kadish, Kevin M. Smith* and *Roger Guilard*. Academic Press, San Diego 2000. 3607 pp., hardcover approx. $ 3500.00.—10-volume set: ISBN 0-12-393200-9;
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This 10-volume work on porphyrin chemistry, edited by Karl M. Kadish, Kevin M. Smith, and Roger Guilard, was published to coincide with the first International Conference on Porphyrins and Phthalocyanines, which took place in Dijon, France, on 25–30 June 2000. The handbook, containing 61 articles by over 100 authors, will certainly become a standard work on porphyrin chemistry, taking the place of older works such as D. Dolphin's *The Porphyrins* and K. M. Smith's *Porphyrins and Metalloporphyrins*. Nevertheless, some existing monographs on aspects of the broad field of porphyrin and tetrapyrrole chemistry will continue to be important, as they contain specialized or more detailed information, or treat topics that are touched on only marginally or not at all in this new work. The great merit of this 10-volume work lies in its competent treatments, by well recognized experts, of the many aspects of the chemistry, physics, biology, and pharmacology of the classical fully unsaturated porphyrins and of the corroles, isocorroles, isoporphyrins, carbaporphyrins, azaporphyrins, "expanded" porphyrins, and heteroporphyrins. The synthetic design of the latter macrocycles is based on the porphyrin as a structural lead.

Volume 1, *Synthesis and Organic Chemistry*, treats the classical porphyrins from the standpoints defined by this title. In the first chapter K. M. Smith gives a useful overview of total and partial syntheses of octaalkylporphyrins and their reduced derivatives. From the vast literature on the subject the author has selected representative examples of different synthetic strategies and discusses their advantages and disadvantages, in a lucid treatment that can also be understood by nonspecialists.

In Chapter 2 J. S. Lindsay describes the synthesis of meso-substituted porphyrins, mainly with aryl groups as substituents. Because these systems can be synthesized easily, numerous compounds of this porphinoid class have been prepared, and are used in most of the many areas of porphyrin chemistry research. The author gives an excellent account of the various synthetic routes to the target structures and the subsequent modifications that are possible, and summarizes the many structural variants in clear and systematic tables with literature references. In such an extensive work it is, of course, not possible for the reviewers to describe all the articles in detail. However, Chapters 4 and 5 deserve a special mention from the standpoint of synthetic chemistry; these contain clear descriptions of methods for the subsequent functionalization of porphyrins and meso-substituted porphyrins. The modification of naturally occurring porphyrins such as heme, chlorophyll, and meso-tetraarylporphyrins opens up many possibilities for synthesizing interesting new structures. In such a large work as this, some errors have inevitably crept in and can mostly be tolerated. However, the confusion between mesomerism arrows and tautomerism arrows should not happen. Also, more attention should have been given to observing the proper conventions in drawing structural formulas. The chapter on "Geochemistry of Porphyrins" makes interesting and enjoyable reading. Geoporphyrins are formed by the partical degradation of "natural" porphyrins in geological formations. The formation and the isolation and identification of the products, as well as their geological importance, are described clearly. However, a separate article about "naturally occurring" porphyrins, as a prelude to this chapter, would have been a useful addition.

Volume 2, *Heteroporphyrins, Expanded Porphyrins and Related Macrocycles*, reviews the chemistry of this new and very active area of research. The individual articles are all very competently written, as the editors have succeeded in attracting authors who initiated this field of work and have had a major influence on it during the past two decades. In particular the chemistry of the corroles, a topic started in the 1960s by A. W. Johnson, has recently undergone a renaissance and is treated in two articles. This area of research arose out of work on the chemistry of vitamin B_{12} and the corrins. Therefore it would have been useful at this point to include a contribution on corrin chemistry, which was further developed after the pioneering work of Eschenmoser and Woodward in the field of vitamin B_{12} synthesis.

The many important chemical functions associated with porphinoid structures mainly depend on complexation with metals, leading to catalytic or redox reactions mediated by the central complexed metal atom. In Volume 3, *Inorganic, Organometallic and Coordination Chemistry*, the chemical, synthetic, structural, electrochemical, and spectroscopic aspects of such functions are covered by various authors who have been active in this area for years and have made

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fundamental contributions. Chapters 22–25 describe recent developments in endowing supramolecular systems with special functions and investigating the organometallic and coordination chemistry of porphyrinogens, the reduced nonconjugated compounds of the porphyrin family.

Volume 4 is entitled *Biochemistry and Binding: Activation of Small Molecules*, and is mainly concerned with the chemistry and biochemistry of oxidation reactions mediated by iron-containing porphyrins (hemes). Building on our knowledge of the oxidation processes involving various heme proteins that occur in nature, a very productive area of chemical research has developed, and includes other metals, in particular manganese and ruthenium. As one might expect, the main focus is on the activation of oxygen for oxidation processes, but appropriate attention is also given to the growing importance of the use of heme systems and other metalloporphyrins for the activation of NO and halogens. The chapters describe in thorough detail the wide diversity of the different metalloporphyrins, their intermediates in higher valence states and their reactions, and the molecules formed by reaction with various substrates. The only complaint about this volume is that it does not include any metalloporphyrinoids with properties corresponding to the chemistry of the naturally occurring cobalt corrins and the nickel-containing factor F-430.

Volume 5 is devoted to NMR and EPR spectroscopies, which are important methods for studying the structure and dynamics of porphyrins and their derivatives. The first third of the volume deals with the NMR spectroscopy of diamagnetic metalloporphyrinoids, while the rest of the volume is devoted to the use of EPR spectroscopy for characterizing paramagnetic metalloporphyrins. The latter method is described in detail, including the theoretical basis, and its applications to various heme systems and heme proteins are described. In this way one can arrive at an accurate picture of the structure, coordination, and function of heme systems in their natural protein environment.

The many different ways in which porphyrins can be modified by introducing structural variations, organizing in oligomers and supramolecular structures, or immobilizing on surfaces by adsorption or polymerization, have led to a correspondingly wide variety of applications. Important examples are systems imitating photosynthesis, new materials with special electrical and optical properties, porphyrins as polymerization catalysts, porphyrinoids as photosensitizers in photodynamic therapy, immobilized porphyrins as electrochemical sensors, and porphyrinoid systems as receptor models for molecular recognition and bonding of anions, all areas in which porphyrinoids are now regarded as indispensable. Volume 6, *Applications: Past, Present and Future*, contains a stimulating and well organized survey of this ever expanding field.

A comprehensive theoretical and physical description of porphyrins provides the basis for understanding their structure, dynamics, and functions, and involves special methods appropriate to the unique properties of this class of compounds. In Volume 7, *Theoretical and Physical Characterization*, specialists in their particular fields describe not only the most familiar methods, such as quantum-mechanical calculations, X-ray crystallography, mass spectrometry, and circular dichroism spectroscopy, but also some less widely used ones such as resonance Raman spectroscopy and X-ray absorption spectroscopy. However, it seems strange that some other spectroscopic methods, such as Mössbauer spectroscopy, are missing.

Although electron transfer processes are mentioned occasionally in the preceding volumes, Volume 8 provides a systematic treatment of all the relevant aspects. Electron transfer in porphyrins can be understood on the basis of their redox properties, which are studied by electrochemical methods. In the introductory chapter to this volume (Chapter 55 of the work as a whole) K. M. Kadish presents a comprehensive and systematic overview of the electrochemistry of porphyrins and their metal complexes. Further chapters expand on the theme in more detail for heme and heme proteins. D. Gust and T. A. Moore, two pioneers in the field of artificial photosynthesis, discuss light-induced electron transfer as the primary step in photosynthesis. Although the authors initiated this area of research and have greatly influenced its progress, more attention should also have been given to the contributions of other investigators.

Volumes 9 and 10 consist entirely of tables, listing redox potentials and bonding constants (Vol. 9) and X-ray crystallographic data (Vol. 10). The comprehensive and lucid compilation of these data provides an extremely valuable resource. However, its usefulness could have been still further improved by also offering the data in an electronic version, thus allowing more efficient searching. Also on this theme, when a new edition of the handbook is planned the editors should consider providing a complete index in electronic form.

To summarize, it is clear that with this handbook we now have a valuable standard work on porphyrin chemistry. At the price of $ 3500.00, the complete work is essentially only within the reach of libraries. Individuals may consider buying just the volumes of interest to them. In a future edition of the handbook it would be desirable to devote an appropriate amount of space to the chemistry of porphinoid natural products, and also to some other aspects such as the chemistry of corrins and some other special spectroscopic methods. Although monographs on the most important porphinoid natural products such as chlorophyll, vitamin B_{12}, and the bile pigments already exist, a handbook on porphyrin chemistry should not neglect these topics, as these structures are derived from porphyrin. To some extent they constitute the roots of the entire field, and recently the biochemistry, bioorganic chemistry, biosynthesis, and prebiotic chemistry of substances such as vitamin B_{12} have provided an important impetus for porphyrin research. In this connection it would also be interesting to have a detailed and systematic description of newly discovered porphinoid natural products from different biological sources, as these structures (e.g., in the case of the porphinoid factor F-430, which is involved in bacterial formation of methane) are associated with unique physiological functions.

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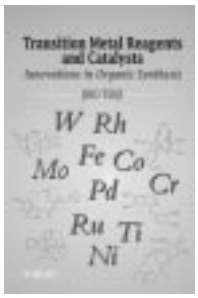
Transition Metal Reagents and Catalysts. Innovations in Organic Synthesis. By *Jiro Tsuji.* John Wiley & Sons Ltd., New York 2000. xv+477 pp., hardcover £ 125.00.—ISBN 0-471-63498-0

The readership for this book, written by a pioneer in the field of organotransition metal chemistry, is mainly intended to be synthetic organic chemists who are not yet intimately familiar with the many developments in the use of transition metals in the past 20 years. Appropriately, the book starts with a brief but insightful discussion of the early industrial processes that formed the very foundation for the development of synthetic applications of homogeneous transition metal catalysts, followed by a useful chapter on the major reaction classes and some mechanistic elaboration of transition metal complexes. Whenever possible, the author tries to draw analogies to organic reaction mechanisms that might be more familiar to the reader. The later chapters are ordered according to types of organic substrates and cover reactions of organic halides, allylic and propargylic compounds, conjugated dienes, alkenes, and alkynes. Finally, transition metal carbene complexes, protection and activation by coordination, catalytic hydrogenation, and Pd^{II} chemistry receive special attention in separate chapters. The metal carbene chapter also contains a section on metathesis processes. The focus lies mostly on catalytic processes in strong preference over stoichiometric transformations. Mechanistic information is presented for the most important transformations, but for many subtle ligand and additive effects the discussion is terse, and the reader will have to consult more specialized books or reviews. Many of the latter are listed as references in the text.



The original Japanese version of this book was published in 1997, and the present English edition has been updated and some examples have been revised. In general, references are well covered up to 1997, with a few mentions of work published in 1998. Accordingly, the book serves very well as a source of fundamentals and recent developments for the newcomer to the field.

Maybe not surprisingly, the coverage of organotransition metal chemistry is overall quite "palladium-centered", and in view of the huge amount of data that this area has produced, the specialist will find gaps and omissions, in particular in areas outside Pd^0 and Pd^{II} catalysis. For example, the coverage of cross-couplings of silicon, aluminum, and zirconium compounds with organic halides is outdated, and Fe-acyl enolates and Stryker's reagent have been omitted. Furthermore, whereas hydroboration, hydromagnesation, hydrozincation, hydroalumination, hydrostannation, and hydrosilylation have their own subchapters, hydrozirconation of alkenes receives only a very cursory treatment. Even the former transformations, while covered in the text, are missing from the index. The index is not nearly comprehensive, and this may be one of the few serious deficiencies in the book, since it is addressed to the novice, who is particularly dependent on extensive indexing and cross-referencing. Since the chapters are mostly ordered according to the organic substrate class, it is difficult to find information on a specific transition metal complex in the absence of some knowledge about its chemistry. The lack of an author index is also a noteworthy omission. In contrast, one of the strengths of this book is a vast and diverse collection of examples, with a good mix of elegant natural product syntheses that provide a reasonably fast assessment of the potential scope of the reaction. The back cover also presents a very nice summary of chiral and achiral phosphine ligands.

Text and structures in this book are of high quality and very reader-friendly. There are only few errors, such as a few reagents left out, or incorrect drawings of substructures in schemes. The accuracy of the references is excellent. Overall, this is a very valuable text for novices who want to gain an overview of the field of organotransition metal chemistry, and in particular in the area of palladium chemistry it could become a significant resource even for the expert.

While the very high retail price ($ 225 here in the USA) is unfortunately likely to severely limit personal acquisitions, *Transition Metal Reagents and Catalysts* can be recommended to anybody who wants to have access to a readable and relevant text to freshen up on current transition metal based technologies in organic synthesis.

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Organofluorine Compounds. Chemistry and Applications. Edited by *Hisashi Yamamoto*. Springer-Verlag, Heidelberg 2000. xii+272 pp., 96 figs., 37 tables, hardcover DM 198.00.—ISBN 3-540-66689-3

This book has been written by T. Hiyama of Kyoto University, a well known and respected scientist in the fluorine community. Mr K. Kanie and Drs. T. Kusumoto, Y. Morizawa, and M. Shimizu have contributed to various chapters of the book. As the title of this eight-chapter book implies, the subject is entirely devoted to C–F-containing compounds, beginning with a discussion on the physicochemical properties of fluorine and fluorine compounds, including a section on toxicity and first aid treatment in case of contact with HF or F_2. This is followed by two chapters on synthetic approaches to C–F bond formation. The first of them involves the transformation of a suitable functional group using electrophilic and nucleophilic fluorinating agents, electrochemistry, and a combination of an electrophile and a fluoride reagent. The second chapter in the sequence covers the burgeoning field of organofluorine building blocks. Chapter 4 describes succinctly key reactions of C–F bonds. Due to the small page format and limited size of the book (just a little over 260 pages) it is understandable that the coverage of building blocks and reactions of C–F bonds cannot be comprehensive. However, because of their importance to a practicing organic synthetic chemist, it is surprising that these topics have not received a wider cover-

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age. The largest section in the book consists of two chapters on applications of fluorine in biologically active compounds and the properties of fluorine-containing materials, including polymers. The final two chapters in the book focus on the new field of organic reactions in fluorous media and on the no less important role of fluorine in organic reactions (e.g., fluoride anion and trifluoroacetic acid).

According to the author, this book was written with the aim of "overviewing the large field of organofluorine chemistry on the basis of organic synthesis." Its merit lies in its conciseness and its readability, as well as in its small size that allows facile access to a variety of subjects through a clear and practical table of contents. Overall, the book offers a "convenience store" type approach to a field that has been reviewed exhaustively and regularly. In this regard, it is more a pocketbook than a treatise, and perhaps it is here where its strength lies. It is practical in the sense that it contains easily retrievable information and useful bibliography for a worker or graduate student entering the field of fluorine chemistry. The book places heavy emphasis on the application aspect of organofluorine compounds, as it dedicates almost 40% of its content to therapeutic and crop protection agents and polymers. Indeed, the author even lists structures of over sixty widely used fluorinated agrochemicals, providing the reader with a one-stop, quick glance at an area, with abundant information.

The bibliography cited throughout the book regularly includes references up to the mid-1990s, but it is thinner on material that appeared in the primary or secondary literature during the last five years. For example, in the section dedicated to ^{19}F NMR spectroscopy the author lists a number of well known sources of data for chemical shifts and coupling constants up to 1995, but fails to mention the more recent and very thorough monograph by Berger, Braun, and Kalinowski published in 1996. Similarly, in Chapter 3, the coverage of building blocks fails to provide important reviews on the subject, such as the one written by J. Percy in *Top. Curr. Chem.* (1997), or the review on fluorinated ylides authored by D. Burton in *Chem. Rev.* (1996).

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