Book Reviews

Solid-Phase Organic Synthesis. Edited by Kevin Burgess (Texas A & M University). Wiley Interscience: New York. 2000. xiv + 277 pp. $69.95. ISBN 0-471-31825-6.

This book seeks to highlight and critique key developments in solid-phase organic synthesis through a series of reviews written by some of the leaders in various aspects of the field. The book focuses primarily on the chemical modification of resin-bound substrates for the generation of products and libraries destined to be employed as drug candidates (Chapters 1−3), oligomers for polymer synthesis (Chapter 4), and natural products (Chapter 8). Polymer-bound reagents are reviewed in Chapter 5, which focuses mainly on resin-supported capture agents. The influence of the supports used for solid-phase chemistry is described in Chapter 6, among others, wherein the Chiron Technologies group reviews synthesis and compound tracking using radiation-grafted polymer surfaces. Unfortunately, the discussion fails to include details on the synthesis of the supports and their influence on reactivity. Analytical approaches for monitoring support-bound chemistry are described in different sections of selected chapters as well as in Chapter 7, which gives a thorough description of the application of IR techniques for monitoring solid-phase chemistry.

Among the eight chapters, many accomplish the goal of highlighting and critiquing key developments by reviewing the literature up to 1998 (with some citations from 1999), by commenting on what methods seem viable for effective library synthesis, and by focusing attention on useful techniques for conducting solid-phase reactions. For example, in Chapter 2 on Pd-catalyzed C−C bond formation on solid support, Todd and Abell cover effectively the developments of this important methodology and are quick to point out when approaches seem "robust and rapid", when attempts failed, and when "no details were given". Similarly, they emphasize useful strategies, such as Ellman's use of KCN/DMSO wash for removing deposited palladium from the resin. Chapters 3 and 4 focus more on the achievements made by their authors in the respective fields of heterocycle synthesis by S_nAr reactions and arylalkyne oligomer synthesis. These chapters include some unpublished results as well as more experimental details concerning the chemistry. Details on the actual techniques for applying polymer-bound reagents are less abundant in the review in Chapter 5, which surprisingly fails to cite pioneering discoveries (such as those made in the 1960s, 1970s, and 1980s by T. Wieland, D. L. Marshall, and E. T. Kaiser) in peptide science that form the foundation for the application of "polymer-supported substrates".

The text is well supported by illustrations that are usually clear and informative presentations of the material reviewed. One common inconvenience concerning the illustrations is their failure to define the type of resin, depicted as a ball, that is employed in each scheme. Sometimes this variable is defined on the scheme; however, in most cases one must consult the text for this pertinent information for understanding solid-phase reactivity.

Overall, the book effectively realizes its goal by providing a series of useful specialized reports. In many respects the book serves as an excellent follow-up to *Combinatorial Chemistry: Synthesis and Application*, edited by S. R. Wilson and A. W. Czarnik (Wiley: New York, 1997), by focusing attention on solid-phase synthesis without repeating material covered in this earlier text. In the Preface, Burgess suggests compilation and publication of such reports annually or biannually. In light of the rapid and growing application of solid-phase synthesis techniques in both the industrial and academic sectors, this suggestion is very reasonable since such books will serve as valuable reference tools for cataloging and reviewing accomplishments in the field.

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Modern Amination Methods. Edited by Alfredo Ricci (University of Bologna). Wiley-VCH: Weinheim. 2000. xvii + 268 pp. $168. ISBN 3-527-29976-9.

Organonitrogen compounds, and amines in particular, are immensely important as chemical intermediates and end-products, especially in the pharmaceutical and agricultural industries. As such, reactions that form C−N bonds are of great significance. This book includes seven chapters by prominent researchers in the field who review recent developments in the synthesis of amines but emphasize non-substitution reactions and stereoselective methods.

In the first chapter, K. A. Jorgensen reviews newer aspects of allylic amination methods, including nucleophilic amination of allylic electrophiles, and direct aminations of olefins, including ene-type and metal-promoted amination reactions. Illustrative examples are given, but extensive tables are not. In Chapter 2, E. Fernandez and J. M. Brown discuss electrophilic amination routes from alkenes, emphasizing net hydroaminations via hydroboration/ammonolysis. Little coverage of metal-promoted hydroamination is provided, despite the substantial activity in this area over the past decade. In Chapter 3, J.-P Genet, C. Greck, and D. Lavergne summarize developments in the area of electrophilic amination of olefins and enol derivatives (ene-type reactions) by sulfonoxycarbamates and azodicarboxylates, emphasizing diastereo- and enantioselective transformations. In the next chapter, H. Tietgen, M. Schultz-Kukula, and H. Kunz draw substantially on their own work to summarize the use of glycosylamines as chiral auxiliaries (usually via imine derivatives) in the stereoselective synthesis of chiral amines, particularly amino acids and heterocycles. C. S. Tomooka, H. Iikura, and E. M. Carreira then cover in Chapter 5 the synthesis of transition metal−nitride complexes (organized by metal). This topic only indirectly fits within the book title theme; however, these compounds are of interest synthetically as potential *N*-transfer agents, which are covered in Chapter 6. In Chapter 6, S. Minakata and M. Komatsu discuss asymmetric *N*-transfer reactions of olefins and enol derivatives with nitrido−Mn complexes. Included is a disappointingly brief coverage of aziridinations via other metal−nitrenoid reagents (e.g., Cu-catalyzed aziridinations) and more complete coverage of the synthesis and stoichiometric reactions of achiral and chiral salen−Mn−nitrido complexes, which generally provide aziridines (or α-amino ketones from enol derivatives). Finally, J. F. Hartwig provides an extensive review of Pd-catalyzed aminations of aryl electrophiles. This very active area is covered from a historical perspective, and first-, second-, and third-generation catalysts are discussed in terms of improved efficiency and scope. Extensive tables are provided that summarize yields with various substrates, aminating agents, and catalysts; applications of these reactions to various areas and a discussion of the state of their mechanistic understanding are also presented.

Overall, the focus of this work is a timely one that should be of interest to a broad segment of the synthetic organic community. By the editor's own admission, "no attempt has been made to present a comprehensive work". As could be expected from such a multiauthored compendium, there are some significant gaps in the coverage of topics, most notably in the areas of copper-catalyzed asymmetric aziridination and metal-catalyzed hydroamination and amino-hydroxylation reactions. Nonetheless, these are generally good quality, mid-depth, reasonably up-to-date reviews (most of the chapters contain references through 1999) of many of the active areas in synthetic methods development for amines. The quality of the text and graphics is very good, with few typos detected. The book should be in the libraries of all institutions where synthetic organic chemistry is practiced as well as in the personal libraries of those who wish to keep abreast of developments in the synthesis of amines.

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Flat Panel Displays. Advanced Organic Materials. By S. M. Kelly (Department of Chemistry, University of Hull, U.K). Royal Society of Chemistry: Cambridge. 2000. xvi + 232 pp. £59.50. ISBN 0-85404-567-8

This monograph provides a good overview of advanced organic materials used as components in flat panel display technologies, including liquid crystal displays (LCDs) and organic light-emitting diodes (OLEDs), with the major focus on the former. In the preface, the author emphasizes that the primary concentration of the monograph is on the development in design and synthesis of these two different classes of organic materials and the correlations between the molecular structure and the physical properties required for applications in LCDs and OLEDs.

The first chapter provides an introduction to different flat panel display technologies by briefly describing the important features and differences between cathode ray tube, plasma, vacuum fluorescence, and field emission displays, as well as LCDs and OLEDs. The second chapter overviews liquid crystalline (LC) organic materials and LCDs. This chapter includes an introduction to the LC state, with examples of nematic, smectic, and cholesteric LC phases, followed by a description of the most important physical properties (birefringence, elastic constants, viscosity, and dielectric anisotropy) of nematic LCs and the importance of these properties to device applications. Finally, general schematics for LC pixels and addressing methods (direct and multiplex) are discussed.

Chapter 3, the longest chapter of the monograph, describes LCD technology in detail with the major focus on nematic LC materials. A good description of several different types of LCDs, including twisted nematic, super-twisted nematic, and guest−host LCDs, is given, including a brief history of each. Numerous examples of nematic LC materials, their important physical properties and display configuration, and an explanation of the on- and off-states are systematically provided for each type of LCD. A discussion of the known structure−function relationships of the constituent organic materials is also presented, but as the author accurately states, there is a limited understanding of these relationships because of the complicated interrelation of properties.

Chapter 4, similar to Chapter 2 for LC materials, provides a general overview of photoluminescence and electroluminescence in organic low molar mass materials (LMMMs) and polymers. A brief description of each phenomenon is provided, and general schematics for single-color OLED configurations and display addressing are presented. The following two chapters focus on LMMMs and polymer-based OLEDs, respectively. Chapter 5 outlines examples of materials used as the hole-transport layer (HTL), electron-transport layer (ETL), and emitting layer (EML), including blue, green, and red emitters in OLEDs. Possible applications for utilizing ordered LC materials as charge-transporting layers in OLEDs are covered in detail. However, a key point that was not emphasized in this chapter is the fact that the most efficient and stable devices (devices currently in the market) are based on LMMMs utilizing sensitized luminescence in dye-doped OLEDs. Unfortunately, Table 5.8, described in the text as a list of organic molecules used primarily as dopants in dye-doped OLEDs, is missing from the monograph. Furthermore, there is no mention of organic phosphorescent materials (Baldo, M. A.; et al. *Nature* **1998**, *395*, 151; *Appl. Phys. Lett.* **1999**, *75*, 4), which have led to some of the highest reported OLED efficiencies to date for red and green electroluminescence.

Chapter 6 focuses on OLEDs based on polymeric materials. The number of examples and the discussion of structure−function relationships are more extensive for polymers—including the utilization of LC polymers for polarized electroluminescence applications—than for the LMMMs.

The key point the author makes in the preface and the conclusion is that advances in the practical applications of advanced organic materials in flat panel display technologies are strongly dependent on the understanding and improvement of the physical properties of the constituent organic materials. Such advances are possible only through the cooperation and collaboration of scientists from different disciplines. Overall, this monograph is written with a good balance of chemistry, physics, and engineering concepts, which makes it applicable for an interdisciplinary audience, including graduate students and scientists in industry and academia. This is the most important attribute of the monograph.

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The Properties of Gases and Liquids, 5th Edition. By Bruce E. Poling (University of Toledo), John M. Prausnitz (University of California at Berkeley), and John P. O'Connell (University of Virginia). McGraw-Hill: New York. 2001. 768 pp. $115.00. ISBN 0-07-011682-2.

This fifth edition of a classic reference has evolved into the "must have" resource for those who rely on thermodynamics and physical property methods to explore process applications of new chemicals or formulations. Chemists and chemical engineers developing new processes and products rely on data describing the physical properties and thermodynamic behavior of molecular mixtures over wide ranges of compositions and conditions of temperature and pressure. Experimental approaches and ab initio calculations can generally provide only a very small portion of the required data. This book is for those who need reliable estimation techniques to bridge the gap between knowledge of molecular structure and macroscopic behavior in mixed systems. It includes property values, estimation techniques, and correlations that are valid over a wide range of temperatures and pressures and for many different compounds.

This book represents a significant extension of the previous edition published in 1987. All the chapters have been revised to reflect the most recent advances. The "property data bank" in the appendix has been completely redone and now contains 60 pages covering nearly 500 organic compounds. Most of the numbers provided in this appendix are actually parameters and not data. However, these parameters do represent fits of validated data, as supplied from the Thermodynamics Research Center (TRC) database.

The authors have prepared this book as a critical review of a select number of properties. Their selection seems most suitable for practicing engineers involved in chemical process design. When several property correlation methods are presented, recommendations are generally made to guide the reader to the method most appropriate to his or her application. Numerical examples of using the methods are provided throughout the text. All methods presented extensively reference both the current literature and historical material. The result is a very usable bibliography that includes references dating from the late 19th century (1890) up to 1999. Although many of the best correlation methods are presented, the text cannot contain all possible methods. For example, the Sanchez−Lacombe equation of state for polymer solutions is not included; however, references are provided to handbooks and reviews that cover such methods.

The chapter on phase equilibria in multicomponent systems, spanning a quarter of the book, is remarkably complete and unique for a publication about physical property estimation. All correlations are presented together with their theoretical foundations. This includes a thorough review of thermodynamics, including equation of state methods. The remainder of the book presents a highly detailed discussion of the fundamentals and correlations used for the estimation of viscosity, thermal conductivity, diffusion coefficients, and surface tension.

While the authors point out that their intended audience is the practicing engineer, much of the material is of general interest to scientists and engineers who have a need for property and thermodynamic description of fluid (gas, vapor, and liquid) phases. The background information should prove generally valuable.

As with any new text, there are typographical errors; however, none that we have found are serious. A minor annoyance is the size and shape of the book. A reference book should lie open on a desk; this book does not because it is small and thick.

Overall, this is an excellent book. It is well written at a level that should be easily comprehended by an individual with only limited exposure to physical property estimation and phase equilibria calculations. This book is also complete in fundamentals, equations, validated data, and bibliographic citation; even the expert should find this book to be a very valuable addition to his or her collection.

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Rhodium Catalyzed Hydroformylation. Edited by Piet W. N. M. van Leeuwen (University of Amsterdam) and Carmen Claver (Universitat Rovira i Virgili, Tarragona, Spain). Kluwer Academic Publishers: Dordrecht/Boston/London. 2000. xii + 286 pp. $125.00. ISBN 0-7923-6551-8.

This is an excellent book covering recent work in the important industrial and academic area of hydroformylation catalysis. Given that approximately 70−75% of all industrial hydroformylation is based on rhodium, not to mention the large majority of academic studies, the book does not miss much by focusing on rhodium, relative to cobalt and other considerably less active metal complexes. The book is well written by a mixture of academic and industrial workers who are highly familiar with hydroformylation catalysis. The editors have done a very good job at maintaining a format and general writing style that are consistent throughout the book. Some of the later chapters on the more practical aspects of industrial hydroformylation could have been slightly improved by the inclusion of more ligand and catalyst structures (many of which were previously discussed, however) to make it a little easier on the reader.

The chapters cover unmodified rhodium systems (i.e., $HRh(CO)_3$), use of phosphite, phosphine, and chelating ligands, asymmetric hydroformylation, organic synthetic applications (more complicated substrates), and new catalyst/ligand developments (bimetallic, micellar, supported aqueous phase, supercritical solvents, fluorous phase, and dendrimer/polymer supported). Two of the later chapters focus on more industrial aspects of aqueous phase hydroformylation and summarize actual industrial processes (past and present). Particularly noteworthy is the inclusion of a very practical chapter on catalyst preparation and decomposition. Many researchers new to hydroformylation catalysis make classic mistakes in their work concerning the use of appropriate starting materials, reaction conditions, and even phosphine ligand concentrations needed to avoid rapid catalyst deactivation. The considerably higher activity of rhodium hydroformylation catalysts relative to cobalt systems demands attention to these important issues. Another area where academic researchers often make mistakes is in assigning the high branched to linear regioselectivity of certain substituted alkenes (e.g., styrene, vinyl esters) to their catalyst/ligand. There is a natural electronic preference for these substituted alkenes that the book makes quite clear in several of the chapters.

The general focus is on work done in the last 10−15 years, with some references as recent as 2000. The authors, however, do an excellent job of succinctly summarizing the history of rhodium-based hydroformylation, while developing a complete picture of the current state-of-the-art. Virtually every major development in rhodium hydroformylation catalysis is covered, making this an unusually complete reference book. The writing is clear and interesting enough to maintain the interest of an undergraduate student, but with a straightforward narrative style that will engage even experts in the field. This is a "must have" reference book for all chemistry libraries and researchers working with hydroformylation catalysts.

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New Trends in Synthetic Medicinal Chemistry. Edited by Fulvio Gualtieri (Università di Firenze). Methods and Principles in Medicinal Chemistry. Volume 7. Wiley-VCH: Weinheim. 2000. xvi + 354 pp. $155.00. ISBN 0-527-29799-5

Medicinal chemistry, the science of drug discovery and development, has evolved over the years as it continues to embrace new disciplines. The field has its roots in pharmacognosy, the traditional practice of isolating crude drug products from plants, and advanced when efforts were made to identify the individual components of these mixtures and to characterize their activities. Total synthesis of many natural products and their analogues followed. Subsequently, computational power enabled medicinal chemists to discern relationships between structure and activity, and rational drug design was born. Structural and molecular biology revolutionized the field because their techniques facilitated the identification and characterization of the macromolecular targets (e.g., enzymes and receptors) for these medicinal agents. One discipline, however, that has remained fundamental to the practice of medicinal chemistry is synthetic organic chemistry. Compounds must be generated by rapid and reasonably straightforward schemes. This volume, part of a series known collectively as *Methods and Principles in Medicinal Chemistry*, emphasizes current synthetic techniques that belong in the modern medicinal chemist's toolbox.

The book consists of nine chapters and covers several themes including combinatorial chemistry, stereoselective and biocatalyzed synthesis, the resolution of racemic mixtures, synthesis and properties of carbohydrate and nucleic acid oligomers, and quantitative structure−activity relationship (QSAR) methodology. The opening chapter presents an overview of the book by describing how each of these strategies has been exploited in the synthesis of complex molecules, including some commonly used drugs. Chapter 2 reviews a chemometric approach to QSAR, so that a maximum amount of information is obtained from the experimental data. After a description of the methodology, the authors provide examples showing how powerful the combination of appropriate regression and design techniques can be. In Chapter 3, the authors discuss several combinatorial methods that rely on organic chemistry. The chapter also includes descriptions of the instruments used for solution- and solid-phase synthesis of the requisite library of compounds. The next chapter relates the experiences of an industrial scientist who describes the generation of various libraries (e.g., benzodiazepine, benzisothiazolone, and a group of tyrosine kinase inhibitors known as tyrphostins) that are produced by solid-phase synthesis. Chapter 5 describes a sampling of methods that can be used for the stereoselective synthesis of compounds, including some drugs such as Naproxen, a nonsteroidal antiinflammatory agent, and Diltiazem, a calcium antagonist. Techniques used for the resolution of racemic mixtures on both the analytical and preparative scale are discussed in Chapter 6, and biocatalysis is the focus of the next chapter. In this latter chapter the author presents an overview of how molecules can be produced using microorganisms or enzymes. The last two chapters are devoted to synthetic methodologies used for the generation of carbohydrates (Chapter 8) and oligonucleotides (Chapter 9). Chapter 8 includes a number of synthetic procedures that reference the original literature. The inclusion of these procedures seems excessive, but other readers may find them useful.

The editor of this volume indicates that medicinal chemists "must continue to excel in synthetic organic chemistry". Accordingly, the topics were carefully chosen so as to review "modern synthetic methods that are likely to be of great interest for medicinal chemists". The volume achieves this objective. It will be useful to graduate students, faculty, and research scientists working in organic and medicinal chemistry who desire an introduction to one of these areas. For researchers with experience in any of these areas, the book is not likely to provide any new insights. The chapters are liberally referenced, however, making the book very useful for the preparation of lectures. For these reasons, this book would be a worthwhile addition to a chemistry library.

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