Book Reviews *

Organic Reactions. Volume 42. Edited by Leo A. Paquette (Ohio State University). J. Wiley and Sons, Inc.: New York. 1992. xxii + 670 pp. ISBN 0-471-54410-8.

This volume of *Organic Reactions* covers two of the most valuable and widely used procedures in synthetic organic chemistry, namely the metal–ammonia reductions of aromatic substrates ("The Birch Reduction") and the activation of alcohols by a mixture of triphenylphosphine and a dialkyl azodicarboxylate followed by substitution with a range of nucleophiles ("The Mitsunobo Reaction"). As with earlier volumes in this most important series, the extensive tabular surveys are invaluable, enabling readers to make not only a best informed assessment of the likelihood of the outcome of these two procedures when applied to their own particular substrates but also an optimal choice of the required reaction conditions. The compilation of these surveys requires an enormous and painstaking effort, both in assembling the material and then ferreting through to extract important details.

The review literature pertaining to the Birch reduction is extensive and reasonably up-to-date. Nevertheless, this further article which provides a comprehensive coverage of the literature through 1988 is welcome, especially as it summarizes recent developments on the reduction of less conventional substrates like aromatic ketones, esters, nitriles, amides, etc. Perhaps because of space constraints, the mechanism, scope, and limitations, as well as the selection of optimal procedures, are not treated as thoroughly as in earlier reviews. These should therefore be consulted for more detailed treatments on particular aspects, e.g. the 1972 article by Dryden (which appears not to have been cited) on the scope of and limitations on the reductions of the more traditional substrates, especially methoxyarenes, in *Organic Reactions in Steroid Chemistry* (Edited by Fried and Edwards). Incidentally, the rate of reduction of anisole is 3 times that of benzene, so it is therefore somewhat misleading to classify it and the class at large as "unactivated". The selection of experimental procedures is less than optimal, and it would have helped to have some figures so that readers did not have to struggle with systematic names or refer to the original articles. The procedures for the reductive alkylation of 2-methoxybenzoic acids exemplified by the 5-isopropyl example lead to significant hydrogenolysis of the 2-methoxy substitutent. This loss stems from the ammonium ion generated from ionization of the substrate and is a more serious problem for substrates lacking a 5-alkyl substituent. The reduction of ethyl benzoate using water as a proton source is not general and is inferior to the use of limited amounts of *tert*-butyl alcohol with potassium (most reliable) or sodium, or even lithium. The decision by the authors to lump together the reduction and the reductive alkylation of bifunctional compounds into two tables is unfortunate, making it difficult to locate compounds of interest readily; the colocation of several aromatic lactams with "heterocyclic substrates" seems inappropriate. In such an extensive survey, errors or omissions are bound to occur. Some may mislead the reader; e.g., the extensive hydrogenolysis that occurs in the reduction of 1-methoxynaphthalene takes place over a 72-h reaction but still constitutes only 40% of the product (p 99), and the C-1 acetal on p 251 should be the C-2 isomer (the C-1 substrate would be expected to undergo hydrogenolysis).

A major review of the Mitsunobo reaction is especially timely and provides a much needed update to Mitsunobo's original review in 1981, providing a comprehensive coverage of the subsequent literature through 1988, with several more references for 1989 and 1990 (a total of almost 900 references!). The section of scope and limitations is excellent, and while the treatment of mechanism is lucid, it possibly draws too heavily on the author's own work. In the summary of experimental conditions it would have been helpful to have a more detailed discussion of the pros and cons of alternative reagents, especially addressing the problems of separating the target compound from the reagent-derived products.

Lew Mander, *The Australian National University*

Ylides and Imines of Phosphorus. By A. William Johnson (University of North Dakota), William C. Kaska (University of California at Santa Barbara), K. Alexander Ostoja Starzewski (Bayer AG), and David A. Dixon (DuPont de Nemours). Wiley: New York. 1993. xxvi + 587 pp. $89.95. ISBN 0-471-52217-1.

The first monograph on ylide chemistry was written by A. William Johnson in 1966, and it was a pioneering book. In 1993, 40 years after Georg Wittig discovered the reaction between phosphonium ylides and carbonyl compounds once again A. William Johnson gives a new monograph which is considerably larger, more documented, highly detailed, and more complex than its predecessor. Without doubt, it is a major tribute to the phenomenon of the "Wittig reaction", whose impact on modern synthetic organic chemistry has been monumental and whose contribution to research has continued unabated to this day.

The book is organized into 14 chapters. Chapter 1 is a short but well-documented history of ylides and imines, where we follow Wittig and his students in pursuit of pentacovalent compounds. Chapter 2 has been written by D. A. Dixon from DuPont de Nemours; it covers a theoretical description (energies, molecular geometries, electronic properties, molecular orbitals) of the bonding in ylides with the simplest phosphonium ylide, $CH_2{=}PH_3$, as a model. Chapter 3 covers the physical properties of phosphonium ylides (bond lengths and bond angles, optical activity, P=C bond rotation, isomerism, ^1H, ^{31}P, and ^{13}C NMR spectroscopy, IR, basicity); additionally the chapter presents the chemistry of several classes of phosphonium ylides having unique structures and properties (allylic ylides, phosphonium ylide anions, carbodiphosphoranes and phosphacumulene ylides, phosphaallene ylides, bis-ylides, and cyclic phosphonium ylides). The chapter is illustrated with well-documented tables which provide examples of the variety of known ylides. The various methods available for the preparation of phosphonium ylides are described in Chapter 4, which goes from the most general method, "the salt method", to more specialized methods, including nucleophilic addition to vinyl phosphonium salts, addition of phosphines to alkenes and alkynes, and reaction of phosphines with carbenes.

In view of their strong nucleophilicity, ylides are able to react with almost any electrophiles; this aspect of phosphonium ylides chemistry which depends on the kind of reagent with which the ylide reacts is presented in Chapters 5–7. In Chapter 5, reactions that result in the cleavage of the carbanion–phosphorus bond, including hydrolysis, oxidation, reduction, thermal decomposition, and photolytic decomposition, are discussed. In Chapter 6, the reactions used for the conversion of relatively simple ylides into more complex ylides are described; these include reactions with trivalent boron compounds, halogens, metal halides, and widely used alkylation and acylation reactions. Chapter 7 covers addition reactions of ylides to multiple-bonded compounds which combine carbon, nitrogen, oxygen, and sulfur (alkenes, alkynes, carbon–nitrogen systems, carbon–sulfur systems, carbon disulfide, nitrogen systems, cumulenes, ketenes, etc.); reactions with three-membered ring systems (oxiranes, aziridines) are also included.

In Chapters 8 and 9, the Wittig reaction receives a detailed treatment. Chapter 8 provides an overview of the reaction including its advantages, the stereochemistry, the phosphorus, and carbanion substituent effects, the experimental conditions (base, solvent, additives, temperature) the Schlosser modifications, etc. followed by examples of its application to a wide variety of compounds, with the objective of serving those who use the reaction for synthetic purposes. Chapter 9 discusses the mechanistic and stereochemical aspects of the reaction in detail. Eight mechanisms (the most recent of which was proposed in 1988 by Vedejs) are discussed in terms of a tremendous wealth of experimental data concerning a variety of nonstabilized, stabilized, and semistabilized ylides.

Chapters 10–12 deal with variants of the Wittig reaction which employ phosphonates, phosphinoxy, and other phosphorus-stabilized carbanions. Chapter 10 presents the various preparations of phosphonates and the properties of their carbanions, the Wadsworth–Emmons reaction, its advantages and disadvantages, reaction conditions, β-hydroxy phosphonates, mechanism (perhaps to form betaines?, possibly to form oxaphosphetanes?) which is very much open, stereochemistry, effect of carbanion substituents and reaction conditions, and applications of the reaction of phosphonate carbanions with alkylating agents, lactones, and oxiranes. Chapter 11 deals with the development of phosphinoxy carbanions since their discovery by Horner in 1958. It includes the preparation of phosphine oxides, a discussion of the mechanism of the Horner reaction (which remains to be proved), the stereochemistry of the one-step or two-step Horner reaction, and the various applications of the reaction. Chapter 12 describes several groups of ylides which are sometimes of significant synthetic value (trisalkoxyphosphonium ylides, tris(dialkylamino)phosphonium ylides, phosphonamide carbanions) or sometimes simple chemical curiosities.

Chapter 13 presents the chemistry of iminophosphoranes and related compounds. It includes the preparation of iminophosphoranes by the Staudinger and Kirsanov reactions, their molecular structures and basicity, and reactions of iminophosphoranes with carbonyl compounds (the aza-Wittig reaction, which has found a large development in its intramolecular version). Reactions with carbon disulfide, ketenes, and carboxylic acid

*Unsigned book reviews are by the Book Review Editor.

derivatives are also reported. A large part has been given over to bis-iminophosphoranes, phosphazines, and phosphoramidates.

Chapter 14, the last chapter, is written by W. C. Kaska and K. Alexander Ostoja Starzewski. It deals with the complexes of transition metals with ylides. Although a little bit removed from the central theme of the book, it represents a welcome opening to the field of transition metal chemistry. Here, the focus is more on homogeneous catalysis (e.g. the SHOP process, p 555) than on the synthetic organic chemistry in the other parts of the book. The complexity of the field is well illustrated by the 13 types of ylide complexes, which are mentioned on p 488. The material is organized according to the various transition metal subclasses. The principal merit of this chapter is to open the eyes of the organic chemists to an interdisciplinary field whose potential development is enormous and will open new and unexpected applications for ylides.

Clearly, this book represents an outstanding addition to the chemical literature and is a must for all libraries and laboratories working on synthetic organic and transition metal chemistry. Throughout these 14 chapters, the coverage is extensive and ranges from traditional topics to emerging fields. Each chapter is highly organized to facilitate access to detailed topics, and many chapters include a complete, chronological list of topical reviews, each one being annotated briefly to assist the readers. A. William Johnson has provided an up-to-date, well-made, very complete encyclopedia with 3150 selected references, including some from 1992, which is both pleasant to read and easy to consult. It will remain a reference and a platform for new research for many years to come. The book is carefully edited, and its cost, taking into account the quality and the size, is reasonable.

François Mathey and Philippe Savignac, *Ecole Polytechnique, Palaiseau, France*

Scanning Tunneling Microscopy and Spectroscopy: Theory, Techniques, and Applications. Edited by Dawn A. Bonnell (University of Pennsylvania). VCH Publishers: New York, Weinheim, and Cambridge. 1993. xiv + 436 pp. ISBN 0-89573-768-X.

This is a well-written book concerned with both the theoretical concerns and practical aspects of scanning tunneling microscopy (STM) and its associated techniques. The book is well-organized and easy to follow, including the chapters dealing with theory. Practical considerations which have not been addressed in previous books on STM are dealt with here in a manner which makes this book an excellent reference for both the expert and novice. The various contributors have assembled a text which clearly advises the reader how to properly carry out and interpret experiments in this challenging research area. Very recent applications of STM and its related techniques are presented and reviewed so that current information can be easily obtained. This is a much-needed book and is invaluable to those already performing STM experiments and those who are interested in finding out if their problem can be addressed with STM.

Chapters 1 and 2, by Bonnell, give the reader a very good introduction to tunneling and tunneling microscopy and also provide some extremely useful information concerning microscope construction. Clear and concise descriptions of piezoelectric materials and microscope electronics are given. I am very happy to see this well-presented section on vibration isolation and the ways to deal with this problem.

Tersoff gives a good explanation of the theory for interpreting nanometer-scale images, as well as atomic-resolution images, in Chapter 3. An introductory discussion of voltage-dependent imaging and tip-sample interactions is presented. In Chapter 4, Hamers picks up where Tersoff left off and goes into very detailed descriptions of voltage-dependent imaging, experimental methods and interpretation for local I–V measurements, and general features of tunneling spectra. Tip effects and anomalies are discussed in the section on tunneling spectra. A reasonable presentation of barrier height and inelastic electron tunneling spectroscopy concludes this chapter.

Unertl presents some information in Chapter 5 concerning crystalline surfaces which is often ignored by those writing about STM and is often confusing for the novice. I was glad to see this area discussed in some detail. Adsorbate structure terminology, surface reconstruction, and the thermodynamics of crystal formation are discussed. In addition, defect structures, diffraction techniques, and surface spectroscopies are briefly reviewed.

The important subject of tip preparation is thoroughly discussed in Chapter 6 by Rohrer. The artifacts associated with variously ill prepared tips are demonstrated using several selected images. The various methodologies of tip fabrication are presented and evaluated. Surface and sample preparation are briefly reviewed.

Burnham and Colton do an excellent job discussing force microscopy in Chapter 7. The fundamentals of surface and interfacial forces are reviewed, and a good discussion of forces between surfaces in liquids is presented. The various types of force microscopy (magnetic, capacitance, etc.) are reviewed, as are the detection methodologies and cantilever designs. A brief, but very good, discussion of surface forces in STM experiments concludes the chapter.

Ballistic electron emission microscopy (BEEM), a recent spin off of STM, is presented in Chapter 8. The application of BEEM to Schottky barriers and how this is performed using STM is discussed.

Bard and Fan provide an excellent review of electrochemical applications of STM in Chapter 9. The design of electrochemical cells and instrumentation for use in STM experiments is well presented, as is a fairly comprehensive literature review of *in situ* electrochemical STM experiments. Various tip insulating techniques and surface preparation methods are discussed. Examples of metal and conducting polymer deposition, corrosion events, and tunneling spectroscopy of semiconductors are presented. The chapter is concluded with a discussion of the relatively new technique scanning electrochemical microscopy.

In Chapter 10, Lindsay discusses STM imaging of biomolecules on surfaces and how one does so in a nondestructive manner. The forces between the tip and the molecules, contrast mechanisms, biopolymer conductivity, and resonant tunneling are discussed. Sample preparation, substrate choice, and electrodeposition of biopolymers is reviewed.

Robin L. McCarley, *Louisiana State University*

Conjugated Polymers and Related Materials. The Interconnection of Chemical and Electronic Structure. Edited by W. R. Salaneck (Linköping University, Sweden), I. Lundström (Linköping University), and B. Rånby (The Royal Institute of Technology, Stockholm). Oxford University Press: Oxford, U.K. 1993. xvi + 502 pp. $98.00. ISBN 0-19-855729-9.

This book was developed from the Nobel Symposium *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*, held on 13–14 June 1991 in Luleå, Sweden. After a preface by the editors and lists of participants and contributors, there are 32 chapters listed under the following headings: Introduction; Chemical Synthesis and Structure; Electronic Structure and Excitations; Applications; Spectroscopies; and Related Concepts and Materials. There is also a subject index.

Annual Review of Physical Chemistry. Volume 43. Edited by Herbert L. Strauss (University of California, Berkeley), Gerald T. Babcock (Michigan State University), and Stephen R. Leone (NIST). Annual Reviews Inc.: Palo Alto, CA. 1992. xii + 806 pp. $48.00. ISBN 0-8243-1043-8.

In the tradition of the popular series Annual Review of Physical Chemistry, this volume (Vol. 43, 1992) covers a wide range of current topics in physical chemistry. From the very old subjects of Atmospheric Ozone and Classical Vibrational Spectroscopy to the emerging fields of Femto-second Dynamic Absorption and Stimulated Emission Pumping Spectroscopy (SEP), this volume presents a well-balanced choice of authoritative reviews, elegantly written by leading researchers in their respective fields.

The areas of dynamics and structure of polymer and Tetrapyrrolic Macrocycles, as well as surface phenomena, continue to attract much attention of physical and biophysical chemists, and they are well represented in this volume. Both the reviews on Mobile Ions in Amorphous Solids and on Molecular Electronics are of academic and practical importance. Perhaps, some day these fields will bring about cross-fertilization and remove some of the limitation in the experimental Electron Densities studies. In the same manner, it is hoped that "Computational Alchemy" may prove to be a versatile tool to compliment experimental studies in the understanding of free energy changes in difficult chemical systems.

Modern techniques such as Transition State Spectroscopy and SEP, and sophisticated studies in "Relaxation of Molecules with Chemically Significant Amount of Vibrational Energy" led to new insights into various aspects of fundamental understanding of chemical reactions. As well, it is reassuring, after some early frustration, that "the future of Laser Control Over Chemical Reactions and Molecular Processes is bright". The authors' statement echoes this reviewer's firm belief that physical chemistry is a living science, with many old and new horizons to be explored.

J. K. S. Wan, *Queen's University*

Kinetic Theory of Living Pattern. By Lionel G. Harrison (University of British Columbia). Cambridge University Press: Cambridge and New York. 1993. xix + 354 pp. $69.95. ISBN 0-521-30691-4.

There is at the present time a deep problem with the presentation of

biological sciences. As scientists we wish to give living systems analyzable constructs much as we describe sodium chloride first as NaCl and then as a structure in space and then in terms of physical and chemical properties. In this vein we approach a living cell in reductive analysis. There are those who present DNA in these terms and would like us to stay with the study of the sequence, structure, and properties of this molecule, believing that this tells the story of life. For Lionel Harrison this attitude is mistaken. He insists, with the support of distinguished names such as Turing, Meinhardt, and Prigogine, that the starting point for the discussion of living systems must be a process, a kinetic form, not an analytical structure. I have not the slightest doubt that he is correct. The difficulty for Harrison and those of his kind is to make their soft singing in the wilderness heard above the noise of the traffic. In this book he sets out in three parts the themes of the song. Part I describes "without mathematics" the kinetic ideas necessary for a spatial–temporal description of the living machinery for development and growth. It is firmly based on morphogen theory, and for a modern biologist, no matter how correct it may be, it hides a deep problem: What molecules is Harrison talking about, and do we know of morphogens for sure or are they just symbols—a way of hiding behind complexity when we can analyze DNA?

The problem then for this book is that there is a danger that the biologist reader will quit before the more mathematical Part II, "Pattern-forming processes". He or she must not. Undoubtedly he or she will struggle with the maths of Part II, but let the biologist try to get the take-home message concerning dynamic interactions, flow and feed-back, and diffusion-reaction before giving up for love of structures and properties rather than algebra. He or she will be rewarded though perhaps not directly by this brave book. Even in Part III, where experiment is introduced, no modern biochemist will find firm-footing on DNA/RNA/protein ground to which ultimately there must be a link. So what reward is there in reading this work? It is simple. Having read the book, stand back from DNA for a while and think, "How could I prove Harrison right or wrong?" Some really good experiments could turn biology to its proper quest—the processes of life.

R. J. P. Williams, *University of Oxford*

Advances in Chemical Engineering. Volume 18. Academic Press: New York. 1992. x + 264 pp. $85.00. ISBN 0-12-008518-6.

This volume represents the latest addition to this ongoing series. In the end pages of each volume are the contents of previous volumes. By scanning the progression of topics from the earliest volumes to the present one, it is possible to gain a perspective on the growth and evolution of chemical engineering from artful practice to rigorous science. During these past two decades the field has become one of the premier applied sciences by virtue of its vigor and scope. The contents of this latest volume provide strong evidence for this evolution.

Microparticles are important in a spectrum of practical problems and technologies. These include air pollution, combustion, catalysis, ceramics, and other advanced materials research topics. To develop fundamental, microscale knowledge of these systems, it is desirable and necessary to examine their physical and physicochemical properties at the level of a single particle. To this end the first chapter by Professor Davis provides a detailed introduction into the field of single, microparticle experimentation via electromagnetic levitation. The discourse begins with a review of the physics and design criteria for single particle traps that is detailed, lucid, and well documented with original references. Appropriately, this section is followed by one devoted to light scattering and spectroscopy, powerful techniques that can be used to determine size, composition, and even rate phenomena with high accuracy. Familiar topics of mass and heat transfer are elucidated for the reader through the choice of useful examples from the literature such as multicomponent droplet evaporation as well as others chosen for their pertinence. The final section is of particular interest to reaction engineers, since it covers what has been done to date to investigate chemical reactions between reactive gases and microparticles. After reading this chapter it seems likely that it should succeed in its goal of sparking interest and new research in the fascinating field of microparticle dynamics.

Chemical reaction engineering and applied kinetics are evolving rapidly away from earlier, elegant methods of clustering and lumping and toward more full-blown, molecule-specific descriptions of complex reacting systems. Several forces are driving the field in this direction including the availability of low-cost, powerful computers and more efficient, robust algorithms and the need for speciation, that is a complete accounting of molecular species. Environmental mandates underlie the latter driving force. In Chapter 2, Professor Senhan has done a superb job of organizing and summarizing the major thrust areas in modern chemical reaction engineering which he aptly calls "detailed chemical kinetic modelling". His choice of topics, progression of presentation, and emphasis is right on target. Students and practitioners alike will benefit from reading this chapter. Especially crucial are his summaries of computational chemistry and its utilization in chemical kinetics. For many chemical engineers this will be new ground, but the explanations are clear, although not oversimplified, and the text is complete with many useful references. Equally well done are the sections on thermochemical calculations using either conventional or quantum mechanical means. In Section VIII, Estimation of Chemical Rate Parameters by Conventional Methods, the reader will find a review of the primary families of reactions and a useful compilation of rate parameters and empirical approaches to the problem of estimating activation energies. This chapter is impressive and will be stimulating to a wide range of readers.

The final chapter provides an up-to-date review of optimization methods and strategies that are employed in process modelling. It is the stated goal of the chapter to demonstrate "that, through the application of powerful optimization strategies, ... optimization of complex process models need not be time-consuming or difficult". Newton-type algorithms are developed for solving nonlinear programs, especially for large-scale problems. This is extended to flow sheet optimization in Section III of the chapter. Section IV deals with the special issue of differential/algebraic equation models and compares this approach to more conventional ones. Applications of the methods are pursued in Section V.

The scope of this volume is impressive—from microparticle physics, through quantum mechanics and absolute rate theory, to advanced algorithms and computational strategies for complex process optimization. It is a scope that is reflective of the current state of chemical engineering science.

Henry C. Foley, *University of Delaware*

Advances in Cycloaddition. Volume 3. By Dennis P. Curran (University of Pittsburgh). JAI Press: Greenwich and London. 1993. xii + 210 pp. $98.25. ISBN 1-55938-319-4.

This is the third volume in a series concerned with various aspects of cycloaddition reactions. The chapter on π-facial diastereoselection covers a broad topic that essentially concerns all cycloaddition reactions. Although primarily concerned with the recent literature, this is an excellent contribution on an important topic of value to synthetic chemists and those generally interested in cycloaddition reactions. The second chapter on the ozonolysis of vinylogous esters is more limited in scope. Although this contribution is concerned with an interesting topic, somewhat related to cycloadditions, it may become lost in this series. The last two chapters are related and focus on the generation of azomethine ylides and their cycloaddition reactions. These are important contributions because they are not just concerned with the broad general area of azomethine chemistry but primarily focus on the generation and reactions of azomethine ylides from imine precursors. The increasing importance of this reaction in synthetic chemistry enhances the utility of these contributions. Although these latter two chapters are closely related, the lack of an overall theme to this volume diminishes the importance of personal ownership of this monograph.

According to the consulting editor, the chapters in this monograph are not intended to be comprehensive reviews but are to focus primarily on the author's own work. However, the degree to which the authors adhere to this principle varies in this volume. Because of the unique character of some of the topics, this series continues to play a valuable role in keeping the specialist and nonspecialist informed of this important field of chemistry.

Frank W. Fowler, *SUNY Stony Brook*

Practical Electron Microscopy. A Beginner's Illustrated Guide. Second Edition. By Elaine Hunter (University Hospital, London, Ontario) with contributions from Peter Maloney and Moïse Bendayan. Cambridge University Press: Cambridge, U.K. 1993. xii + 174 pp. $34.95. ISBN 0521-38539-3.

This book is designed for the novice as an illustrated workbench manual of electron microscopy techniques. After a forward by M. D. Silver and a preface by the author, there are seven chapters each outlining the following techniques: Fixation; Dehydration and Embedding; Cutting; Immunoelectron Microscopy (by Moïse Bendayan); Special Methods; The Electron Microscope (by Peter Maloney); and Photography. There is an appendix and an index.