

Additions and Corrections

Stereochemistry and Reactions of Presilphiperfolanol: A Branch Point Marker in Triquinane Sesquiterpene Biogenesis [*J. Am. Chem. Soc.* **1996**, *118*, 9249–9254]. ROBERT M. COATES,* ZHANQI HO, MICHAEL KLOBUS, AND SCOTT R. WILSON

Page 9252: The temperature and kinetic data in Table 2 for *cis*-hydrindanyl and *trans*-bicyclo[3.3.0]octanyl *p*-nitrobenzoates should be reversed—*cis*-hydrindanyl pNB: $t = 80\text{ }^{\circ}\text{C}$, $k = 2.11 \times 10^{-5}\text{ s}^{-1}$ and $t = 50\text{ }^{\circ}\text{C}$, $k = 0.054 \times 10^{-5}\text{ s}^{-1}$, $k_{\text{rel}} = 19$; *trans*-bicyclo[3.3.0]octyl pNB: $t = 50\text{ }^{\circ}\text{C}$, $k = 6.18 \times 10^{-5}\text{ s}^{-1}$, $k_{\text{rel}} = 2200$.

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Book Reviews

Current Trends in Polymer Photochemistry. Edited by Norman S. Allen and Michele Edge (Manchester Metro University) and Ignazio R. Bellobono and Elena Selli (University Degli Studi di Milano). Ellis Horwood: New York. 1995. x + 382 pp. ISBN 0-13-138785.

When an overall up-to-date summary of the relevant advances in a given field is being searched for, it is fortunate to be able to find such a thorough and informative collection of articles as the editors have assembled in this treatise on polymer photochemistry. One of the most impressive aspects of this book is the broadness of the coverage, ranging from articles on photoimaging systems to those on weathering of relevant industrial polymers. All aspects of polymer photochemistry, photophysics, photodegradation, and photoinitiated polymerization are covered by the leading researchers in the field. As well, complimentary topics involving pulse radiolysis and photooxidation are presented. More specifically, the photodegradation of numerous polymers, including styrene-based polymers, polyolefins, and lignin are reviewed, and chapters on stabilizers are included. Coverage of photoinitiated polymerization includes polymerization and grafting in organic and aqueous media, photopolymerizable adhesives and membranes, laser curing, and photoinduced cationic/anionic polymerization. Special photochemical topics are included in chapters on imaging, photoconductivity, luminescence spectroscopy, topochemical photopolymerization, photostability of conductive polymers, nonlinear optical processes in conjugated polymers, and the use of microwave measurements to investigate titanium dioxide photoactivity. Finally, the pulse radiolysis of polymer/acceptor systems and liquid crystalline phthalocyanines is described in separate chapters. Overall, the book is an exciting, up to date account of some of the latest work in the rapidly developing polymer photochemistry field. It should be equally appealing to industrial and academic scientists, and is highly recommended for anyone wanting to catch up on the most recent activity in the field.

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Stereochemistry of Radical Reactions: Concepts, Guidelines, and Synthetic Applications. By Dennis P. Curran (University of Pittsburgh), Ned A. Porter (Duke University), and Bernd Giese (University of Basel). VCH: New York. 1995. xii + 280 pp. \$95.00. ISBN 3-527-29372-8.

This well-written book reviews the status of stereoselective radical reactions and serves as a welcome companion to other books on stereoselective reactions which focus almost exclusively on ionic processes. Each of the authors of the present book has made significant contributions to the development and understanding of stereoselective radical reactions. They have now come together to produce the first comprehensive book in which the principles of conformational analysis

of organic molecules and the structure and reactivity of radicals are used to understand and even to predict the stereochemical outcome of the various classes of stereoselective radical reactions.

After a short introductory chapter recapitulating some of the more important features of radical reactions, the various classes of stereoselective radical reaction are surveyed in five additional chapters. Chapter 2 is the longest of these and reviews substrate-controlled radical cyclization in which an achiral radical bearing prostereogenic radical and alkene centers can lead by way of kinetically controlled cyclizations to achiral or chiral diastereomers in differing amounts. If an enantiomer of a chiral radical is used and if the radical or alkene centers are prostereogenic, then cyclization can occur with asymmetric induction, leading to single enantiomers of two chiral diastereomers in unequal amounts. An outstanding feature of this chapter is the excellent discussion of the Beckwith–Houk model for the prediction of the diastereomeric excess in the cyclization of 1-, 2-, 3-, and 4-substituted hexenyl radicals, and the utilization of the process for the synthesis of a variety of ring systems.

Chapters 3 and 4 survey stereoselectivity of other substrate-controlled reactions of, respectively, cyclic and acyclic radicals. With cyclic radicals the number of reactive conformers is reduced, and because of steric reasons, the attack occurs preferentially *anti* to the shielding substituent, while a prerequisite for stereoselective reactions of acyclic radicals is the existence of a preferred conformation in which the substituents shield the two faces of the prochiral radical to a different extent. The configuration of new stereogenic centers formed from acyclic prostereogenic radical centers may be controlled by a chiral group attached to the radical or attached to the alkene. If the chiral group may be subsequently removed after the stereochemically defining reaction, the chiral group is designated a chiral auxiliary, and as discussed in Chapter 5, the chiral group intended to control the configuration of the newly formed stereogenic center must be fixed relative to the prostereogenic radical center. In Chapter 5, much attention is devoted to the use as chiral auxiliaries of enamines prepared from Whitesell's pyrrolidine (2,5-dimethylpyrrolidine), amides from Whitsell's pyrrolidine and related chiral pyrrolidines each with C_2 symmetry, Oppolzer's sultam, chiral oxazolidines, and esters prepared from chiral alcohols. Both the usefulness for stereoselectivity and the problems for removal encountered with these and other chiral auxiliaries are discussed in some detail. One section in Chapter 5 is concerned with chiral auxiliary-controlled addition reaction of radicals to alkenes leading to telomerization and polymerization with good to excellent stereoselectivity, resulting in the reinvestigation of the control of the stereochemistry in radical polymerization. Finally, Chapter 6 reviews three additional classes of stereoselective radical reactions: radical pair coupling reactions leading to the ground state product or two alkenes by radical pair disproportionation, radical rearrangements, and alkene-forming reactions.

The book is well organized, and the very few typographical errors

are easily accommodated by the lavish use of clearly-drawn perspective formulas for molecules and transition states, free standing and in the great number of reaction sequences. At the end of each chapter there is a list of references, 480 in all, many containing two, three, or more literature citations. Of these, only a very few are dated prior to 1980 with a great number from the 1990s and some even from 1995. The book then will be of interest to a wide range of organic chemists, is an absolute necessity for every chemistry departmental library, and will serve as a valuable supplement for both undergraduate and graduate courses in synthetic organic chemistry. Synthetic chemists will also want to read this book and to have it at the ready on his or her bookshelf.

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Polymers and Other Advanced Materials. Emerging Technologies and Business Opportunities. Edited by Paras N. Prasad (State University of New York at Buffalo), James E. Mark (University of Cincinnati), and Ting Joo Fai (Standard and Industrial Research Institute of Malaysia, Kuala Lumpur, Malaysia). Plenum Press: New York. 1995. xviii + 791 pp. \$65.00. ISBN 0-306-45210-3.

This large and impressive proceedings volume follows the Third International Conference on Frontiers of Polymers and Advanced Materials, held January 16–20, 1995, in Kuala Lumpur, Malaysia. As explained in the Preface, it succeeds earlier proceedings volumes (also published by Plenum) covering conferences held in 1991 in New Delhi and 1993 in Jakarta. The stated goals of the conference and, hence, the book are threefold: (i) to highlight advances and new findings in polymers and advanced materials; (ii) to assemble leading international scientists, engineers, and top-level industrial management for discussions on the current status of advanced materials, new technologies, and industrial opportunities; and (iii) to foster global communication in polymers and advanced materials technology. After inspection of the contents of this book, one must conclude that the conference organizers and participants ably fulfilled their goals. The 81 separate articles contained in this volume are authored by an international cast of scientists spanning a wide range of disciplines including polymer chemistry and physics, mechanical and aerospace engineering, electronics and optoelectronics, bioengineering, and even industrial business management. Clearly, there is something here for everyone.

The contents of the volume are divided into ten headings, namely, Composites and Blends (17), High Performance Polymers (11), Materials for Electronics (12), Materials for Photonics (12), Biomaterials (6), Recycling of Materials (5), Sol-Gel and Chemically Processed Materials (4), Materials from Natural Products (5), Multifunction and Smart Materials (4), and Business Opportunities (5), where the figure in parentheses refers to the number of articles under each heading. In the present age of striving toward diversity, this book cannot be accused of being noninclusive. The conscious effort of the book to cover so many of the emerging technologies in materials/polymer science is an exceptional feat and should attract wide interest among scientists and engineers, project managers, and even entrepreneurs in the field.

The articles themselves are difficult to describe collectively. They vary considerably in length, technical content, and style. Many are written as typical research articles (i.e., Introduction, Experimental, Results and Discussion, Conclusions, and Literature Citations), while some can be described as overviews or commentaries with few or no references. Although only a small fraction of the articles provide Abstracts, the literature citations are up-to-date (as recent as 1995). The quality of the contributions is very good overall and excellent in some cases. A substantial amount of useful information and data is presented in tables and figures, although the figures themselves vary in quality somewhat.

Space limitations prevent even a partial listing of the many informative and interesting articles in this book. Just a select few are cited here: on high-performance polymer composites by J.-M. Berthelot (Université du Maine, France), on vibration control in fibre-reinforced composite structures by A. R. Roslan and M. S. Leong (Universiti Teknologi Malaysia, Malaysia), on biodegradable polymer blends by M. Yasin, A. J. Amass, and B. J. Tighe (Aston University, U.K.), on non-linear optical materials for optical devices by J. R. Davy et al. (Department of Defense, Salisbury, Australia), on polymers as multi-role materials for photonic technology by P. Prasad (State University

of New York at Buffalo), on electro-optic polyimide and polyamide side chain polymers by U. W. Suter and co-workers (Swiss Federal Institute of Technology, Zürich, Switzerland), on bioartificial polymeric materials by P. Giusti et al. (University of Pisa, Italy), and on the design of "intelligent" ceramic materials for chemical sensors by E. Traversa (University of Rome, Italy).

As one might expect, this book is not intended as an introduction for the newcomer to polymers and materials science. It is, however, a superb choice for the professional wishing to expand his/her familiarity with the subject technologies from a worldwide perspective.

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Advances in Metal-Organic Chemistry, Vol. 4. Edited by Lanny S. Liebeskind (Emory University). JAI: Greenwich, CT. 1995. x + 317 pp. \$97.50. ISBN 1-55938-709-2.

This is the fourth in a series of volumes which are dedicated to the application of catalytic and stoichiometric transition metal-based processes in organic chemistry. There are five chapters in this volume, covering a variety of subjects.

The first chapter, by Bruce Lipshutz, addresses the generation and reactivity of what are presumed to be the higher order cyanocuprates. This is a very personal, and most entertaining, account of recent developments, with emphasis on results from the group at Santa Barbara. Reactions considered include transmetalation of silicon, tin, and zirconium compounds with cuprates, and ligand exchange between copper(I) reagents and unsaturated alanes. The nature of the "higher order" cyanocuprates is a contentious issue, and Lipshutz is to be commended for tackling this subject in a forthright manner.

Scientists at Searle Laboratories have developed practical routes for the synthesis of misoprostol, an antiulcer agent, and other prostaglandins. The pivotal step involves conjugate addition of an *in situ* generated cuprate (from a vinylstannane and $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$) to an appropriate cyclopentenone. The brief, succinct account by James Behling, Paul Collins, and John Ng illustrates the creative approach by this team of industrial chemists.

Cycloaddition reactions promoted or catalyzed by metal complexes are an exciting research area, and Jim Rigby has made pioneering contributions to this subject. In this chapter, he describes the use of (cycloheptatriene)chromium complexes and either dienes or olefins in $[6\pi + 4\pi]$ and in $[6\pi + 2\pi]$ cycloaddition reactions. These photochemically induced processes often proceed in excellent yield, providing access to compounds not easily available or inaccessible by other means.

A quite comprehensive review of the chemistry of acyclic-diene tricarbonylation complexes, by René Grée and Jean Paul Lellouche, accounts for nearly half the material in this book. These complexes together with the η^2 -pentadienyliiron cations derived therefrom are useful intermediates in the synthesis of important natural products including leukotrienes, HETEs (which are part of the arachidonic cascade), and toxins (e.g., AF and AK host specific toxins). The use of the iron complexes for the preparation of interesting heterocycles is also described. The synthetic potential of these complexes has, in the opinion of this reviewer, been underappreciated by the organic chemistry community, and this chapter may contribute to a greater awareness of the subject.

The final chapter, by Masanobu Hidai and Youichi Ishii, is concerned with several carbonylation reactions including the intramolecular cyclocarbonylation of allylic acetates, affording aromatic and heterocyclic compounds, and the formation of aldehydes from olefins or iodoarenes by means of a dual catalytic system (e.g., $\text{Ru}_3(\text{CO})_{12}$ – $\text{PdCl}_2(\text{PPh}_3)_2$). While much work is still needed to elucidate the mechanisms of these reactions, the synthetic potential, particularly of the cyclocarbonylation reactions, is well-documented.

In summary, this book is recommended for purchase by organic and organometallic chemists, and should be in university and corporate research and development libraries.

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