

Book Reviews

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BOOK REVIEWS

Organic Reactions, Volume 39. Edited by L.A. PAQUETTE *ET AL.*, John Wiley and Sons, 605 Third Avenue, New York, NY 10158. 1990. xvii + 585 pp. 16 × 23 cm. \$85.00. ISBN 0471-52632-0.

Volume 39 of *Organic Reactions* contains three highly useful chapters on important synthetic methods. The first surveys the preparation of lithioalkenes from carbonyl compounds via the corresponding arenosulfonylhydronones. This is a very useful review, addressing chemistry that is important in the context of the Shapiro reaction and complementary to the Stille coupling of enol triflates. Appropriate comparisons with other methods are made. The mechanism and the scope of the reaction are reviewed, and over 20 experimental procedures are provided. The Tabular Survey is organized according to structure (acyclic, cyclic carbonyl compounds) and the mode of reaction (dianion alkylation followed by acyclic or cyclic vinyl lithium formation and intramolecular cyclization reactions of acyclic and cyclic reagents). It is well written and eminently useful as an updated reference.

The second chapter, on the Polonovski reaction, reviews the mechanistic options of this process in detail, especially with regard to stereo- and regiochemical implications of the intermediate immonium ions and their subsequent trapping. Alkaloids are used as examples since much of this work has historical foundation in alkaloid synthesis. The scope and limitations section and the synthetic application section contain many examples of alkaloid synthesis via intramolecular immonium ion trapping. Formation of pyrroles is also reviewed as a separate section. The SO₂- and ion-mediated aldehyde synthesis from amines (via *N*-oxides and hemiaminals) is surveyed separately with emphasis on the importance of these processes in demethylating reactions. Other applications that are addressed include silicon- and selenium-promoted Polonovski reactions. About 20 experimental procedures are provided, and seven tables are organized according to the type of Polonovski reaction (those requiring an acylating agent, and those that do not), iron-, silicon-, selenium-, and SO₂-mediated reactions (separate tables for each), and according to class of compounds made (i.e., dimeric alkaloids vs. macrolides). Thus the chapter also provides a fine complement to an overview of alkaloid synthesis, especially of the indole type.

The third chapter reviews those oxidations of alcohols based on alkoxyulfonium ylides. It discusses Moffatt, Swern and related oxidations from the perspective of the ylides used (including those derived from selenium), activating catalysts, bases, and substrates. An important feature is the discussion of side reactions encountered. Comparison is made with other methods. The Experimental Conditions section mentions solvent, reagent, apparatus, and isolation parameters in a general sense and lists more than 20 different conditions. Tables are organized to list 1° alcohols, 1° sugar alcohols, 2° alcohols, 2° sugar alcohols, and diol/polyol oxidations. This is an extremely timely chapter providing an up-to-date review of important technology.

Overall, Volume 39 continues the usual excellent standards of the series and provides an outstanding reference source for important and widely used processes.

TOMAS HUDLICKY, *Virginia Polytechnic Institute and State University*

Lipid Biochemistry: An Introduction. MICHAEL I. BURR and JOHN L. HARWOOD. Chapman and Hall, 29 West 35th St., New York, NY 10001. 1991. ii + 406 pp. 15.5 × 23.3 cm. \$39.95 in paper. ISBN 0-412-26620-2.

This book maintains an excellent balance between basic lipid information available as early as the 1950–60 period and the flood of information developed in the post-1980 era. A vestige of the former era is the use of clupanodonic acid as a common name for all-*cis*-7,10,13,16,19-docosapentaenoic acid. Together with "timnodonic" acid this common name usage is best forgotten, especially as there are two docosapentaenoic all-*cis* acid isomers, respectively of the n-6 and n-3 families.

The mention of a role for fatty acids of the linolenic acid family, in the form of PGI₃ production on page 179, or as a source on "eicosanoids" on page 65, is easily overlooked. While there is a wealth of information on the "essential fatty acid" functions of the n-6 family, the n-3 family is otherwise almost ignored. Excellent and lucid summaries of the biochemical role of the longer-chain n-3 (omega-3) fatty acids have appeared as early as 1982 (e.g., Goodnight *et al.*, *Arteriosclerosis*, **2**, 87–113), and it is disturbing to find their biochemistry virtually ignored in a 1991 book. Many references in this book do in fact date to as late as 1988, and the system of breaking down the references for each chapter by subsections is an interesting and useful style of presentation.

This book is strong on plant and microbial enzymes and occasionally weaker in animal systems. For

example, Refsum's syndrome is discussed in two places (pages 93 and 375–376), but the omega oxidation pathway to degrade phytanic acid is not mentioned. Similarly the peroxisomal mode of chain shortening of long chain fatty acids not readily catabolized by mitochondria is clearly laid out on page 368 but is not brought into focus to explain the failure of docosenoic acids to create health hazards in humans (pages 377–378). In an age where "guilt-free" foods, especially in terms of fats, are avidly sought by a vocal minority of consumers, there is good coverage of the role of trans acids as part of an extensive discussion of dietary fats in human health. The hydrogenation process is reasonably well outlined but contains an element of confusion in a table on page 168 since *cis*-9, *trans*-12-18:2 is repeated twice as an ingredient in hydrogenated soybean oil. On the other hand the inclusion of trans acids in a section on toxicity fairly points out that arterial lesions in pigs fed trans acids may have been due to a dietary fatty acid imbalance, and goes on to question whether any one species is representative of another in this complex area of fats in health.

The diagrams in this book are numerous and first-class. This feature and the low price of the paper cover edition (\$39.95 US) make it a very attractive proposition for student use, but the average lipid chemist should also find it sufficiently comprehensive to be useful as a refresher on many specific points of lipid biochemistry.

ROBERT G. ACKMAN, *Technical University of Nova Scotia*

Stereochemistry of Organic Compounds. D. NAISPURI. Wiley Eastern, John Wiley and Sons, 605 Third Avenue, New York, NY 10158. 1991. xx+527 pp. 15×23 cm. \$41.95. ISBN 0-470-21639-5.

In the thirty years since the appearance of Eliel's *Stereochemistry of Carbon Compounds*, we have witnessed an explosive growth of the subject. Stereoselective synthesis has come of age, nmr has been applied in numerous elegant ways to solve stereochemical problems, computers have been programmed to perform molecular mechanics calculations, and almost the entire language of stereochemistry has been re-written. But until now, no one has written an upper-level text covering both the basics and these new developments. Thus Nasipuri's book is greeted with enthusiasm. He writes in the Eliel tradition and the ordering of topics and the selection of material is similar to that found to Eliel's 1962 book, but he has done a good job of incorporating new material.

The first five chapters cover symmetry, chirality, and classification, occurrence, and nomenclature of stereoisomerism. Chapter 6 deals with homotopic, enantiotopic, and diastereotopic groups, prochirality, and a plethora of related topics. Chapter 7 addresses enantiomer mixtures: formation and resolution of racemates and methods for determination of enantiomeric composition. Questions of relative and absolute configuration are covered in Chapter 8. Conformational analysis and the relationship of conformation to reactivity are found in Chapters 9–12. Chapters 13 and 14 cover many of the recent advances in stereoselective reactions, including pericyclic reactions. Chapter 15 is a rather brief treatment of chiroptical measurements, with most of the reference at least 20 years old.

The book is recommended for anyone wishing to further his knowledge of organic stereochemistry. It is suitable for individual use and as a text in an advanced undergraduate organic course or beginning graduate course. Selection of topics is good, and the depth of coverage is appropriate for the intended audience. For the most part, the treatment is technically correct, but as usual, there are places where the author's quest for brevity (or lack of expertise) results in a less-than-ideal presentation. This reviewer would have preferred a more thorough coverage of molecular mechanics, more clarity in the section on nmr lineshape analysis of exchanging systems, additional detail on the use of chemical shift reagents to solve stereochemical problems, and some discussion of chiral recognition of enantiomers (solute-solute interactions).

Considerable attention to detail appears to have been exercised in the production of this book, with one exception. Figures and tables are clearly drawn and placed where they belong in the book, and very few errors are in evidence. The one glaring problem is that the literature citations at the end of each chapter are not properly arranged. They are listed by number, but the numbers are not used in the text. Probably they should have been alphabetized, but someone forgot to do so.

HAROLD M. BELL, *Virginia Polytechnic Institute and State University*

Eucalyptus Leaf Oils, Edited by D.J. BOLAND, J.J. BROPHY, and A.P.N. HOUSE, Inkata Press, Melbourne, P.O. Box 345, North Ryde, N.S.W. 2113, Australia. 1991. xii+252 pp. 17×24.5 cm. \$65.00. ISBN 0-909605-69-6.

This book was prepared as a reference source for developing countries interested in growing Australian eucalypt species for fuelwood, poles, or other uses and distilling the essential oils as a value-added product. Chapter 1 provides a brief history of the early eucalyptus essential oil research and industrial developments

in Australia. Once an important rural industry for Australia, today most eucalyptus essential oil is produced in developing countries with Australia maintaining a commercial advantage in upgrading oils for the world market. Chapter 2 begins with a discussion of commercial uses and botanical sources of the most common oils. The remaining portion of the chapter is devoted to oil gland biology, biosynthesis of terpenoids, and the genetic and environmental factors influencing oil quality and quantity.

Chapter 3 presents new data on the essential oil composition of 111 eucalyptus species collected from northern and eastern Australia. A full page is dedicated to each species and includes a map, a list of terpenoids with their percentage composition in the oil, and two or more paragraphs of text including a description of the tree and habitat where it grows. Each map outlines the general species distribution and locations of samples collected for chemical analysis. Chapter 4 is an updated version of Penfold and Willis's 1961 table listing all eucalypt species analyzed to date for essential oil constituents. Included in the table are percent oil yields, major terpenoid components, and literature references.

Chapter 5 describes the design and operation of simple stills with utility for rural areas of developing countries, and the modern mobile vats. Chapter 6 presents the realities and practical aspects of marketing essential oils. Anyone wishing to enter the essential oil industry would be well advised to read this chapter and the checklist in Appendix 6 carefully. There are six Appendices listing sample collection sites, chemical structures and molecular formulas, names and addresses of analytical services, essential oil brokers and dealers, and a start-up check list for prospective oil producers. In addition, there is a one-page glossary and species index.

Using a condensed format, the editors have managed to pack a significant amount of information into 252 pages. Eucalyptus essential oil chemistry has been integrated with practical concerns of building a still and the realities of the essential oil markets and industry. The judicious use of subject headings and subheadings within chapters makes it easy to find topics of interest. Furthermore, many of the problems associated with the essential oil industry have been candidly identified and discussed. The authors and editors have achieved their goal of preparing a useful guide for scientists and businessmen in developing countries.

In addition, this book is a valuable reference source for economic botanists, terpene chemists, flavor and fragrance scientists, chemotaxonomists, and eucalypt biologists, among others. Because of its general appeal this book should be purchased by major research libraries, particularly those specializing in flavors and fragrances, phytochemistry, or terpenoids. Libraries of major herbaria would find this book a useful reference. Individual scientists in these disciplines may want to add this book to their personal collection, depending on their involvement and interest in the eucalypts.

RICK G. KELSEY, *USDA Forest Service*

Studies in Natural Products Chemistry, Volume 8, Stereoselective Synthesis (Part E). ATTA-UR-RAHMAN. Elsevier Science Publishers, P.O. Box 882, Madison Square Station, New York, NY 10159. 1990. xviii + 499 pp. 16.5 × 24 cm. \$200.00. ISBN 0-444-88967-1.

Stereocontrol in natural product synthesis is essential for the efficient construction of a wide range of target molecules. This volume contains eclectic topics of current interest within the field which have been investigated by an impressive group of researchers. Composed of 22 chapters, the number and diversity of which are likely to cause the book to possess something of use to most workers in the area, this latest addition to the series will prove to be a valuable acquisition to any library devoted to the study of natural products.

Four of the chapters focus on the chemistry of macrocycles. The chapter by J.E. McMurry and R.G. Dushin describes the enhanced chemoselectivity of low-temperature McMurry couplings and the judicious application of this methodology to the synthesis of several members of the structurally challenging cembranoid family, including the first total synthesis of (\pm)-crassin. T. Takahashi's chapter details useful C-C bond forming reactions leading to macrocycles via intramolecular alkylation, as well as skillful evaluations of the preferred conformations of large ring compounds for predicting the stereochemical outcome of the peripheral functionalization and cycloadditions of such systems. Among the syntheses described in this chapter are routes to (\pm)-periplanone B and (\pm)-haageanolide. In the E. Vedejs chapter, the reader is presented with versatile ring expansion chemistry of heterocyclic sulfur ylides that Vedejs has ingeniously applied, together with (4 + 2) cycloaddition chemistry of thiocarbonyl compounds, to the synthesis of C₁₈-desmethylcytochalasin D and other targets. The review by E. Czyżewska and A.C. Oehlschlager, "Occurrence and synthesis of macrocyclic semiochemicals," is well written and informative and should be of use to those interested in both pheromones and the assemblage of large ring natural products.

Eight chapters of the volume concern the synthesis and chemistry of non-macrocyclic terpenoids. A. Krief, J.L. Laboureur, M. Hobe, and Ph. Barbeaux contribute a chapter that delineates several novel approaches to the cuparenes by means of metalated organoselenium reagents. Application of this

methodology to the synthesis of permethylated cycloalkanones is also described. "Terpene synthesis" by E. Wenkert contains concise approaches to the copanenes and longipinenes in which the strained cyclobutane subunits are installed via intramolecular alkylations of ketone enolates. W. Kriesel's chapter documents the elegant use of nmr and synthesis to corroborate the structure of many members of the bisabolone class of monoterpene. The partial synthesis of rare natural gibberellins from gibberellic acid is the focus of the chapter by G. Adam, B. Voigt, M. Lischewski, A. Schierhorn, A. Priess, and L. Kutschabsky. The utility of photochemical skeletal modifications of gibberellic-acid-derived 7-aldehydes and the preparation of thiogibberellins are among the many interesting features of this chapter. A variety of useful chiral auxiliaries for the synthesis of enantiomerically pure five-membered carbocycles are highlighted in the chapter by G. Helmchen, A. Goeke, S. Kreis, A. Krotz, G. H. Lauer, and G. Linz. The diastereomeric excesses of the cycloadditions are generally excellent, and imaginative stereocontrolled manipulations of [2.2.1] bicycloheptenes leading to a variety of terpenoids are described. Electrochemistry of polyoxygenated arenes is the topic of the chapter by Y. Shizuri, H. Shigemori, K. Suyama, K. Nakamura, Y. Okuro, M. Ohkubo, and S. Yamamura. Intermolecular and intramolecular [5 + 2] and [4 + 2] annulations employing intermediates of phenolic oxidation allow the facile construction of [3.2.1] and [2.2.2] bicyclo-octenones, which are then converted to natural products such as denudatin A and silydianin. B. Trost's chapter covers the innovative palladium-catalyzed cyclization of acetylenic olefins. Synthetic elaboration of the resulting carbocyclic and heterocyclic systems to challenging targets is illustrated. For example, a convergent 13-step approach to the sesquiterpene picrotoxinin is presented. The D. Spitzner chapter demonstrates the utility of successive Michael reactions in syntheses of seychellene, patchouliol; and isoeremolactone. The use of cyclopropylidene acetates as functional equivalents of β,β -dimethylacrylate Michael acceptors is particularly noteworthy.

Synthesis of alkaloid natural products is featured in two chapters of the volume. H. H. Wasserman and C. B. Yu's contribution details the creative application of exotic 1,2,3-tricarbonyl systems to the synthesis of β -lactam antibiotics, prodigiosin, and various polycyclic indole and isoquinoline alkaloids. F. Soti, M. Incze, Zs. Kardos-Balogh, and Cs. Szantay present progress toward the total synthesis of the hexacyclic indole alkaloid cuanzine. The synthesis of (\pm)-desmethoxycuanzine has been achieved in a convergent approach from tryptamine and a 3-(1-oxoprop-2-enyl)- γ -butyrolactone derivative. Work is underway to repeat the synthetic plan with incorporation of the requisite C-12 methoxy substituent.

Bioorganic topics dominate seven chapters of the volume. The L. L. Danilov and V. N. Shibaev chapter, "Phosphopolyprenols and their glycosylesters: chemical synthesis and biochemical application," provides a thorough coverage of the subject. Although lengthy and not particularly germane to stereoselective synthesis, it is a carefully composed manuscript complete with experimental details. G. W. Kirby and R. B. Cain contribute the chapter "The methylmuconate pathways, stereochemistry and mechanism of enzymic reactions." Elegant stereochemical structure proofs of many intermediates of the pathways are discussed, and interesting organism dependent divergencies in the pathways are elucidated. "Thiooligosaccharides: their synthesis and reactions with enzymes," submitted by J. Defaye and J. Gelas, illustrates a wide variety of stereocontrolled syntheses of sulfur-carbon bonds between appropriately functionalized sugar units. An interesting stereocontrolled glycosylation methodology is the subject of the chapter by M. Nishizawa. A wide range of $\alpha:\beta$ glycoside ratios are obtained, the best α -selective glycosylations being those carried out on pyranose derivatives with axial C-2 oxygenation. The F. Johnson chapter, "Synthesis and chemistry of carcinogenic adducts of DNA," offers among other investigations of chemically altered nucleic acids, a fascinating study of the unusual heterocyclic chemistry of 8-(2-fluorenylamino)-2'-deoxyguanosine. F. Z. Basha reports on "Novel conformationally restricted analogues of norepinephrine: synthesis and structure activity." An interesting spatial relationship of atoms within rigid norepinephrine models that appears to influence the selectivity of binding to α_1 or α_2 adrenergic receptors is described. Synthesis of immunologically significant polypeptides is addressed in the chapter by W. Voelter and A. Kapurniotu entitled "Strategies for the total synthesis of thymosins."

The final chapter of the volume, "Asymmetric synthesis via chiral organoboranes—an unexpected bonus from a half-century of borane research," by H. C. Brown, is a delightful decade-by-decade account of this master chemist's enormous contributions to the field of organic synthesis. In addition to its focus on the utility of isopinocampheylboranes in asymmetric synthesis, the chapter provides an intriguing historical perspective on Brown's work and contains several entertaining anecdotes.

As a whole, this volume has much to offer those interested in natural products and synthetic organic chemistry. However, not all of the chapters are largely concerned with stereoselective synthesis, as the title would imply. Fortunately, a substantial number of the chapters do address the issue of stereocontrol in synthesis, and the broad scope of the book is highly commendable. Typographical errors are few, although parts of the book do contain broken English. With these minor grievances aside, the book is enthusiastically recommended.