asymmetric synthesis,[3] and therefore the assignments of stereochemistry are secure.

The allylic alcohols **16a** and **16b** prepared from **14a** and **14b**, respectively (step i), were subjected to asymmetric epoxidations,[18] each with (+)-DET and (−)-DET (another set of double asymmetric syntheses) to provide four diastereomers, one of which was expected to be **7**. Comparison of the $[\alpha]_D$ and ^1H NMR spectra of each isomer with the degradation product **7** revealed that the configuration of **1** at C(7) was *S* and that the epoxide was syn with respect to the C(7) hydroxyl group.

Synthesis of 4b from 7. The only stereochemistry of **1** yet to be established concerned the C(25) stereogenic center, and this task was readily achieved by isolating the C(23)–C(26) fragment of **1** as 1,3-butanediol and comparing it to authentic material as summarized in the supplementary material. With the assignment of the 25*R* configuration the synthesis of the C(17)–C(2) fragment **19** (see **1** for numbering) started with (*R*)-methyl 3-hydroxybutyrate and involved a Horner–Wadsworth reaction with **17**[19] (step a, reaction 3) and a DMAP-mediated transesterification of triethyl phosphonoacetate[20] with the 25-hydroxyl compound derived from **18** (step b, reaction 4) (Scheme III).

The construction of the macrocycle was achieved through the double Horner–Wadsworth coupling of **19** with the aldehyde derived from **7**. All of the steps proceded smoothly,[21] and it was noted that under the conditions of the Sarrett oxidation (step e) the expected oxidation of the 15-hydroxyl group was accompanied by THP-like cleavage and oxidation to provide the desired ketoaldehyde (**22**). The synthetic macrolactone **3** was identical with that obtained from the natural source and its conversion into the pimarolide methyl ester proceeded in the manner shown in Scheme I, steps c and g.[22,23]

Supplementary Material Available: ^1H NMR spectra of all new compounds and experimental procedures of selected reactions (21 pages). Ordering information is given on any current masthead page.

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[18] Gao, Y.; Hanson, R. M.; Klunder, R. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

[19] DeKoning, H.; Mallo, G. N.; Springer-Fidder, A.; Subramanian-Erhart, K. E. C.; Huisman, H. O. *Recl. Trav. Chim. Pays-Bas* **1973**, 683, and references quoted therein.

[20] Hatakeyama, S.; Satoh, K.; Sakurai, K. and Takano, S. *Tetrahedron Lett.* **1987**, *28*, 2713.

[21] Cf.: refs 7b and 8b for steps d–f.

[22] All new compounds showed mass spectra consistent with the structures assigned as shown above.

[23] We are grateful to Gist-Brocades (The Netherlands) for a generous gift of pimaricin. The work at M.I.T. was supported through a grant from the National Institutes of Health (Grant GM 35879).

Additions and Corrections

Theoretical Study on the Electronic Structure of Si–Ge Copolymers [*J. Am. Chem. Soc.* **1990**, *112*, 5043–5052]. KYOZABURO TAKEDA,* KENJI SHIRAISHI, and NOBUO MATSUMOTO

Page 5044, Reference 27: The last three sentences in this reference should be replaced by the following.

Note that, in the present and our previous works, the *x* axis is set to the main axis of the polymer skeleton chain. This is different from the usual setting of the coordinates, in which the *z* axis is set to the main axis. Therefore, one should change our *x*, *y*, and *z* coordinates to *z*, *x*, and *y* when referring to the usual character table.

Book Reviews

Studies in Organic Chemistry 39. Carbon-13 NMR of Flavonoids. By P. K. Agrawal (Central Institute of Medicinal and Aromatic Plants). Elsevier: Amsterdam and New York. 1989. XVI + 564 pp. $184.25. ISBN 0-444-87449-6.

P. K. Agrawal and his coauthors have made a significant scientific contribution by assembling this large data base for the carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra of flavonoid compounds. This extensive collection is an essential reference for anyone studying the flavonoids. The book should also be useful to chemists outside this specialized field of natural products chemistry. Carbon-13 NMR methods have been especially important to advances in the chemistry of plant phenolic compounds. The phenomenal growth of ^{13}C NMR spectra of flavonoids, from the several hundred entries presented in Markham's 1982 review to the nearly 2000 compounds listed in this volume, attests to the power of ^{13}C NMR in clarifying the structure of these compounds.

When compiling a large data base such as this, it is understandable that errors might be found. A partial check on selected compounds revealed some errors but most are immediately obvious. To assist in evaluating solvent effects, the authors often present spectral data from more than one reference for a compound. To extract chemical shift data for a compound, the reader must expend considerable effort by working between drawn structures and the tabular data. The most interesting data are often those presented for the vast array of substituent structures. Unfortunately, presentation of this valuable information is in a footnoted format that can be disconcerting. However, the novelty of the data makes it worthwhile to work through this difficult presentation. The vast array of structures represented by these compounds makes this volume a valuable reference for all organic chemists faced with the problem of structure elucidation.

Perhaps there is no better way to present such a vast amount of data and still keep the book to a manageable size. But, now that all these spectra have been assembled, the development of a computer-searchable file should not be too difficult. While one hesitates to ask the editor to add further to the huge effort that went into producing this book, the development of such a file would add substantially to its usefulness.

Because modern high-field instruments have not been readily available to many chemists studying plant phenolics, the data presented in this book are concentrated on the proton-decoupled spectra. Therefore, some caution must be exercised when using these assignments which, in many instances, have not been proven by other experiments. The text, however, summarizes the results of a number of two-dimensional experiments that have been employed to solve problems in assignments that are resolved with empirical rules. This book has already been very helpful in solving the interpretation of spectra of some compounds made recently in our laboratory, and others will find it a very helpful reference.

Richard W. Hemingway, *Southern Forest Experiment Station, USDA Forest Service*

Physical Organic Chemistry: The Fundamental Concepts. Second Edition. By Calvin D. Ritchie (State University of New York at Buffalo). Marcel Dekker: New York and Basel. 1990. v + 357 pp. $59.75. ISBN 0-8247-8307-7.

There are chapters on kinetics and interpretation of rate equations, transition-state theory, structural effects on reactivity (linear free energy relationships), molecular orbitals and reactivity, acid–base equilibria and catalysis (including Marcus theory), and isotope effects.

The first chapter, on kinetics and the interpretation of rate data, also introduces the basics of matrix algebra. This is used immediately to derive a general solution for any set of consecutive or simultaneous first-order elementary steps. The latter is then used to illustrate the limits of the Bodenstein steady-state approximation.

The use of matrix algebra continues in later chapters, not only in connection with quantum mechanics but also in connection with transition states and molecular vibrations. Although matrix algebra may seem formidable to most students when encountered in Chapter 1, its use becomes easier with each application and its value more obvious.

Chapter 5, on quantum mechanics and state functions, uses matrix algebra and connectivity matrices to develop molecular orbital theory. Operator algebra is introduced to facilitate the treatment of orbital symmetry, reactions, and the non-crossing rule. The chapter closes with a discussion of Slater determinants, configuration interaction, self-consistent field calculations, and density matrices.

The clarity of the writing and organization in this book are a testimony to the clear thinking, and probably hard work, of the author. I particularly liked his simple but rigorous definitions of such concepts as *elementary step, intermediate*, and *transition state*.

John E. Leffler, *Florida State University*

Diffusion at Interfaces: Microscopic Concepts. Springer Series in Surface Sciences 12. Edited by M. Grunze, H. J. Kreuzer, and J. J. Weimer. Springer-Verlag: New York and Berlin. 1988. vi + 205 pp. $59.50. ISBN 0-387-19212-3.

This slim volume is a collection of papers presented at a workshop on interface phenomena in 1987. As usual in such collections, the papers vary in length and nature, ranging from what amounts to an extended abstract (Blakely and Umbach, Surface Self-Diffusion, Capillarity and Surface Steps, or Doll, Freeman and Voter, Recent Developments in the Theory of Many-Body Processes: Implications for the Theory of Surface Dynamics) to a full-scale review of a relatively mature research area (Fleischmann, Electrochemical Processes in Small Systems). The most interesting contributions combine selected new results with a minireview of the technique used and the relevant theory. Prominent among these are articles on the use of laser-induced desorption to measure diffusion at the gas–solid interface (by S. George and by Seebauer and L. Schmidt) plus descriptions of measurement of diffusion on metal surfaces by field-emission microscopy (Fine) and by scanning tunnelling microscopy (Behm). The remaining contributions deal with diffusion at the solid–solid interface as well as the gas–solid interface; for example, two of the papers discuss the dynamics of alloy surface segregation in Ca/Ni (Hofmann, Borgmann, and Wedler) and Pb/Sn (Unertl, Grunze, and Weimer).

There are a total of 16 articles plus two commentaries in the book. They combine to give an excellent impression of the new ideas and new techniques being brought to bear on the long-standing problem of the characterization of atomic motion at interfaces involving one or two solids (mostly metals, in this collection). On balance, the book is timely, informative, and well worth purchasing by workers interested in time-dependent changes in the structure of metal surfaces, in chemical reactions on these materials or in related areas.

William Steele, *Penn State University*

Inorganic Chemistry Concepts. 12: Crystallographic Statistics in Chemical Physics. By F. Valach and M. Melnik (Slovak Technical University) and J. Ondracek (Institute of Chemical Technology). Springer-Verlag: New York and Berlin. 1988. x + 185 pp. $99.50. ISBN 0-387-18921-1.

Chemists are only recently recognizing the value of large crystallographic data bases as research tools and have now begun to search data bases, such as the Cambridge Crystallographic Database, for new insights into bonding and chemical connectivity. In order to draw valid conclusions from such searches, the data must be treated with the proper statistical methods. Many chemists who may wish to pursue this new form of research have a limited background in statistics, and a book directed to the proper use of statistical methods in the extraction of chemical information from the systematic study of data bases is indeed most timely.

It is the goal of the authors of this small book to provide just that. Unfortunately, the presentation of the material is such that it does not succeed. The use of the English language is so inadequate that many key sentences are incomprehensible. In addition, a general sloppiness prevails which involves punctuation, spelling, and the inconsistent use of symbols. Unfortunately, the problem is exacerbated by the fact that the authors cast their discussion in the more general and precise terminology of mathematics, rather than a terminology more familiar to chemists.

The general topics covered in the book are reasonably well chosen. They are (i) a review of basic statistics, (ii) the application of statistics to a study of the distribution of the lengths of non-bonded interatomic vectors from transition-metal ions, (iii) a study of distributions of the site symmetries adopted by transition-metal ions, and (iv) a study of the distributions of bond lengths from transition-metal ions, with particular reference to the effects of the degeneracy of orbitals.

One is left wondering how this book slipped past the watchful eye of the publisher.

Beverly E. Robertson, *University of Regina*

A Practical Guide to Protein and Peptide Purification for Microsequencing. Edited by P. T. Matsudaira (Massachusetts Institute of Technology). Academic: San Diego. 1989. xiii + 131 pp. $24.95. ISBN 0-12-480280-X.

This book is an expanded version of a handbook from a workshop on protein microsequencing conducted at the 1989 joint meeting of the American Society for Cell Biology and American Society for Biochemistry and Molecular Biology.

The Introduction, by Paul Matsudaira, presents an overview of the Edman degradation reactions and requirements for sample preparation prior to sequencing. Commonly encountered agents or contaminants that interfere with Edman chemistry or create problems in detection of sequence products are identified. Chapter 1, by Harry Charbonneau, outlines strategies for obtaining amino acid sequence data from small quantities (<5 nmol) of protein. HPLC and SDS gel electrophoresis approaches for purifying proteins for microsequencing are compared. Protocols for limited proteolysis and complete fragmentation of both nanomole and picomole quantities of protein are presented. Chapter 2, by Kathryn L. Stone and co-workers, surveys strategies for optimization of HPLC purification of picomole quantities of peptide following enzyme digestion. General HPLC conditions for both analytical and narrowbore columns are described. Protocols for sample preparation and enzymatic digestion of proteins are included.

Chapter 3, by Nancy LeGendre and Paul Matsudaira, gives protocols for protein isolation by SDS gel electrophoresis and subsequent blotting and sequencing. Electrophoretic techniques that enhance separation are discussed. Technical details for optimization of electroblotting to PVDF membranes as well as aspects of electroelution from gels are reviewed. In situ CNBr cleavage of PVDF blotted proteins is described. Chapter 4, by Ruedi Aebersold, contains a method for in situ digestion of blotted protein and subsequent N-terminal sequence determination of peptides eluted from the blot. This chapter concludes with a multipage table listing symptoms, diagnosis, and trouble shooting remedies for unique problems encountered in microsequencing of peptides and associated isolation and cleavage procedures.

Chapter 5, by Hubert A. Scoble, describes how mass spectrometry can be utilized for rapid confirmation of sequence, sequences of blocked N-termini, or identification of modified amino acids.

The book contains practical technical details and rationale for the procedures involved in microsequencing. There are over 110 up-to-date references. This text is an excellent source of technical insights for graduate students, technicians, and postdoctoral fellows who are interested in microsequencing.

L. Dale Snow, *Louisiana Tech University*