Scheme III. Hydroboration of the exocyclic methylene function (C-16) with 9-BBN occurred stereospecifically from the β-face of the double bond and on oxidative workup (3 N NaOH/H_2O_2/40 °C/2 h) provided the triol **11** in 85% yield. Direct hydroboration of the β-dicarbonyl compound **9** with 9-BBN furnished the triol **11**; however, the yield was somewhat lower. As shown in Scheme III (structure **11**), 9-BBN has attacked the β-face of the exocyclic methylene function in order to minimize steric repulsion (1,3) between the axial N_b-methyl function and the incoming hydroboration reagent. This is opposite to the stereochemical outcome of the hydroboration at C-16 observed during the synthesis of (±)-suaveoline.[4b]

The optically active triol (−)-**11** was regioselectively cyclized to the desired (−)-tetrahydroalstonerine monol **12** on stirring with tosyl chloride (1 equiv) in pyridine followed by the addition of either triethylamine or potassium hydroxide. This process gave (−)-**12** in 60% yield, accompanied by starting triol **11** (33%), which could be recycled to provide additional quantities of (−)-tetrahydroalstonerine **12**. When monol **12** was stirred with pyridinium dichromate, an 86% yield of (−)-dihydroalstonerine (**3b**) was realized; however, treatment of **12** under modified Swern[9] conditions [$(COCl)_2$/DMSO/CH_2Cl_2/−78 °C → −10 °C/1.5 h; Et_3N] gave (−)-alstonerine (**2a**) (mp 171–172 °C) in 51% yield, accompanied by dihydroalstonerine (**3b**) (31%). The spectral data for (−)-**2a** (^1H NMR, ^{13}C NMR,[10] IR, UV, MS)[2a] were in complete agreement with those published for natural (−)-alstonerine (mp 172–173 °C); moreover, the optical rotation {$[\alpha]^{25}_D$ −190° (*c* 0.32, EtOH)} of synthetic **2a** indicates that it has been prepared in at least 98% ee.

The synthesis described above represents the first chirally controlled preparation of a member of the macroline-related alkaloids.[11] The stereospecific preparation of tetracyclic ketone **5a**,[4a,b] coupled with the execution of both the Claisen rearrangement (C-15) and the hydroboration process (C-16) in the desired fashion, provides a route for the enantiospecific synthesis of the macroline/sarpagine alkaloids. Further work is in progress to extend this approach to the synthesis of alstophylline (**2b**), as well as a number of bisindole alkaloids,[1-3] including the hypotensive bisindole alkaloid macralstonine (**1**).[1a,b]

Note Added in Proof. Recently, base-catalyzed (NaOMe, CH_3OH, Δ) epimerization of synthetic **3b** gave the epimeric **3a** which had been previously converted into macroline **4** by LeQuesne et al.[3a] Consequently, the synthesis of (−)-**3b** also constitutes a formal total synthesis of **4**, although the yield of this conversion has not been maximized.

(9) Mancuso, A. J.; Huang, S.-L.; Swern, S. *J. Org. Chem.* **1978**, *43*, 2480.

(10) Ratnayake, C.; Lakshimi, S. R.; Arambewela, K. T.; Silva, D.; Rahman, A.; Alvi, K. A. *Phytochemistry* **1987**, *26*, 868.

(11) The optical purity (>97% ee) of **5a** as well as other intermediates was proven by the use of chiral shift reagents as detailed in the following: Campbell, J. *Aldrichimica Acta* **1972**, *5*, 2. All compounds including (−)-**2a** gave satisfactory NMR, IR, and mass spectral data.

Additions and Corrections

Phosphate Ester and Phosphinate Binding to the (μ-Oxo)diiron(III) Core: Synthesis and Characterization of $[Fe_2O\{O_2P(OC_6H_5)_2\}_2(HBpz_3)_2]$ and $[Fe_2O\{O_2P(C_6H_5)_2\}_2(HBpz_3)_2]$ [*J. Am. Chem. Soc.* **1990**, *112*, 681–690]. PETRA N. TUROWSKI, WILLIAM H. ARMSTRONG, MARY E. ROTH, and STEPHEN J. LIPPARD*

Page 687: The minus sign in eq 2 should be a plus sign. This change does not affect any results of the paper, for which the correct equation was used.

Characterization of (Methylcyclopentadienyl)trimethylplatinum and Low-Temperature Organometallic Chemical Vapor Deposition of Platinum Metal [*J. Am. Chem. Soc.* **1989**, *111*, 8779]. ZILING XUE, M. JANE STROUSE, DAVID K. SHUH, CAROLYN B. KNOBLER, HERBERT D. KAESZ,* ROBERT F. HICKS, and R. STANLEY WILLIAMS

Page 8780: We have learned of new evidence from NOESY spectra that suggests that the assignment of H_a and H_b (Figure 1) and C_a and C_b (Figure 2) in (MeCp)$PtMe_3$ should be *reversed* (private communication from Richard A. Newmark, Larry D. Boardman, and Allen R. Siedle, 3M Corporate Research Laboratories, Bldg. 201-BS-05, Box 33221, St. Paul, MN 55144-1000). Arguments and supporting data that involve a series of compounds including the one mentioned above are being prepared for publication.

X-ray Structures of Cubylcubane and 2-*tert*-Butylcubylcubane: Short Cage–Cage Bonds [*J. Am. Chem. Soc.* **1988**, *110*, 7232]. R. GILARDI,* M. MAGGINI, and P. E. EATON

Page 7232, footnote 3: the *c* dimension should be 13.431 (1) Å rather than 13.341 (1) Å.

Mechanism of Grignard Reagent Formation. The Surface Nature of the Reaction [*J. Am. Chem. Soc.* **1989**, *111*, 1896]. H. M. WALBORSKY* and JANUSZ RACHON

Page 1896: The label for structure **4** should read (*S*)-(+)-**4**.

Evidence for a 1,2-Fluoride Shift in a Gaseous Cation [*J. Am. Chem. Soc.* **1989**, *111*, 6868]. THOMAS A. SHALER and THOMAS HELLMAN MORTON*

Page 6869, Table I: The first entry should be −216.227 24 au for ion **5**. Footnote *b* should refer to the following reference: Stams, D. A.; Thomas, T. D.; Maclaren, D. C.; Ji, D.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1427–1434.

Computer Software Reviews

Material Safety Data Sheets on CD-Rom. Sigma/Aldrich: 940 West St. Paul Ave., Milwaukee, WI 53233. $1300 annual subscription rate.

Material Safety Data Sheets[1] on CD-ROM is a single compact disk that provides access to over 38 000 complete MSDSs including chemical structure with printing options. This CD-ROM and its companion software run on an IBM PC or Apple Macintosh computer equipped with CD-ROM drive. Hardware necessary for using this software, including CD-ROM Drive, IBM Cable and Interface Kit, or Apple Macintosh Cable Kit, can be purchased through Aldrich. For Macintosh computers Finder 6.1 and System 6.0.2 or later versions must be used. The CD-ROM provides information on the majority of Sigma/Aldrich chemicals (industries or universities with multiple users in need of quick access to chemical handling and safety information can be accommodated by

(1) A Material Safety Data Sheet, MSDS, includes a detailed description of a chemical's physical properties, fire, explosive, and reactivity data, health hazard and toxicity information, required protective equipment, spill procedures, and waste disposal methods.

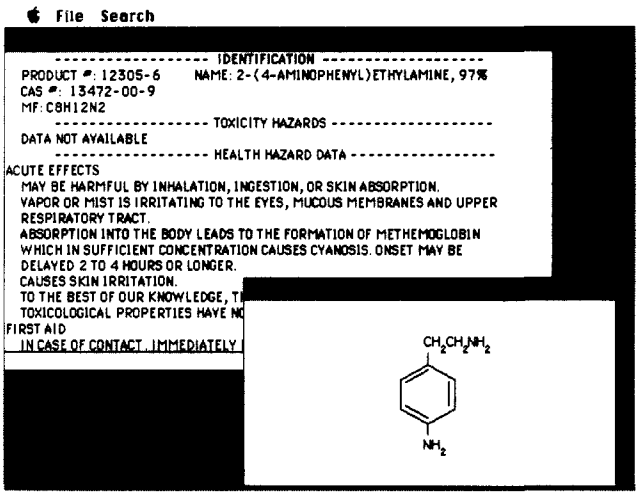

Figure 1.

special licensing agreements). One CD-ROM player will support an entire Mac network. The annual subscription rate includes quarterly disk updates with additional safety data and new Sigma/Aldrich products (approximately 3000 additions/changes per quarter). Information in this review pertains to the Macintosh version.

The MSDS program is relatively user friendly and the instruction manual is explicit, although this is a new software package and some minor bugs do exist. The program allows searches for an MSDS by a variety of methods (Sigma/Aldrich catalog number, CAS number, chemical name, or molecular formula) by choosing the desired option under the SEARCH menu. Some search options are more consistent than others and yield faster results. Searching by molecular formula can be tedious; the software requires the atoms to be entered in alphabetical order. Searching by CAS number or Aldrich/Sigma catalog number will yield the fastest results.

Data can be viewed on-screen, printed, or saved as text files. When viewing on-screen data, the user can toggle between two windows, the MSDS data and the chemical structure. The MSDS print out gives the most pertinent safety information first, along with a clear depiction of the chemical structure, which is not found in most MSDSs. The multi-print option under the FILE menu allows the user to print up to 30 MSDSs by the Sigma/Aldrich Product numbers. Saving the MSDS as text is convenient, since it enables the user to extract data from the MSDS to use in reports. This software is a straightforward, cost effective way to obtain fast access to the most up-to-date federally required chemical hazard information for single or multiple users.

Cynthia A. Markle, *E.I. DuPont de Nemours & Co.*

CHEM-CALC. Version 1.0. Paul Haberfield: 1666 52nd Street, Brooklyn, NY 11204. IBM PC, 1 disk. Suggested shareware price: $35.00.

CHEM-CALC is designed to provide a single, simple package that will help the working chemist with some of the common, everyday computations that Dr. Haberfield has found useful in his daily work. Although some of the components can be found elsewhere, the packaging of a conglomeration of types of calculation and conversion types into a single unit should be a time-saver as opposed to searching through a variety of programs and operating features.

The author has divided the components into 5 types. I. Unit conversions. (1) Energy and spectroscopy: Converts units from one to another. Typing "400, nm, kcal" will give the kilocalorie equivalent of one mole of blue (400 nm) photons. (2) Solvent mixture, composition: Converts between three common ways of specifying solvent composition in binary mixtures. Thus, type "e,w" then "40,v" will inform you that 40 vol % ethanol-water is equivalent to 34.5 wt % and 17.1 mol %.

II. Equilibrium. (1) Weak acid and strong base: Calculates one variable from the other three (K_a, [acid], [base], [conjugate base]). (2) Weak acid and weak base: Calculates any one of the five variables from the other four (as above plus K_b). (3) Thermodynamic parameters: Calculates ΔG from K of vice versa, also ΔH and ΔS from K's at two temperatures.

III. Kinetics. (1) Rate constants: Calculates 0, 1st, or 2nd order rate constants from up to 25 experimental data points. (2) Activation parameters: Calculates free energies of activation, activation enthalpies, and entropies from appropriate rate constants. (3) Enzyme kinetics: Calculates the Michaelis-Menten constant and V_{max} from rates and substrate concentrations using the Lineweaver-Burk method as well as inhibitor constant, K_i, in the presence of a competitive inhibitor.

IV. Numerical. (1) Quadratic equation: Solves quadratics. (2) Least-squares line: Does a linear regression calculation, giving the slope, the intercept, and the standard deviation of the slope (but not the correlation coefficient). Calculates a new x or y value and gives a rough graph of the data.

V. Other. (1) Formula weight and percent composition: Calculates the formula weight from the empirical formula and keeps a running total for some 21 elements, but does not recognize others (B, Be, Sn, Si, Al, Sc, etc.). Also calculates the C, H, and N percent composition. (2) Isotopic abundance ratios: Gives the ratio of the abundance of the molecular ion to the M + 1, M + 2, etc. peaks for the most common 9 elements as well as the high precision mass of the molecular ion.

In general, the calculations are accurate, fast, and easy to learn, with some exceptions. In energy conversions, typing "425, kcal, cal" gives 424989.8 cal, but typing "424989.8, cal, kcal" gives 424.9974 kcal; typing "425, j, cal" gives 101.575 cal (not 101.5774), and typing "101.575, cal, j" gives 424.9898 J. Typing "425, Joule, cal" (using Joule rather than j) gives 0 calories, not an error message. Typing "1, cal, cal" gives 0.99976 cal. As noted by the author, the calculation of isotopic abundance ratios for larger molecules is slow without a math coprocessor chip. Thus, sucrose requires 30 min without the chip (on an 8088 machine), under 1 min with the chip. Ethyl cinnamate requires 2.5 min without the chip. Also, for the lower abundance M + ? peaks, although they are unlikely to be useful, the output flies by too quickly to be read.

There is a typographical error in the thermodynamic parameters, 3rd option instructions. "andS" should read "and dS". Under the weak acid and strong base section of the equilibrium calculations, if you make a mistake in entering the data (leave out a comma) and do not see your error, it would be helpful if you could return to the main menu without rebooting.

Programs can be run off the floppy or loaded onto a hard disk. The system is set up to be used with a color monitor; monochrome monitors may or may not work well. On a Zenith ZMM-149 with an amber screen and a VGA video card some of the instructions (tints) are invisible regardless of the monitor's settings.

This is a useful bit of software for those chemists who make many and varied calculations.

Charles N. Robinson, *Memphis State University*

Papyrus. Version 6.0. Research Design Software: 2718 SW Kelly St., Suite 181, Portland, OR 97201. List price: $99. Site license: $200.

Papyrus is an extensive and powerful program for building a database of bibliographic references, allowing input and editing, and inserting these references into a manuscript, as needed. The program is sophisticated enough to allow the user to set up styles for each journal to which manuscripts are to be submitted and to save these styles for future use. The flexibility of output formatting is impressive, with separate citation styles for books, chapters, articles, patents, etc. In addition, a library of reference styles for an array of journals is included.

The program is not difficult to install or use, and the documentation is not only useful, it is actually literate and interesting to read! Papyrus requires an IBM compatable computer with 512K of ram and DOS 2.0 or higher. A hard drive is strongly recommended as each 1200 references will occupy about 1MB of disk space. According to the supplier, a VAX version is available, and a Macintosh version will be coming later this year.

With use of the program, a bibliography is created and filled with entries typed in or imported from other databases, from on-line searches, or just from listings created on a word processor. An initial test of the import facility, using a typed bibliography, shows that the program has a great deal of sophistication, being able to distinguish the type of reference, but it must be supplied with nicely consistent listings to begin with. If you specify that the date will be in parentheses and will follow the page numbers, it had better do so in each reference. Actually, some more flexible ways to set up these import formats are provided, with conditional inputs, which should make importing a bit more certain. However, a "reject" file of those listings Papyrus could not deal with is kept, so these can be entered by hand or just cleaned up a bit and re-imported. Input files from mainframe databases should be even less of a problem, since these are quite rigidly formatted to begin with. Import formats for many of the common on-line systems are also supplied.

After the references are stored, they can be listed in various ways, sorted into specific-purpose groups, such as the bibliography for a certain manuscript, edited, and printed. Partial references can be entered, and the program automatically tags these with the keyword "incomplete" so they are easy to find when the missing information becomes available.

The program is designed to work in conjunction with a word processor, with a pop-up mini-program supplied, in two versions, to allow the searching of the database and insertion of references without leaving the word processor. The larger of the two pop-ups, which provides for references to be added to the main database or edited, will not work with a large word processor, unless the computer has extended memory. I was able to load and use the larger of the pop-ups in conjunction with XYwrite with a computer having 1 megabyte of RAM, but I ran out of memory when I tried to open a second document simultaneously. The program can be specifically set up to work with Microsoft Word, Wordperfect, Wordstar, and PC-Write, although I used it with XYwrite with little problem. However, with an unsupported word processor, the bibliography must be printed from Papyrus, rather than from the word processor, unless you want to add all the underlines, bold faces, etc. to the bibliography file after you read it into the word processor. I assume that any word processor that writes ASCII files without strange formatting characters should give no more trouble than that.

There are several thoughtful little features in Papyrus. If you begin to enter a reference that is similar to one already in the database, it shows the first reference and inquires if it is the same one and if you wish to continue. It also checks such things as capitalization of authors names and remembers what journals you have entered before, so you can just give an abbreviation the next time. It also keeps a dictionary of keywords for searching your database, as well as abstracts or comments on each paper, if you care to enter them.

The major question with such a powerful and specific-purpose program is "Who needs it?" One can certainly keep a decent bibliography using a word processor, but that would not allow sophisticated searches, and it might need hand labor to reformat it if a different journal required a different format for references. A flat file database, though, could do most searching, and a reasonable job of reformatting. However, it would not supply the instant response inside your word processing program to tell you what that reference by Smith and Jones was, insert the footnote marker automatically, and print the bibliographic listing in specified order. This program, I think, will find its niche in active research groups that publish many papers in a variety of journals, with many people contributing references to a common database, and all using it to extract data as needed.

The license agreement for the program, which is not copy protected, coupled with its relatively modest price, makes it practical for a research group, small company, or academic department to use it easily. The purchaser is permitted to develop up to four distinct databases or can purchase a site license if more are needed. There is no limit specified as to the number of computers that can use copies of these databases. The documentation is included on disk, in addition to the printed manual, to make it easy for each user to have a copy. This is the sort of program that can inspire one to finally dispose of those old 3 × 5 index cards and get those references organized at last!

Barbara B. Kebbekus, *New Jersey Institute of Technology*

*Book Reviews**

Dynamics of Proteins and Nucleic Acids. By J. Andrew McCammon (University of Houston) and Stephen C. Harvey (University of Alabama—Birmingham). Cambridge University: Cambridge and New York. 1988. xii + 234 pp. $42.50. ISBN 0-521-35654-0.

The authors of this book have a long-standing interest and are recognized experts in the field of atomic motions in proteins and nucleic acids. They have written a well-organized book which introduces the reader to the various aspects of internal dynamics in macromolecules.

After reviewing the structural and energetic properties of proteins and nucleic acids and their relationships with the surrounding solvent, the authors present various mathematical models which are used to simulate the different levels of motions allowed in these systems, along with the advantages and limitations of each. The application of these theoretical approaches for the establishment of correlations between structure and function in protein and nucleic acids is illustrated and critically evaluated. This approach ultimately will allow the design of biomolecules endowed of specific activities which can be produced by molecular engineering.

This is a superbly self-contained book which can be understood not only by researchers who wish to gain some insight into the molecular dynamics of macromolecules, but also offers a variety of information and provides an excellent reference source to the scientists already in the field. It is rewarding reading for those of us interested in the structure–function relationships in macromolecules, using either theoretical or experimental approaches.

This book should make a valuable addition to both institutional and personal libraries and is suitable for adoption on a graduate level course list in biophysical chemistry.

Clara Fronticelli, *University of Maryland*

Chromatographic Separations. Analytical Chemistry by Open Learning. By Peter A. Sewell (Liverpool Polytechnic) and Brian Clarke (Neath College). John Wiley & Sons: Chichester and New York. 1988. xix + 335 pp. $29.95 (paperback). ISBN 0-471-91371-5.

This text is one of a 30-volume series in the basics of analytical chemistry written by staff members of the Polytechnic Chemistry Departments in the United Kingdom and designed to train those "who, for a variety of reasons cannot use conventional education courses".

Chromatographic Separations includes the techniques of gas and liquid chromatography, ion exchange, paper and thin-layer chromatography, and size-exclusion chromatography in varying depths of thoroughness in its five chapters. Chapter 1 introduces the several techniques and covers basic terminology, distribution coefficients, and an elementary discussion of sorption mechanisms. The theory of chromatography, particularly that related to retention in column chromatography and in the paper and thin-layer techniques, is presented in Chapter 2 as well as various factors affecting retention. Peak shape, sorption isotherms, column efficiency, band broadening, and resolution are the subjects in Chapter 3, while Chapter 4 covers some aspects of qualitative and quantitative analysis but restricts the qualitative discussion to retention measurements, neglecting the important ancillary techniques, GC/MS, LC/MS, GC/FTIR, etc. Chapter 5 is devoted to classical column chromatography, adsorption column packings, and applications of ion-exchange and size-exclusion chromatography. Fifty-nine pages at the end of the text are devoted to answering self assessment questions raised throughout the volume.

This text is of limited value to the research scientist since no references are given, thus depriving the reader of the opportunity to pursue a topic in greater depth. Also no index is provided making the text of marginal value as a reference. Moreover, such important subjects as detectors, sample introduction methods, choosing the best liquid phase in partition chromatography, programmed temperature operation, and the instrumentation for GC and HPLC are either ignored or considered only briefly. More serious than the few typographical errors noted (e.g., in eq 2.16, page 43, and in the reference to Figure 2.5, which does not exist, on page 54) are more fundamental ones found on page 49, where it is suggested that retention data at different temperatures can be compared using the definition of the specific retention volume, in which V_g is proportional to the reciprocal of column temperature, and the conclusion on page 72 that retention is inversely proportional to the square of the temperature. Both conclusions are incorrect since it is the *logarithm* of the specific retention volume that is proportional to the reciprocal of the absolute column temperature as given by the well-established expression, $\log V_g = -\Delta H_s/2.3RT_c + c$.

In this reviewer's opinion this text is written well below a level desirable for graduate students or research scientists in analytical chemistry; however, it should be of interest to those in other disciplines who desire only an overview of the several chromatographic techniques.

Richard S. Juvet, Jr., *Arizona State University*

Ben Franklin Stilled the Waves: An Informal History of Pouring Oil on Water with Reflections on the Ups and Downs of Scientific Life in General. By Charles Tanford (Duke University). Duke University: Durham. 1989. ix + 228 pp. $38.50. ISBN 0-8223-0876-2.

The author, an emeritus professor of physiology, has written this account of a simple and insightful experiment by Benjamin Franklin, the

*Unsigned book reviews are by the Book Review Editor.