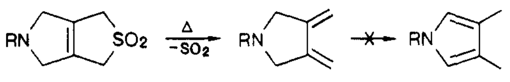
cyclohexane ring and oxoalkyl-substituted cyclopentene, cyclohexene, and pyrrole derivatives.

Clarification of the reaction mechanism is an interesting subject of a further study. One possible reaction path[2,10] is depicted in Scheme I. The strained 1,2-bis(alkylidene)cycloalkane intermediates **3** and **12** are transformed into various cyclic products **6**–**9** via different hydrogen transfer isomerizations.

The 400 MHz ^1H NMR spectra of the bicyclic α-pyrans **6b**–**e** show that they are sterically congested molecules, in which the free rotation of the ethyl group on the 2-C atom is restricted. Thus the methylene hydrogen atoms H_B and H_C (Scheme I) of **6b**–**e** are not equivalent (J_{BC} = 14–15 Hz) and exhibit the different coupling constants (J = 9 and 3 Hz) to the methine hydrogen H_A, which appears as a broad doublet (J = 9 Hz). Furthermore, the methylene hydrogens of the ethyl group on the 5-C atom of **6e** are not equivalent. The free rotation of the butyl group on the 5-C atom of **6f** is also restricted. However, it may be inferred that, in comparison with the dienone **11** which is a highly strained molecule owing to the steric repulsion arising from H vs O, H vs R^2, R^1 vs O, or R^1 vs R^2, the bicyclic α-pyrans **6b**–**f** are relatively stable and can exist without undergoing the ring-opening isomerization to **11**.

The formation of **7** from the unsubstituted diyne **1a** indicates that an alkyl substituent is necessary at least on the 5-C atom for the existence of the bicyclic α-pyran **6** (Z = CH_2CH_2). The transformation of **6** (Z = CH_2 and ^nPrN) to **8** and **9** via the dienone key intermediate **12**[11] (Z = CH_2 and ^nPrN) suggests that the α-pyran ring fused with a five-membered ring is unstable and undergoes the electrocyclic ring cleavage to the dienone. The conjugated δ-amino-α,β,γ,δ-dienone intermediate **13** may play an important role in the formation of **9** because it is known that 3,4-dimethylenepyrrolidine (**14**) does not isomerize to 3,4-dimethylpyrrole (**15**)[12] (eq 4).



14 **15**

(4)

Supplementary Material Available: Typical experimental procedures and characterization (IR, ^1H NMR, ^{13}C NMR, MS, and HRMS) data for the products **6a**–**f** and **7**–**9** listed in Table I (5 pages). Ordering information is given on any current masthead page.

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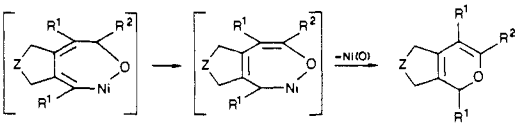
(10) Another possible reaction path may be the one involving the hydrogen transfer isomerization via a metallacycle containing the nickel atom: for example



10 **6**

(11) Equilibration of **12** (Z = CH_2 and ^nPrN) ⇋ **6** (Z = CH_2 and ^nPrN) may be possible.[8b]

(12) Ottenbrite, R. M.; Alston, P. V. *J. Org. Chem.* **1974**, *39*, 1115.

Additions and Corrections

pH Dependence of the Mechanism of Hydrolysis of Benzo[*a*]pyrene-*cis*-7,8-diol 9,10-Epoxide Catalyzed by DNA, Poly(G), and Poly(A) [*J. Am. Chem. Soc.* **1987**, *109*, 2108–2111]. NAFISA B. ISLAM, DALE L. WHALEN,* H. YAGI, and DONALD M. JERINA

Page 2109, Table I: The values of k_{cat}^{H} (M^{-1} s^{-1}) and k_{cat}^{0} (s^{-1}) for the reaction of **DE-1** in solutions of Poly(G) should be >6.3 × 10^5 and >0.20, respectively, and not <6.3 × 10^5 and <0.20 as reported.

Reaction of Dinitrogen Pentoxide with Fluoranthene [*J. Am. Chem. Soc.* **1986**, *108*, 4126–4132]. BARBARA ZIELINSKA,* JANET AREY, ROGER ATKINSON, THOMAS RAMDAHL, ARTHUR M. WINER, and JAMES N. PITTS, JR.

The ^1H NMR spectrum reported for 1,2,5-trinitrofluoranthene was actually that of 2,3,5-trinitrofluoranthene. The correct ^1H NMR spectrum of 1,2,5-trinitrofluoranthene is as follows ($CDCl_3$): δ 8.95 (d, 1, $J_{(4,6)}$ = 1.6 Hz, C_6H), 8.85 (s, 1, C_3H), 8.83 (d, 1, C_4H), 8.02 (d, 1, $J_{(7,8)}$ = 6.4 Hz, C_7H), 7.86 (d, 1, $J_{(9,10)}$ = 7.6 Hz, $C_{10}H$), 7.63 (t, 1, C_8H), 7.55 (t, 1, C_9H). Both trinitrofluoranthenes are formed in the reaction of 2-nitrofluoranthene with N_2O_5 in CCl_4 solution, with 1,2,5-trinitrofluoranthene being the major trinitro isomer formed.

Computer Software Reviews

Number Cruncher Statistical System. Version 5.01. Dr. Jerry L. Hintze: 865 East 400 North, Kaysville, UT 84037. List price $99.00. Optional NCSS 5.1 Graphics ($59.00) and NCSS 5.3 Power Pack ($49.00) require NCSS 5.0.

Number Cruncher Statistical system (NCSS) is an advanced statistical analysis software package. The program requires an IBM-PC, XT, AT, or close compatible machine. NCSS 5.1 Graphics is an integrated statistical analysis and graphics accessory for NCSS and requires a CGA, EGA, VGA, and Hercules compatible graphics board and was designed to output to an HP-compatible plotter. Other plotters require special drivers, not supplied by NCSS. NCSS Power Pack is an accessory designed to perform advanced statistical procedures. This review was conducted on a Leading Edge Model D (8088, 4.7 MHz) and an Acer 1100 (80386, 16 MHz) equipped with an HP Color Pro Plotter.

The basic NCSS package comes on three 360 Kb floppy disks and is designed to run on either a floppy-disk or hard-disk system with at least 450 Kb of memory. NCSS Graphics needs 512 Kb of memory, two floppy disk drives or a hard-disk, and graphics equipment. NCSS is not copy protected.

NCSS offers a surprising repertoire of statistical techniques, probably well in excess of the needs of the average chemist. At first glance, the organization of the package seems lacking. However, the sheer volume of features presented in NCSS is probably to blame, and closer examination reveals a simply organized system centered around a transfer menu packed with options. A statement of the organizational scheme of the program early in the manual would alleviate this confusion, although this is not a serious flaw. The documentation is otherwise straightforward and able to be followed even by the computer novice. The statistical options of NCSS are thoroughly described, with tutorials for the major features appended. Installation is accomplished easily and quickly by copying the driver files to a hard or floppy disk, running the supplied INSTALL program, and redirecting the PLOT file to the proper COM port for the plotter.

Data manipulation is achieved through a "Lotus-123-like" spreadsheet, complete with all the mathematical transformation ability, including logic statements, that one would expect from a good spreadsheet program. NCSS's spreadsheet data system is particularly useful for handling large data sets, allows for clear data labeling within the set, and provides for both spreadsheet and individual data cell editing.

The statistical options provided by NCSS include descriptive statistics, cross tabulation, scatter plots, multiple regression, discriminant analysis, factor analysis, cluster analysis, T-test, ANOVA, nonparameteric tests, and forecasting. With the NCSS Power Pack, the options are expanded to include linear logistic regression, response surface regression, correlation analysis, nonlinear regression, advanced ANOVA, and MANOVA.

Only a fraction of the statistical options offered by NCSS were actually tested in the course of this review, and probably the true power of the package can only be appreciated by a statistician. However, even the most rigorous of statistical procedures was easy to accomplish with NCSS. The program responded admirably to the routine treatment of chemical data and to multiple linear regression analysis of large data sets. However, the large amount of statistics generated became burdensome on routine analysis where extensive statistical data treatment was not required.

The truly impressive part of NCSS lies in its graphics capability. In addition to generating two- and three-dimensional plots in a variety of forms and orientations, NCSS provides the unique ability to easily rotate three-dimensional data vertically and horizontally, and to plot in multidimensional space through star and parallel coordinate plots. Plotter output is achieved through DOS, enabling multiple users of a single plotter.

In some respects NCSS may be cumbersome for routine statistics in the chemistry laboratory, since all of the statistical results are presented on the screen. A useful modification for future revisions would be the ability to create templates, presenting only the desired data and results. This is a fairly minor point, however, and overall, NCSS should prove to be a valuable tool for handling large data sets and for manipulating data where rigorous statistical treatment is required. If for no other reason than its outstanding graphics capabilities, NCSS is a valuable addition to the modern chemistry laboratory and an invaluable aid in the presentation and publication of data.

During the course of this review, we were unaware of the cost of the NCSS package. The price is the biggest surprise of all. We know of no better statistics/graphics software value for $200.00. It is worth $200.00 in graphics capability alone, not to mention the power of NCSS's statistical operations. Its power and ease of use surpass packages costing 10 times as much. It is fun and simple to use, and we highly recommend it to chemists, statisticians, and software junkies, alike.

Barbara J. Bassler, *Hoechst-Celanese Corporation*
Richard A. Hartwick, *Rutgers University*

*Book Reviews**

Applied Geochemical Analysis. Volume 88. By C. O. Ingamells and F. F. Pitard. John Wiley and Sons: New York. 1986. VII + 733 pp. $89.95. ISBN 0-471-83279-0.

In the preface, the authors state the hope that this book will be of value to a wide variety of specialists ranging from mining engineers to academic geochemists. This review is from the perspective of the latter. The book emphasizes classical types of analysis, in part because of the aim of being useful for low-budget labs. However, a pervasive theme in the text is a mistrust of recent innovations in analytical instrumentation. To a degree this is a healthy attitude. I fully agree that—"Modern instrumentation (especially computer output) gives a false sense of security to the analyst." It is also true that even for sophisticated instruments, data quality depends critically on the skills of the analyst. Moreover, even an accurate analysis is only useful if the sample analyzed was chosen with a clear definition of the problem being addressed. In fact, the major message of Chapter 1 is that the sampling process can legitimately be considered the most important aspect of an analytical problem in geochemistry. Precise and accurate data on unsuitable samples are useless. Most of the chapter is devoted to semiempirical approaches to the important problem of obtaining a representative small sample of a large body. This is not a trivial problem, but it is too often ignored. It is an important and relevant chapter, but it is not easy to read.

Chapter 2 emphasizes many important laboratory skills that are essential to analytical geochemists, but too often ignored in modern chemical curricula. However, the authors seem out of touch with the real world in their rejection of single-pan digital-readout balances in favor of a two-pan balance. Usually weighing errors are minor relative to other sources of error, especially with the authors' endorsement of the relatively imprecise (±5%) technique of emission spectroscopy. Discussion of analytical techniques is very uneven. While the relatively new (to geochemistry) technique of inductively coupled plasma-emission spectrometry is endorsed, they downgrade the usefulness of X-ray fluorescence and electron microprobes, two instruments that have had major positive impacts on geochemistry.

Chapters 3 and 4 on classical analysis techniques are, I am sure, the "heart" of the book to the authors. They note that "classical analysis" is not the "old" approach but the "hard core" of well-tried methods of maximum accuracy. They state that when a new technique is developed and proven more accurate it is incorporated into the classical analysis scheme. I question whether the authors are open-minded in this respect. Much of the innovation in analytical chemistry is now done by geochemists. A plethora of new instruments developed over the last 10–20 years have enabled geochemistry, especially trace-element geochemistry, to develop dramatically. Accurate and precise data now enable formulation and testing of hypotheses, something that could not be previously done.

It is interesting to have documented what can be done with limited instrumentation. However, I suspect that all geochemists are aware of instrumentation advances that can be as precise and accurate and more rapid than wet chemical techniques. What geochemists need to know is what analytical approach is best for a specific element or sample, or problem? Indeed their own lab may not have the appropriate equipment, but increasingly it is possible to visit other facilities to learn about and utilize new equipment.

Chapter 6 is a pot-pourri that left me bewildered by its diverse and unrelated topics. Chapter 7 addresses the important issue of geochemical standards, an important topic when studying natural rocks and minerals.

In summary, there is a wealth of practical analytical chemistry information in this book. We are indebted to the authors for passing on their lessons learned from experience. All of this expertise is needed whether one does a gravimetric analysis or uses the latest in new instrumentation. However, this book is not a well-rounded summary of the state of the art in Geochemical Analysis.

Frederick A. Frey, *Massachusetts Institute of Technology*

Vapor–Liquid Equilibrium Data Bibliography. Supplement IV. Edited by Ivan Wichterle, Jan Linek, and Eduard Hãla (Institute of Chemical Process Fundamentals, Czechoslovak Academy of Science). Elsevier Science Publishers: Amsterdam and New York. 1985. vii + 274 pp. $92.50. ISBN 0-444-42518-7.

This supplemental volume is an uncritical compilation of the literature in which liquid–vapor equilibrium data were reported for the period January 1982 through December 1984. It includes binary and higher order systems of both organic and inorganic substances. Entries are arranged according to the Hill system used in the Chemical Abstracts Formula Index. Following the names and formulae of the constituents are numbers, in order of publication, corresponding to the 780 bibliographical entries at the end of the text. These are arranged alphabetically and are in the standard format found in the chemical literature.

This compilation will undoubtedly be useful to chemists and chemical engineers involved in the design and operation of separation and distillation equipment and will find use in other disciplines concerned with fluid phase equilibria such as experimental and theoretical geochemistry. However, I believe that the references could have been made more complete. While the compact version is acceptable for journals concerned with saving space, in a reference work whose sole purpose is to provide a list of articles to be investigated by the reader I believe that the full reference, including the title (translated into English if in another lan-

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*Unsigned book reviews are by the Book Review Editor.