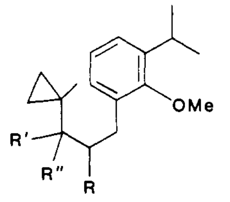
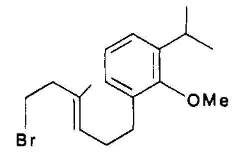
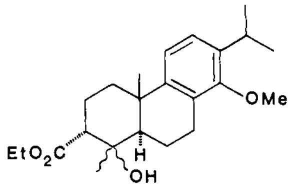
by the action of PBr_3 in ether at 0 °C) was used to alkylate (NaH; THF; 0 °C to room temperature) the cyclopropyl ketoester **7**,[6] thereby generating **8** (99%).[7] Removal of the ester function by means of $Ba(OH)_2$ saponification and concurrent decarboxylation (H_2O/Et_2O for 17 h at 90 °C) led to ketone **9** (92%), which was reduced with LAH (dry ether, 0 °C) to the cyclopropyl carbinol **10**. Conversion of the latter to homoallylic bromide **11**[8] was accomplished in 70% yield by the method of Julia (LiBr, PBr_3, collidine in Et_2O at -40 to 0 °C; then $ZnBr_2$ in Et_2O at 0 °C).[9] Alkylation of ethyl acetoacetate with bromide **11** (LiH; DMF; 75 °C)[10] gave rise to the substituted β-ketoester (**3**)[11] (90%) desired for cyclization.



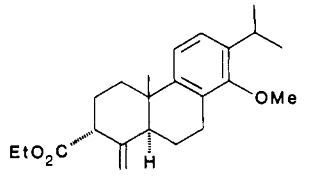
8 R=COOMe; R',R''=O
9 R=H; R',R''=O
10 R=R'=H; R''=OH



11

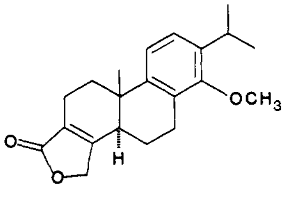


12



13

In the best procedure for cyclization, β-ketoester **3** was exposed to the action of $SnCl_4$ in CH_2Cl_2 at 0 °C for 1–1.5 h, generating tricycle **12**,[12] which was transformable without purification to the unsaturated ester **13**[12] by treatment with 7–8 equiv of $MeSO_2Cl$ and 10 equiv of $(C_2H_5)_3N$ in CH_2Cl_2 at 0 °C. In order to generate the butenolide moiety, crude olefinic ester **13** was directly oxidized (m-$ClC_6H_4CO_3H$; CH_2Cl_2; room temperature) to the corresponding β,γ-epoxy ester; subjection of the latter, without isolation, to elimination conditions (n-C_4H_9Li/i-C_3H_7NH; -78 °C) presumably generates the γ-hydroxy α,β-unsaturated ester, which cyclizes *in situ* to the (±) tetracycle **14**[14] (51% from keto ester 3), identical in all respects (NMR, IR, and mass spectroscopy and TLC) with material of structure **14** produced by means of earlier routes.[4] In view of the prior conversion of **14** to the corresponding 7-ketone[4] and thence to (±)-triptonide (**2**) and (±)-triptolide (**1**),[2,4] the transformations described herein constitute a new synthesis of these natural products (in the racemic form).[15] Overall, this synthesis of **14** requires 12 steps from available materials, necessitates the purification of only 4 intermediates, and proceeds in a yield of ~15%, compared to 20–30 steps and ~0.3–15% yields in prior approaches.[4]



14

Acknowledgment. Grant support from the National Science Foundation (CHE-8002661) is gratefully acknowledged.

Registry No. 1, 73414-46-7; **2**, 73465-88-0; **3**, 80865-60-7; **4**, 2944-47-0; **5**, 80865-61-8; **6**, 80865-62-9; **7**, 61185-33-9; **8**, 80865-63-0; **9**, 80865-64-1; **10**, 80865-65-2; **11**, 80865-66-3; **12**, 80865-67-4; **13**, 80865-68-5; **14**, 73414-41-2; 2-isopropylphenol, 99-89-8; ethyl acetoacetate, 141-97-9.

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(6) Rhoads, S. J.; Gilbert, J. C.; Decora, A. W.; Garland, T. R.; Spangler, R. J.; Urbigkit, M. J. *Tetrahedron* **1963**, *19*, 1625.

(7) **8**: ^1H NMR ($CDCl_3$) δ 0.60 (m, 2 H, cyclopropyl H), 1.21 (s, 3 H, CH_3), 1.11, 1.25 (dd, 6 H, J = 3.6, 6.9 Hz, $CHMe_2$), 1.20 (m, 2 H, cyclopropyl H), 3.17 (m, 2 H, CH_2), 3.21 (m, 1 H, $CHMe_2$), 3.67 (s, 3 H, CO_2Me), 3.74 (s, 3 H, OMe), 4.0 (m, 1 H, CH), 6.91–7.22 (m, 3 H, aromatic H).

(8) **11**: ^1H NMR ($CDCl_3$) δ 1.23 (d, 6 H, J = 6.9 Hz, $CHMe_2$), 1.58 (br s, 3 H, CH_3), 3.74 (s, 3 H, OCH_3), 5.33 (br t, 1 H, vinyl H), 7.0–7.2 (m, 3 H, aromatic H).

(9) Julia, M.; Julia, S.; Tchen, S.-Y. *Bull. Soc. Chim. Fr.* **1961**, 1849.

(10) Hoye, T. R.; Kurth, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 5065.

(11) **3**: ^1H NMR ($CDCl_3$) δ 1.23 (d, 6 H, J = 6.9 Hz, $CHMe_2$), 1.27 (t, 3 H, J = 7.1 Hz, $CO_2CH_2CH_3$), 1.57 (br s, 3 H, CH_3), 2.20 (s, 3 H, C(O)CH_3), 3.74 (s, 3 H, OMe), 4.19 (quart, 2 H, J = 7.1 Hz, $CO_2CH_2\mu$), 5.23 (br t, 1 H, vinyl H), 7.0–7.2 (m, 3 H, aromatic H).

(12) Sterochemical assignments are based on comparison of the NMR spectrum of crude tricyclic ester with the spectra of well-characterized counterparts encountered in earlier, related studies.[13]

(13) van Tamelen, E. E.; Taylor, E. G. *J. Am. Chem. Soc.* **1979**, *102*, 1202.

(14) **14**: mp 175.5–176 °C; IR (CCl_4) 2962, 1763, 1678, 1033 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (s, 3 H, CH_3), 1.22 (d, 3 H, J = 6.8 Hz, $CHMe_2$), 1.23 (d, 3 H, J = 6.8 Hz, $CHMe_2$), 3.30 (sept, 1 H, J = 6.8 Hz, $CHMe_2$), 3.74 (s, 3 H, OCH_3), 4.7, (m, 2 H, OCH_2), 7.11(s, 2 H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 174.0 (=O), 162.9 (C=C), 1.55.5, 144.1, 139.1, 128.0 (aryl), 124.8 (C=C), 124.0, 120.2 (aryl), 70.4 (OCH_2), 60.4 (OMe).

(15) For the production of tripdiolide by tissue culture of *Tripterygium wilfordii* see: Kutney, J. P.; Beale, M. H.; Salisbury, P. J.; Sindelar, R. D.; Stuart, K. L.; Worth, B. R.; Townsley, P. M.; Chalmers, W. T.; Donnelly, D. J.; Nilsson, K.; Jacoli, G. G. *Heterocycles* **1980**, *14*, 1465.

Book Reviews[*]

Polymer Catalysts and Affinants—Polymers in Chromatography. Edited by B. Sědlacëk (Institute of Macromolecular Chemistry, Prague), C. G. Overberger (University of Michigan) and H. F. Mark (Polytechnic Institute of New York). John Wiley and Sons, Inc., New York. 1980. v + 254 pp.

This is No. 68 in the Polymer Symposium Series of the Journal of Polymer Science and represents part of the proceedings of an IUPAC meeting on macromolecules held in 1978 in Prague. It is a collection of 28 papers ranging in length from 6 to 12 pages and covering topics in two somewhat related fields. The first field includes examples of the use of polymeric or polymer-bound catalysts, while the second is concerned with affinity chromatography and applications of polymers in chromatography. Of the 28 papers, most are written by authors from European and Communist countries, and most are concerned with chromatography. Much of the work described is reasonably up-to-data as of 1978 and ranges in quality from acceptable to excellent. The subjects range from polymer-bound transition metal catalysts to immobilized enzymes and whole cells, and from chromatography of peptides and nucleic acid derivatives to TLC of synthetic macromolecules. A number of papers deal with various aspects of gel permeation chromatography and there are even two papers on inverse GC. While this book is a must for all reference and university libraries, the concise nature of the reports will make this book of specific interest only to those workers in the titled fields.

Lon J. Mathias, *University of Southern Mississippi*

Techniques and Applications of Path Integration. By Lawrence S. Schulman. John Wiley & Sons, New York. 1981. xv + 359 pp. $31.95.

Path integration arose as a mathematical technique in quantum the-

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[*] Unsigned book reviews are by the Book Review Editor.

ory, with the heuristic justification that the propagation of a quantum particle between two points might be thought of as involving a coherent sum over all paths between the points. Passing from this heuristic argument to a rigorous mathematical treatment is neither trivial nor, in the author's view, a solved problem. Schulman does a good job of distinguishing between rigor and handwaving, and of indicating where the latter fails to achieve the standards of the former. Applications of particular interest to chemists will include the relation of path integrals to Brownian motion (which involves real integrals over paths) and a brief discussion of applications to statistical mechanics, including a computation of the second virial coefficient for the quantum mechanical hard sphere gas. The value of the extensive references to other books and papers is greatly enhanced by the author's annotations.

George D. J. Phillies, *The University of Michigan*

Spectrometric Identification of Organic Compounds. Fourth Edition. By R. M. Silverstein (SUNY College of Environmental Science and Forestry), G. C. Bassler (Los Altos, California), and T. C. Morrill (Rochester Institute of Technology). John Wiley & Sons, Inc., New York. 1981. 442 pp. $23.95.

The revised fourth edition of this popular text uses an integrated approach to the spectroscopic elucidation of organic structure by mass spectrometry, infrared spectroscopy, proton and carbon-13 NMR spectroscopy, and ultraviolet spectrometry. The chapters on IR and ^{1}H NMR are essentially unchanged from whose of the third edition, and the chapter on UV is similar except for the deletion of the section on instrumentation. The major changes in this edition are an updating of the chapter on mass spectroscopy and the addition of a new chapter on ^{13}C NMR spectroscopy. The mass spectroscopy chapter includes a description of new techniques, such as chemical ionization, field ionization, and field desorption, and of the spectra of new compound classes (amino acids, steroids, and triglycerides). The chapter on ^{13}C NMR spectra is a good introduction to the interpretation of these spectra. It includes a brief introduction to pulse Fourier transform NMR, a comparison of proton coupled to proton noise decoupled and off-resonance decoupled spectra, the effect of specific deuteration on spectra, and a good discussion of additivity rules and functional group correlations for chemical shift assignment. An introductory section on spin–spin coupling of carbon to other nuclei lists representative coupling constant values, but the authors deemphasize the utility of $^1J_{\mathrm{CH}}$ values and do not describe how these can be routinely obtained, with appreciable NOE retention, on modern instruments. The final section of this chapter is a brief description of quantitative ^{13}C NMR methodology (use of long pulse delays, inverse gated decoupling, and relaxation reagents).

This book is an excellent introduction to spectral interpretation and a valuable reference source. The various spectra are more clearly reproduced in this edition, and the tables and appendices to each chapter are considerably easier to read; indeed, the quality of printing in this edition is greatly improved. Each chapter has a revised list of references and a series of problems. There are integrated sets of analyzed spectra and of spectra of unknowns, some with *Beilstein* references, at the end of the text.

Louis Messerle, *University of Michigan*

Chemical Reaction Engineering: Nice. Volume I. Contributed Papers. Edited by J. Villermaux and P. Trambouze. Pergamon Press, New York and Oxford. 1980. x + 532 pp.

This is a special issue of "Chemical Engineering Science" (Vol. 35, No. 1/2) and constitutes the proceedings of the Sixth International Symposium, held at Nice in March 1980. The papers are reproduced for the author's original typescripts and include figures and references. A keyword and an author index are included. The former has some fascinating entries, such as "band-bang control", "cusp catastrophe", "unsteady state", etc.

Treatment of Domestic and Industrial Wastewaters in Large Plants. Edited by S. H. Jenkins (Executive Editor, IAWPR Publications). Pergamon Press, Elmsford, New York. 1981. ii + 773 pp. $90.00.

This collection of 60 papers constitutes the proceedings of an international workshop held in Vienna, Austria, September 3–7, 1979. The volume contains a brief editorial introduction, a subject index, and 68 pages of discussion and replies.

The contributions are largely wastewater treatment facility case studies and are of mixed quality owing to the large number of contributors, typical of such symposium proceedings.

Topics covered relate mainly to the usual problems that plague biological wastewater treatment, viz., sludge disposal, inhibition of biodegradation due to toxic substrates, sludge settling problems, odor control, etc. A few of the papers deal with physical–chemical treatment or chemically assisted biological treatment; these are among the more interesting contributions.

The volume would seem to be of greatest interest to practitioners who are directly involved in the detailed design and construction of treatment plants. It contains little of fundamental interest and as such should have relatively narrow readership appeal.

Lloyd A. Spielman, *University of Delaware*

Solubility Series. Volume 18. Tetraphenylborates. Compiled by O. Popovych (CUNY). Pergamon Press, New York & Oxford. 1981. xxii + 242 pp. $100.00.

Tetraphenylborate salts, $\mathrm{MBPh_4}$, have been known only since 1947 but have assumed importance in analytical chemistry because of the very low solubility of some, such as the potassium salt, and because of the value of the ion as a reference ion in physical chemistry. Altogether, 29 salts, from lithium to tetraphenylphosphonium, are included; the solvent considered is water in most instances, but some organic solvent systems are also considered. Solubilities or solubility products are given, along with the source, the experimental method, purity of materials used, and estimated error. There is a system index and a registry number index.

Solution Equilibria. By F. R. Hartley (Royal Military College of Science), C. Burgess (Gloxco Operations UK Ltd.), R. M. Alcock (Severn-Trent Water Authority). Ellis Horwood Limited, Chichester, UK. 1980. 361 pp. $79.95.

This ambitious and well written volume attempts (1) to give a state of the art treatise on methods used in defining metal-complex solution equilibria, (2) to provide experimental techniques for choosing the "best" method for individual systems, and (3) to introduce readers to matrix algebra so that modern computing techniques may be understood. Unfortunately, the coverage is somewhat uneven. A large amount of space is devoted to the application of matrix algebra, weighting, and error analyses for the treatment of potentiometric and spectroscopic data used in determining formation (stability) constants for metal complexes. Most "amateurs" in the area will probably find this material to be of value only if complicated (polymeric or weak) complexes are formed. More simple systems do not necessitate such powerful mathematical techniques. However, there are useful discussions of the various non-linear least-squares computer programs available and their relative merits and drawbacks and of matrix algebra techniques.

The authors describe in reasonable detail how one can determine the number and types of metal complexes formed in solution. Detailed but brief discussions of experimental techniques for potentiometric and visible-spectroscopic determination of stability constants are included along with less detailed accounts for infrared, NMR, ESR, spectropolarimetric, distribution, electrochemical, and calorimetric methods.

Four "case studies" are included, which cover linear treatment of pH data, Leden and nonlinear treatment of potentiometric data, qualitative and quantitative analysis of spectrophotometric data, and model building and testing using a computer. These are interesting and informative chapters and cover the most widely used techniques. However, a detailed treatment and discussion of a polymeric metal–ligand system would have been of value since simple approaches are usually unsatisfactory.

The last two chapters contain a too brief discussion on the interpretation and application of stability constant data; however, the chapters are well referenced so that one may find more detailed discussions elsewhere. The appendix contains useful computer programs for determining the number of species in solution and DALSFEK, a non-linear least-squares program for spectrophotometric and potentiometric determination of stability constants.

The authors are very careful to point out various pitfalls and common errors that occur in the determination of stability constants via potentiometry and/or spectrophotometry. The suggestion that spectrophotometric data (it should read spectral, i.e., NMR, IR, UV–VIS, etc.) should always accompany potentiometric data cannot be stressed enough, since high-powered computer treatment of the data may yield incorrect analyses which could easily be recognized to be incorrect if spectral data had been obtained.

Robert Nakon, *West Virginia University*

James Prescott Joule and the Concept of Energy. By Henry John Steffens. Science History Publications/USA, New York. 1979. x + 173 pp.

This volume treats the progress of James Joule as an experimenter, beginning with his early efforts on electric motors and culminating in his quantitative studies on the conversion of work into heat. As discussed here, Joule began his work with an effort to build an electric motor capable of replacing the steam engines then in general use. He failed; the author argues that the experimental discipline and technique, which Joule learned in his work on motors, served him well in his later work.

The relationships between Joule and the bulk of the English scientific community, and the reception which his work had prior to its notice by William Thompson, while now only of historical importance, may still have some educational value. Certainly, they show the very fine line between sophisticated work made in advance of general understanding and crackpot work undertaken in scientific backwaters. Joule's isolation from the accepted English doctrine on heat allowed him to find his own results—one may contrast with a modern worker bathed in seminars, summer schools, etc., all forcing the accepted doctrine to his attention. Furthermore, Joule can now be recognized as an exceptionally good experimentalist, who knew the limits of his data. Steffens makes clear, though, why Joule's contemporaries would reasonably have concluded that he was a crackpot. His work claimed fabulous experimental accuracy; there were still large discrepancies between the data and the theory said to have been proved. Worse, Joule's papers commonly built on each other, so that one had to know the entire body of his work to understand the importance of each new paper. While the problems which Joule studied are now well understood, sorting good science from rubbish is still important. Readers of this clearly written volume may perhaps consider how our modern Joules would fare against the present day scheme for journal and grant peer review. Certainly, the final acceptance of Joule's work seems to have been appreciably aided by well placed supporters.

George D. J. Phillies, *The University of Michigan*

Toxicants and Drugs. Kinetics and Dynamics. By E. J. O'Flaherty (University of Cincinnati). John Wiley & Sons, Inc., New York. 1981. VII + 398 pp. $42.50.

During the past two decades, biological scientists have become increasingly aware of the utility of mathematics to quantitatively describe the actions of chemicals and drugs on living organisms.

Dr. E. J. O'Flaherty has made a significant contribution to investigators who need to become acquainted with fundamental mathematical applications to the dynamics and kinetics of drug action. This book focuses on the mathematics of absorption, distribution, and elimination of drugs, including the relationships between drug concentration and time, drug dose and effect, and drug effect and time. The initial chapter includes a review of basic mathematics. Subsequent chapters discuss saturable systems, kinetics of drug action, dose effect relationships, and dose response relationships. Each chapter is well written and is replete with recent literature references. At the end of each chapter, a number of problems taken from the literature are given for the reader to solve. Included also is a separate glossary of symbols and definitions used in the text. The mathematical theories and literature citations are very current and update nicely an earlier text by D. S. Riggs ("The Mathematical Approach to Physiological Problems", M.I.T. Press, Cambridge, MA) published in 1963.

Although the author has suggested that nonmathematicians should be able to assimilate the material contained within the text, the reader should have a minimal level of mathematics including an introductory calculus course to fully appreciate or comprehend the equations. The problems at the end of each section are excellent. However, a discussion or presentation of the solution or even a partial solution to some of these problems would be useful to the novice reader who is doing an independent study. Furthermore, the author might consider including in the next edition a broader discussion on the use of mathematic models and its general application to drug dynamics.

The author has suggested that this text is to be suitable for graduate and/or advanced undergraduate students in pharmacology, toxicology, or related disciplines. Certainly, this book should be an excellent choice for a course in kinetics and dynamics of drug action. In summary, the author has very aptly accomplished her goals as stated in the preface. This text gives an excellent review of the recent literature and mathematical approaches to drug kinetics and dynamics and therefore should be useful for young students and scientists alike.

Leon Shargel, *Northeastern University*
College of Pharmacy and Allied Health Professions

Anionic Surfactants: Physical Chemistry of Surfactant Action. Volume 11. Edited by E. H. Lucassen-Reynders (Merseyside, England). Marcel Dekker, Inc., New York. 1981. xi + 412 pp. $55.00.

Because the physical chemistry of surfaces bears on important problems in biology and technology, this book will have broad appeal. One immediately thinks of the structure and function of cell membranes that control many biological processes, as well as the broad fields of detergency, emulsification, evaporation, extraction, flotation, foaming, and tertiary oil recovery. Discussions bearing on micelles and microemulsions are also included.

It is somewhat odd that this volume, which is one of the most basic of the "Surfactant Science Series", should be Volume 11. However, the book was well worth the delay. The contributions are of high quality and cover in detail a great deal of the subject matter. They have both breadth and depth. The discussions are about equally divided between the equilibrium and the dynamic properties of interfaces. There is relatively little overlapping of the chapters. Dr. Lucassen-Reynders, who is the editor and who in addition has contributed two of the most basic chapters, deserves great credit for the overall organization and consistently high quality of the discussions.

The topics covered include: adsorption at fluid-fluid and solid-fluid interfaces, dilute and concentrated surfactant solutions, polymer–surfactant interactions, surface elasticity and viscosity, liquid films and foams, detergency, and contact angles and wetting. The book is clearly a valuable reference work for the relatively recent thinking in these areas.

Nevertheless, a few constructive criticisms may be in order. Although the contributions are quite thoroughly documented and the author index is extensive, the subject index is disappointingly brief and incomplete. For example, neither "monolayer" nor "monomolecular film" is found in the index whereas a great deal of Chapter 1 and other parts of the book are concerned with monolayers. Clearly this volume would be far more valuable if the subject index were more detailed. Furthermore, there is some unevenness in the documentation. For example, the important classical studies of surface phenomena by three giants in the field, Harkins, Langmuir, and McBain, are given relatively little space. The more recent and extensive work of J. H. Schulman is also rather completely ignored. On the other hand, J. W. J. Henneberg may well have made some pioneering contributions, but devoting almost a full page to a picture of his bust (the only photo in the book) seems somewhat inappropriate.

In conclusion, the discussions make clear that to understand and apply surface chemistry in its broadest sense more work is needed on simple systems and mixtures of pure compounds under controlled conditions. The book provides much food for thought and various indications of the directions in which future academic and industrial research might move. The authors clearly indicate that if fundamental surface chemistry and physics fail to solve some problems the fundamental approach should not be abandoned but should be intensified and broadened to bear better on the phenomena under consideration. The authors and the editors are to be congratulated on a major contribution to the literature of surface chemistry.

Herman E. Ries, *The University of Chicago*

Biological Fluidised Bed Treatment of Water and Wastewater. Edited by P. F. Cooper (Water Research Centre, Stevenage Laboratory) and B. Atkinson (University of Manchester Institute of Science and Technology). Ellis Horwood Limited Publishers, Chichester, England. 1981. 411 pp. $99.95.

The book provides an excellent overview of the application of biological fluidized bed technology to water and wastewater treatment. The book is probably as complete a compilation of information on this topic as is currently in existence.

This book is composed of chapters derived from papers given at a conference in Manchester, Great Britain, in April 1980. Consequently, the book lacks the coherence that might be found if only two or three authors were involved. Nonetheless, each of the individual chapters are generally well prepared. A more direct coupling of theory to experiment to actual plant experience would have been desirable.

The book includes after each section a synopsis of the discussion of the papers. Since many of the reader's questions will coincide with questions raised in the discussion, the inclusion of the discussion greatly assists the reader in critically evaluating material presented in each paper.

This reviewer was somewhat disappointed that the conference did not include papers on immobilized cell technology as being developed in other areas of biochemical engineering. The cross-fertilization would have been useful. The papers in the book, except for a supplementary contribution by Hakulinen and Salkinoja-Salonen, do not consider the explicit nature of the biological catalyst and changes that might occur in that catalyst due to immobilization and changes in process variables. Finally, a more detailed summary of the theoretical background of such reactors would have been useful to the novice.

Overall the book will provide a useful overview for the expert and a good introduction for those developing an interest in this technology.

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School of Chemical Engineering