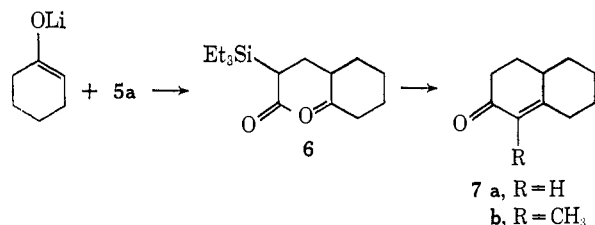
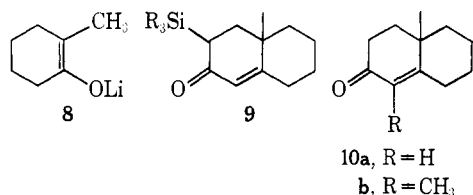


had thus been demonstrated, but for the activating group to be of practical value, it must be easily removed, and we expected cleavage of the triethylsilyl moiety during completion of the annelation process. Indeed, heating the crude adduct **6** in 5% sodium methoxide-methanol afforded $\Delta^{1,9}$ -2-octalone **7a** in



an overall yield of 80%.¹² The use of **5b** in the annelation reaction similarly led to the octalone **7b** in ~70% yield.

With 2-methylcyclohexanone, conjugate addition at the more substituted position could be carried out either using the pure lithium enolate **8**, derived from the silyl ether, or more simply by mixing equimolar amounts of annelating agent **5a** and 2-methylcyclohexanone in *tert*-butyl alcohol containing a catalytic amount of potassium *tert*-butoxide. This latter technique afforded primarily the silylated enone **9** which was easily transformed into the known methyl-octalone **10a** (60% yield by vpc calibration, using **10a**

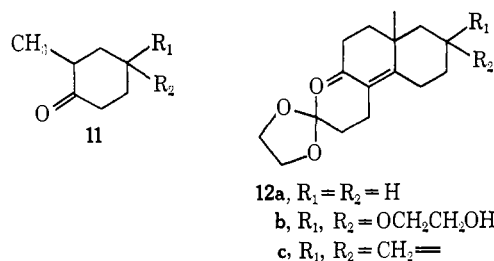


as a standard) by boiling with sodium hydroxide-isopropyl alcohol solution.¹² Reaction of the lithium enolate **8** with the silylated enone **5b** similarly gave the octalone **10b** in ~60% yield.

α -Silyl vinyl ketones such as **5c** allow the preparation of highly functionalized octalones such as **12a-c** in good yields. The following represents a typical experimental procedure. A solution of **11b** (1.2 g, 7 mmol,¹³ in *tert*-butyl alcohol) (15 ml) was treated

(12) This material was shown to be identical with an authentic sample, prepared by published procedures.

(13) S. A. Narang and P. C. Dutta, *J. Chem. Soc.*, 2842 (1960).



with the enone **5c** (2.25 g, 7 mmol, in 10 ml of *tert*-butyl alcohol) at room temperature under an inert atmosphere. Later (2.5 hr), the deep red solution was poured into ether (150 ml) and washed successively with water and brine. After drying and concentration, the crude product was taken up in 10% aqueous sodium hydroxide (6 ml) and isopropyl alcohol (9 ml) and then refluxed for 12 hr. Ether extraction afforded a dark oil which was heated under vacuum in a Kugelrohr oven at 120° (0.2 mm) to remove triethylsilanol. Column chromatography of the residue furnished 1.7 g (73%) of **12b** as a clear oil.⁵

The contrast with the classical method is worth emphasizing. For instance, condensation as just described of **8** with the silylated enone **5c** led in about 70% yield to **12a**. On the other hand we were unable to isolate any enone **12a** from the condensation of 2-methylcyclohexanone with the unsilylated analog of the vinyl ketone **5c** in the presence of potassium *tert*-butoxide-*tert*-butyl alcohol, conditions which had proved very satisfactory for the synthesis of **10a** from methylcyclohexanone and the silylated enone **5a**.

The feasibility of carrying Michael additions under aprotic conditions, by the use of silylated vinyl ketones, is a step forward. Nevertheless, the method presented here is not suitable at the present time for the trapping of kinetically generated, *regio-unstable*, lithium enolates because they equilibrate faster (*via* proton transfers) than they undergo Michael addition. In such situations alkylation with reactive halides is, of course, a feasible alternative.

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Book Reviews*

Crystal Data Determinative Tables. Third Edition. Volume I: Organic Compounds. Volume II: Inorganic Compounds. Edited by J. D. H. DONNAY and H. M. ONDIK. U. S. Department of Commerce, National Bureau of Standards, and the Joint Committee on Powder Diffraction Standards, Swarthmore, Pa. 1972 and 1973. Vol. I: ix + 865 pp. \$30.00. Vol. II: ix + 2106 pp. \$50.00.

The previous edition of this important work of reference appeared in 1963 and 1967, and the number of entries has increased from 13,000 to 24,000. An impressive international group of

crystallographers compiled the data, which for the first time have been placed on magnetic tape to make possible computer searches. The editors express the hope that having the data on tape will also facilitate preparing later editions, and particularly to reduce the time lag (six years for this edition!) between the end of literature coverage and publication. Entries are arranged according to crystal type, but formula, chemical name, and mineral name indexes facilitate manual access to particular data.

Determination of Organic Structures by Physical Methods. Volume 5. Edited by F. C. NACHOD and J. J. ZUCKERMAN. Academic Press, New York, N. Y. 1973. xv + 367 pp. \$26.00.

* Unsigned book reviews are by the Book Review Editor.

This volume continues in the path of the earlier ones, which have been reviewed in previous numbers of this journal. The selection of subjects indicates a broadening interpretation of the term "structures" in the title, for several of the chapters are concerned with methods of primary value for studying reaction mechanisms, e.g., Spin Saturation Labeling (J. W. Faller) and Ion Cyclotron Resonance Spectroscopy (J. L. Brauman and L. R. Blair). There are chapters on Mössbauer Spectra of Organometallics (N. W. G. Debye and J. J. Zuckerman), Automated Chemical Structure Analysis Systems (S.-I. Sasaki), Electron Diffraction (J. Karle), Chemically and Electromagnetically Induced Dynamic Nuclear Polarization (R. G. Lawler and H. R. Ward), and Nuclear Quadrupole Resonance (M. G. Voronkov and V. P. Feshin). As heretofore, the chapters start with short orienting introductions and lead rather rapidly into full-fledged treatments of methods, capabilities, and results, amply documented.

Heterocyclic Compounds. Volume 9. Acridines. Second Edition. Edited by R. M. ACHESON (University of Oxford). **Volume 27. Condensed Pyridazines, Including Cinnolines and Phthalazines.** Edited by R. N. CASTLE (Brigham Young University). Wiley-Interscience, New York, N. Y. 1973. Volume 9: xii + 878 pp. \$75.00. Volume 27: xii + 1124 pp. \$80.00.

Volume 9 of this standard work has been completely revised, and considerably expanded, with the help of an international group of fifteen collaborators. In addition to the chapters on ordinary chemistry, such subjects as Chemiluminescent Reactions of Acridines, the Mass Spectra of Acridines, Acridines, and Enzymes, etc., are treated separately.

Volume 27 consists of but three whopping chapters: Cinnolines (G. M. Singerman), Phthalazines (N. R. Patel), and Azolo- and Azinopyridazines and Some Oxa and Thia Analogs (M. Tisler and B. Stanovnik). Printing the references in convenient groups throughout the chapters makes consulting them easier.

As in previous volumes, the treatment is both encyclopedic and authoritative, and the amount of information compressed into tables is enormous.

In neither volume is the cut-off data for the literature given, but the editors' prefaces are dated March and April 1972, respectively, and 1971 references are present. Both volumes have good subject indexes, but, curiously, only Volume 27 has an author index.

Organic Reaction Mechanisms. 1971. Edited by B. CAPON (University of Glasgow) and C. W. REES (University of Liverpool). Wiley-Interscience, New York, N. Y. 1973. x + 648 pp. \$39.00.

The literature on reaction mechanisms appearing between November 1970 and November 1971, comprising approximately 5000 papers, is summarized in fourteen chapters by thirteen devoted contributors. An author index, a cumulative subject index for 1970 and 1971, together with prompt publication, help to maintain the value of this series as an aid to current awareness.

Pharmacological and Chemical Synonyms. 5th Edition. Compiled by E. E. J. MARLER. American Elsevier, New York, N. Y. 1973. vii + 456 pp. \$32.00.

This is a kind of dictionary, in which nonproprietary names and codes of drugs and "other compounds drawn from the medical literature" are listed and defined by giving systematic chemical names or a cross-index leading to one. This compendium is a valuable guide in an area where proliferation of synonyms has reached irresponsible and horrifying proportions. The anti-alcoholic drug disulfiram (bis(diethylthiocarbamoyl) disulfide), for example, has no less than twenty-nine synonyms, ranging from TTD to "Contrapot."

Physical Constants. 9th Edition. By W. H. J. CHILDS. Halsted/Wiley, New York, N. Y. 1973. 107 pp. \$6.95 (cloth); \$3.50 (paper).

The newest edition of this book now uses SI units wherever practicable, among other improvements.

Specific Energies of Galvanic Reactions and Related Thermodynamic Data. By J. G. GIBSON and J. L. SUDWORTH (British Railways Board Railway Technical Centre). Wiley-Halsted, New York, N. Y., and Chapman and Hall, London. 1973. xvi + 819 pp. \$30.00.

This is a book of tables giving specific energies, cell voltages, and temperature coefficients of a comprehensive variety of inorganic galvanic reactions. The derived data were calculated from pub-

lished values using a digital computer and photographic reproduction of the print-out to avoid errors in transcription. The reactions considered are formation and displacements involving oxides, sulfides, and the halides, with, apparently, all reasonable oxidation states of all metals. This compilation should be of much value to chemists concerned with electrochemical energy conversion and battery research.

The Vapour Pressures of Pure Substances. Compiled by T. BOUBLIK (Czechoslovak Academy of Sciences), V. FRIED (Brooklyn College), and E. HALA (Czechoslovak Academy of Sciences). American Elsevier, New York, N. Y. 1973. 626 pp. \$25.50.

In formula-index order are tabulated vapor-pressure data for a large group of largely organic compounds. For each is given the literature reference, the constants for the Antoine equation ($\log P^0 = A + B/(T + C)$), and columns of experimental and calculated vapor pressures at various temperatures. There is also a compound index in alphabetical order of the name (not always systematic and not cross-indexed).

Water and Water Pollution Handbook. Volume 4. Edited by L. L. CIACCIO (GTE Laboratories, Inc.). Marcel Dekker, Inc. New York, N. Y. 1973. xi + 630 pp. \$29.50.

Water chemists throughout the world will welcome the "Water and Water Pollution Handbook" and its interdisciplinary approach to the subject of water analysis and water treatment. Volume 4 is a comprehensive review of the various instrumental techniques applied to the measurement of organic and inorganic substances and radionuclides in water. Techniques reviewed include atomic fluorescence, atomic absorption, and flame, emission, infrared, luminescence, mass, and X-ray spectroscopy. Also included are activation analysis and automated instrumental, electrochemical, and gas chromatographic methods. Chapters covering Determination of Minor Metallic Elements and Gas Chromatographic Methods are outstanding in the orderly presentation of two very complex subjects. References are abundantly given throughout the text.

The chapters on Monitoring of Water Systems and Automated and Instrumental Methods in Water Analysis present the subject in a very thorough and positive manner but are severely lacking in emphasis on the limitations of present technology in this field. Most of the equipment available for water monitoring has been designed to provide stream monitoring rather than waste discharge evaluation. While the analysis method is the same in both situations, the concentration of the measured constituent is generally greater in the waste. Interference, corrosion, and suspended solids are more significant in waste monitoring requiring more rugged construction and modification of flow systems. At present there is a lack of reliable sensor systems for many of the chemical constituents to be measured in industrial wastes. Because of this restraint, most of the analytical work for monitoring wastes will be done in the laboratory.

The author attempts to comprehensively cover an extensive spectrum of water analysis and has met with reasonable success in this endeavor. The overview of this broad subject will serve as an excellent reference for those engaged in monitoring the aquatic environment.

Dolores O. Bassett, *Calgon Corporation*

Chemistry of Marine Natural Products. By PAUL J. SCHEUER (University of Hawaii). Academic Press, New York, N. Y. 1973. xi + 201 pp. \$14.00.

This monograph is the first comprehensive treatment of the chemistry of secondary metabolites from marine organisms to appear in book form. The material has been organized according to approximate biogenetic guidelines, which appears to be the most logical presentation. This does, however, present problems for those who want an account of the biosynthetic ability of a particular organism.

The highlights of this book are undoubtedly the chapters on marine sterols and benzenoid pigments, areas in which the author has made major contributions to the research literature. Other subjects receive a less rigorous treatment.

A lack of continuity between many of the topics covered reflects the youthful status of marine natural products research. One suspects that the publication of this book may be premature, for its coverage of several topics has been rendered out-of-date by recent research.

D. John Faulkner, *Scripps Institution of Oceanography*