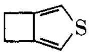
λ_{max} 258, 285 (sh) nm), and mass spectrum (molecular ion at m/e 216), this material was assigned the symmetrical dimer structure **12**.[8]

As in the case of its oxygen analog,[2a] the high-field chemical shift of the α protons in **6** relative to that in other substituted thiophenes (*e.g.*, **13**),[9] despite the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presence of an additional double bond, strongly indicates the contribution of a pronounced paramagnetic component to its ring current. The chemical shift in **12**, however, appears to be normal, suggesting that it exists in a nonplanar "tub" conformation, like cyclooctatetraene itself. The uv spectrum is also consistent with such a structure.

With regard to the mechanism of thiirane desulfurization,[10] the observation of complex kinetics under some conditions indicates that at relatively high concentrations a bimolecular process dominates; this competes with a somewhat slower unimolecular desulfurization which becomes the major pathway as the concentration of thiirane decreases during the reaction. This behavior provides kinetic evidence for the suggestion[10a] that thiirane desulfurizations can (in some cases at least) involve a more complicated mechanism than simple cheletropic extrusion of the sulfur atom. The apparently strong dependence of stereochemistry on temperature, however, suggests that these reactions cannot be classified as "stereospecific,"[10a] and mechanistic interpretation should perhaps be considered with this cautionary observation in mind.

Acknowledgments. We are grateful to the National Science Foundation and the Chevron Research Co. for financial support and to Professor Michael A. Raftery for the use of his scintillation counting equipment.

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[8] For the oxygen analog, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 973 (1970), and ref 2a.

[9] (a) P. J. Garratt and D. N. Nicolaides, *J. Chem. Soc., Chem. Commun.*, 1014 (1972); (b) S. W. Longworth and J. F. W. McOmie, *ibid.*, 623 (1972).

[10] (a) E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7164 (1968); (b) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966); O. P. Strausz, H. E. Gunning, A. S. Denes, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **94**, 8317 (1972).

[11] (a) Alfred P. Sloan Foundation Fellow, 1970–1972; (b) Camille and Henry Dreyfus Teacher–Scholar, 1970–1975.

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Book Reviews

Organic Reactions and Orbital Symmetry. By T. L. GILCHRIST and R. C. STORR (University of Liverpool). Cambridge University Press, London. 1972. viii + 271 pp. £1.80 (UK); $6.95 (USA).

This book presents a good cross section of cycloreaction chemistry in a highly readable manner. Introductory chapters on classifications and experimental indicators for reaction mechanisms, and on theoretical treatments of concerted processes, are followed by descriptive accounts of electrocyclic isomerizations, cycloadditions, and sigmatropic rearrangements. A brief coverage of substitutions, additions, and eliminations completes the text.

It may be recommended to readers at every level of familiarity with the cycloreaction literature: it informs efficiently and provokes thought effectively through a judicious alternation between specific examples and summarizing generalizations.

Inevitably, "Organic Reactions and Orbital Symmetry" and other recent books on similar matters, such as those by Anh, Lehr and Marchand, Maier, Wieland and Kaufmann, and Woodward and Hoffmann, are in part duplicative; yet no one of them is redundant. Each has a unique emphasis, balance, and level of mechanistic sophistication.

John E. Baldwin, *University of Oregon*

Selective Ion Sensitive Electrodes. By G. J. MOODY and J. D. R. THOMAS (University of Wales). Merrow Publishing Co., Watford, Herts, England (U.S. Distributor: Bonn Industries, Inc., Plainfield, N. J. 07061). 1972. vii + 140 pp. $6.90.

In this short, concise monograph, Moody and Thomas survey various characteristics of the ion-selective electrodes which have appeared since Ross rekindled interest in this area with the 1967 publication of the performance of the liquid ion exchange electrode for calcium ion. The authors make no pretext at presenting a theoretical framework or historical development. Their primary concern is the methods by which electrode selectivity is determined and the tabulation of various properties of the many commercially available electrodes. It is written as a practical guide to the selection and use of ion-selective electrodes. The book suffers from lack of depth and a paucity of specific examples with experimental details of the actual use of these electrodes. If one's bookshelf already contains Helferich's "Ion Exchange," Eisenman's "Glass Electrodes of Hydrogen and Other Cations," and Durst's Special Publication No. 314 (NBS), this book would be a suitable companion as a guide to the characteristics of commercially available electrodes.

George Baum, *Corning Glass Works*

Metal Pi-Complexes. Volume II: Complexes with Mono-Olefinic Ligands. Part 1: General Survey. By M. HERBERHOLD (Technical University of Munich). American Elsevier, New York, N. Y. 1972. xv + 643 pp. $86.00.

The stated objective of this monograph is to survey completely the literature concerning monoolefin π complexes of transition metals from 1830 (when W. C. Zeise first described his platinum–ethylene complexes) through 1968. Part 1 is mainly descriptive in nature and is devoted to syntheses and properties of the complexes. It is to be followed by Part 2 which is to be devoted to spectroscopy, structure, and bonding in the monoolefin π complexes.

The book begins with a brief introduction which is followed by a short historical survey of olefin–transition metal complexes. Next there is a chapter which surveys the various methods used to synthesize olefin–transition metal complexes. Chapter IV describes the known nonfunctionally substituted olefin–π complexes. It is organized according to groups of the periodic table, beginning with group VIb metals and ending with a discussion of group Ib metal complexes.

Finally, Chapter V describes the complexes of functionally substituted monoolefins. Here the organization is according to functional group. Virtually all types of functionally substituted olefins are included (*e.g.*, cyanoolefins, α,β-unsaturated carbonyl compounds, haloolefins, vinyl alcohols, ethers and esters, allyl compounds, unsaturated amines, phosphines, arsines, and sulfides). Chapters IV and V together contain 85 tables which list spectral and physical properties for many of the compounds discussed.

In the opinion of this reviewer, this book represents a very significant contribution in the area of transition metal π complexes and is heartily recommended for anyone interested in this area. Professor Herberhold has succeeded in organizing a large amount of material (1879 references) in a clear and orderly fashion. Although the coverage is complete only through 1968, a considerable number of references from 1969 and 1970 are included in an appendix and are mentioned in the body of the text. It is, however, unfortunate that the sizable cost of this volume will probably prevent it from attaining the distribution it deserves.

John W. Fitch III, *Southwest Texas State University*

Natural Rubber and the Synthetics. By P. W. ALLEN (Natural Rubber Producers' Research Association). John Wiley & Sons, New York, N. Y. 1972. xi + 255 pp. $15.75.

The title of this book gives absolutely no clue to its contents. Thus the reader who expects the usual technical book on the chemical make-up and physical properties of various rubbers, natural and synthetic, will most certainly be surprised, but not necessarily disappointed. It might be best to quote from the author's own preface, which states as the purpose of the book "...to describe in terms intelligible to the layman, and acceptable to the technical reader, the present-day technical and economic status of the rubbers, the organizational structure of the various sectors of the industry, the reasons underlying choice of rubber for a particular product and, most important, to provide a balanced perspective which takes account not only of historical forces but also of present trends and future possibilities."

The above description speaks for itself. The use of the word "layman" is somewhat of a euphemism, since at least a basic knowledge of chemistry is required from the reader who wishes to understand the differences between the various rubbers. But there is no doubt that the author succeeds in accomplishing his goal; and to the best of this reviewer's knowledge, this is the only book of its type in existence.

Despite its brevity, this book covers much territory, and does it intelligently and correctly, in the technical sense. After an introduction which defines and classifies various rubbers, both chemically and physically, the subsequent seven chapters treat such topics as history of rubbers, methods of production of natural and synthetic rubbers, kinds of rubbers (in more detail), markets for raw rubbers, the rubber manufacturing industry, and, finally, patterns for the future ("toward 2000 A.D."). Obviously, the most interesting parts and aspects of the book deal with the interplay of world economics (and politics) with natural rubber and the various synthetic rubbers, and what we may expect in future as these factors exert their influence. Here one senses a subtle, yet pervasive, bias toward natural rubber. This is perhaps to be expected if one takes into account the origins and affiliation of the author. After all, someone from the synthetic rubber "camp" would undoubtedly show an opposite bias with the truth probably lying somewhere in between. It is interesting, in this connection, that the author's somewhat grudging concession to the inevitable pressures of the man-made product is to predict an eventual synthetic rubber *via* the biosynthesis reactor!

Despite the above "human" failings, this book is an excellent and valuable contribution to the rubber literature.

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The University of Akron

Nucleic Acid Sequence Analysis. By STANLEY MANDELES (Rutgers University). Columbia University Press, New York, N. Y. 1972. 282 pp. $15.00.

This book provides a useful survey of the nucleic acid sequencing methods currently in use and those that are being developed, as well as separation techniques for oligonucleotides. The most impressive results, the sequencing of several tRNAs and 5S RNAs, have been achieved *via* the overlap method, and numerous examples of the strategy and experimental problems are discussed. The overlap method involves the sequencing of a polynucleotide by using fragments of overlapping sequences obtained by enzymatic cleavage of the nucleic acid at specific points. Chemical and enzymatic methods of stepwise degradation are described with thorough evaluation. Special attention is given to the more sophisticated end labeling method which has been useful in the analysis of large RNAs. Promising physical methods of nucleic acid sequencing which rely on the use of electron microscopy, optical rotatory dispersion, X-ray diffraction, mass spectrometry, and nuclear magnetic resonance spectroscopy are briefly considered.

The longest chapter is dedicated to the most formidable task which is the sequence analysis of high molecular weight RNAs, *i.e.*, messenger, viral, and ribosomal RNAs. Possible approaches to their analysis, such as formation of subunits and use of a replication system which could be limited to the synthesis of specific segments of an RNA template, are presented.

The author has made a special effort to use simple analogies in places where a newcomer might experience difficulty with commonly used terminology. However, in his attempt to simplify the description of the terminal positions of nucleotide chains, the author disregards the currently accepted convention by using "5′-hydroxyl-linked terminal" for the 3′-end and "3-hydroxyl-linked terminal" for the 5′-end. This could lead to confusion should the outsider refer to other literature in this field. This point notwithstanding, Mandeles' book is as authoritative as it is well written. It will fill the needs of those who teach nucleic acids chemistry and have more than an academic interest in the subject. In the opinion of a Ph.D. candidate, Robert H. Hayashikawa, Mandeles might have succeeded in challenging some uncommitted young scientist to join in further research on this seemingly endless frontier.

Joseph Nagyvary, *Texas A&M University*

Determination of pH, Theory and Practice. Second Edition. By ROGER G. BATES (University of Florida). Wiley-Interscience, New York, N. Y. 1973. xv + 479 pp. $19.95.

No physical property of solutions is more frequently measured than is the apparent pH value. And perhaps no other common physical property is more generally misunderstood and misinterpreted.

As the former head of the Analytical Section of the National Bureau of Standards and one of the world's most influential individuals in promoting the establishment of current standard pH scales, Bates writes with authority in this revision to his classic text. The critical issues are quickly brought into focus by an examination of the many definitions of pH which have been proposed and a discussion of the theoretical and/or practical limitations of each defined pH scale. In this section Bates emphasizes his central theme that *no* theoretical pH scale can be matched exactly with experimental numbers. Thus extrathermodynamic assumptions must be adopted for the establishment of any practical pH scale. The main point of controversy then centers on which assumptions are to be made. Following a chapter dealing with liquid junction potentials and ionic activities, the importance of these extrathermodynamic assumptions is stressed in a chapter on the various pH standards which have been adopted by official bodies. As Bates notes, it is important that these inherent assumptions be recognized when interpreting measured pH values.

One of the main features of the current revised edition is the expansion of the two chapters dealing with nonaqueous acid-base phenomena and recent developments in the establishment of viable pH scales in nonaqueous and mixed solvent media. Commencing with a thorough discussion of the medium effect, the general concepts of nonaqueous pH scales are considered with specific emphasis on the recently established pH* scales for methanol-water and ethanol-water mixtures as well as a standard pD scale for deuterium oxide. It is unfortunate, however, that Bates has not seen fit to include information on practical pH scales in other solvent media, even though these may not be as soundly based as are the alcoholic scales.

A new feature in this edition involves the inclusion of a chapter devoted to the measurement of hydrogen ion concentration (as contrasted to activity). This latter material should be of particular interest to coordination chemists and others concerned with the determination of equilibrium constants in units of concentration (rather than in activity or mixed units.) The concluding chapters of the book deal with revised discussions on electrodes and pH instrumentation reflecting the current state of the art.

In its revised form, this book remains as *the* authoritative source of information regarding the determination of pH. As such it is highly recommended to all individuals for whom the quantitative interpretation of measured pH values is important.

David B. Rorabacher, *Wayne State University*