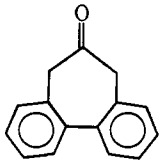
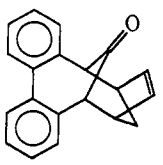
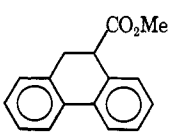
Treatment of MBK with a variety of bases (pyridine, triethylamine, 2,6-di-*tert*-butylpyridine, proton sponge, lithium tetramethylpiperidide) at low and high temperatures failed to give spectral evidence of CE or CE′. Trapping experiments with dienes were more successful, however. Elimination of MBK with triethylamine in methylene chloride containing excess cyclopentadiene yields a 1:1 adduct (A): mp 138°, nmr ($CDCl_3$) τ 2.01–2.11 (m, 2 H), 2.61–2.88 (m, 6 H), 3.77 (s, 2 H), 6.17 (d, J = 3 Hz, 2 H), 6.99 (brs, 2 H), 8.00 (d, J = 12 Hz, 1 H), 8.42–8.68 (m, 1 H); mass spectrum *m/e* 272.1207 (M). The adduct was shown to have exo stereochemistry at a 99.5% confidence level by *R* factor analysis of nmr shifts induced by $Eu(fod)_3$-d_{30}.[4-6] Exo stereochemistry is also found in the tropone–cyclopentadiene [6 + 4] adduct[7,8] and is in accord with theory.[9] As expected CE is much more reactive in {6 + 4} cycloadditions than is tropone; the addition of cyclopentadiene to CE is complete within minutes at


K


A

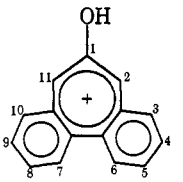


F

most, at ambient temperatures, whereas the same diene requires 3 days to accomplish addition to tropone.[8] A {6 + 4} furan adduct was prepared in the same manner as for A. However, benzene ({6 + 4}) and heptafulvalene ({6 + 14}) failed to yield adducts, the former even though it was present as a solvent excess. The scope of the cycloadditive reactivity of CE is evidently circumscribed by its facile oligomerization. Nevertheless, it appears to be the most reactive trienic component presently available. As expected, it is not intercepted by dienophiles, such as *N*-phenylmaleimide, in {6 + 2} cycloadditions.

Addition of MBK to methanolic sodium methoxide gives product F, characterized (*inter alia*) by dehydrogenation (DDQ, refluxing toluene) and comparison of the latter product with authentic methyl 9-phenanthroate. Though alternative mechanisms are conceivable, this result suggests a Favorskii reaction of the valence tautomer CE′. It is interesting that DBK upon reaction with triethylamine gives a Favorskii-type product (9-phenanthroyl bromide).[2] We find that it does so even in the presence of excess cyclopentadiene. Thus, intermolecular cycloadditions of α-bromodibenzo[*c*,*e*]tropone could not be elicited.

Extraction of a CCl_4 solution of MBK with FSO_3H resulted in an intensely red solution displaying multiplets centered at τ 0.7 and 1.5. The low field multiplet is comprised of three lines which appear to be a singlet ($H_{2,11}$) surrounded by the A portion of an AXYZ spin system in which the A resonance ($H_{6,7}$) is coupled to only one ($H_{5,8}$) of X,Y,Z. HMO calculations indicate that the 2,11 positions of CA should be



CA

by far the most electron deficient. The 6,7 protons are of the planar biphenyl type (such as the 4,5 positions of phenanthrene) and are expected to be anisotropically shifted to low field. The ratio of the areas of the τ 1.5 and 0.7 absorptions is nearer to 2.0 than to the theoretical 1.5. Nevertheless, the evidence suggests that the predominant species in these solutions is, in fact, CA, though some impurity evidently contributes absorptions underlying the λ 1.5 peak.

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(4) The *R* factor analysis was executed by Professor Davis, whom we warmly thank. The details will be presented elsewhere by Professors Davis and Willcott, though it may be noteworthy that the raw data had appeared more consistent with an endo addition. This further accentuates the importance of their method[5,6] for analyzing nmr shift data.

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Book Reviews

Challenging Problems in Organic Reaction Mechanisms. By D. RANGANATHAN and S. RANGANATHAN (Indian Institute of Technology). Academic Press, New York, N. Y. 1972. xi + 160. $7.50.

This second book of problems by the authors partially reviews the literature from 1966 through 1971. There are 417 examples taken from over 460 references. The selection, not intended to be comprehensive, reflects the authors' interests and has been limited to no more than ten journals published in England, Germany, and the United States. Over 40% of the references came from *Tetrahedron Letters*. Three journals (*Chemical Communications*, *Journal of Organic Chemistry*, and *Journal of the American Chemical Society*) tied for second place with each providing about 12% of the references. Multiple selections from the work of any one individual were generally avoided; however, seven selections describe results one of the authors had previously published.

Material is easily located by either the Author Index, or the Compound Type Index, or the Reaction Type Index. A Problem Classification Index places each problem into one of three levels ranging from easy to very difficult. Just under 100 examples have Woodward–Hoffmann classifications.

An organic chemist will enjoy working the problems and will

find them instructive. Surely each reader will "discover" new ideas as he seeks the explanations. For this rewarding experience the book is highly recommended.

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Standard Methods of Clinical Chemistry. Volume 7. By the American Association of Clinical Chemists. Editor-in-Chief: G. R. Cooper. Series Editor: J. S. King, Jr. Academic Press, New York, N. Y. 1972. vii + 333 pp. $16.00.

The seventh volume of this excellent series, dedicated to Miriam Reiner, is organized into seven sections, namely, enzymes, lipids, minerals, proteins, toxicology, vitamins and hormones, and special techniques. From one to six specific methods are described in each section. Each procedure included has been critically evaluated and checked by independent experts. Suggestions from the checkers are included in the text including possible sources of error and helpful precautions. Underlying principles are presented and, where appropriate, the specificity is discussed along with the interpretation of the data. The various sections are strengthened by a reasonable number of carefully selected references.

In general, this book maintains the high standards of its predecessors. A useful memorandum on the classification of the Hyperlipidaemias and the Hyperlipoproteinaemias prepared at an informal consultation arranged by the World Health Organization is particularly timely. It is included along with methods for the measurement of phospholipids, triglycerides, and lipoproteins. Another area given particularly thorough coverage is the assay of serum thyroxine including two procedures for the estimation of thyroxine by competitive protein-binding and a semiautomated procedure. General articles on immunoelectrophoresis, on gel-diffusion techniques in the clinical laboratory, and on methods for assuring quality data from continuous flow analyzers are all clear, brief, and practical.

This volume is strongly recommended for medical schools, hospitals, and clinical laboratories.

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Methods and Techniques in Clinical Chemistry. By Paul L. Wolf, Dorothy Williams, Tashiko Tsudaku, and Leticia Acosta (Stanford University Medical Center). Wiley-Interscience, New York, N. Y. 1972. 417 pp. $11.50.

This book is intended as a laboratory manual, primarily for medical technologists, and for others concerned with the daily practical problems of the clinical chemical laboratory. It contains directions for the determinations of 75 constituents frequently measured in clinical laboratories. With a few exceptions (*e.g.*, acid phosphatase, glucose, and chloride), one method only is given for estimating each constituent. Autoanalyzer methods are given for some estimations, including CO_2, cholesterol, creatinine, phenylalanine, thyroxine, glucose, and urea N. Microbiological methods are followed in the estimation of folic acid and vitamin B_{12}. The more common enzyme assays are described, *e.g.*, transaminases, phosphatases, and lactic dehydrogenases.

The directions for the procedures included are unusually clear and complete and can be followed by persons of limited experience. The sections on "Clinical Interpretation" are admirable for their clarity and brevity. In general the authors succeed in providing clear, practical information in regard to the procedures described, which are those in use at the Stanford Clinical Laboratory of the Stanford University Medical Center.

Obviously, no book on this subject of convenient size can also be comprehensive. This book's limitations arise largely from its intended size and scope. Many widely used procedures are not included; the basis for choosing those which are given is their established usefulness in a particular laboratory. It is primarily a technologist's manual and does not include such material as quality control or principles of instrumentation. In this reviewer's opinion the inclusion of an index, in addition to the alphabetized Table of Contents, and also a glossary of abbreviations would enhance the book's usefulness.

In general, this book can be recommended for its intended use, that is, as a practical manual in a clinical chemical laboratory where both manual and automated procedures are used.

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Methods in Cyclic Nucleotide Research (Methods in Molecular Biology Series. Volume 3). By Mark Chasin (Squibb Institute for Medical Research). Marcel Dekker, Inc., New York, N. Y. 1972. x + 315 pp. $17.50.

This book consists of several techniques currently being used by different laboratories involved in cyclic nucleotide (particularly, cyclic AMP) research. The object of the book is to serve as a laboratory manual and this end has been achieved. The first section describes some of the many methods for measuring cyclic AMP in biological material. Methods for determining activities of adenylate cyclase, guanyl cyclase, and cyclic 3′,5′-phosphodiesterase are described in section 2. In addition, in this section there is a chapter describing methods for purification and assay of cyclic AMP-dependent and cyclic GMP-dependent protein kinases. The final 75 pages of the book deal with some special techniques for studying cyclic AMP in specific biological systems.

As with most multi-authored texts, quality and style are quite variable, but this reviewer found most of the chapters to be clearly written. In general, most of the methods are outlined in sufficient detail to allow one to initiate some studies of cyclic nucleotide metabolism. However, many aspects of each method are not completely detailed and explained. Consequently, additional sources of information will be needed for "trouble shooting" and when special problems arise. For these reasons new investigators in the cyclic nucleotide field will find the text very useful, but individuals who already have some experience may not find the book to be of great value. The methods and techniques will be of more interest to the biological chemist than to organic or physical chemists, with the exception of one chapter on high-pressure liquid chromatography for analysis of cyclic nucleotides.

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Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation Method. By William G. Fateley, Francis R. Dollish (Mellon Institute), Neil T. McDevitt, and Freeman F. Bentley (Air Force Materials Laboratory). Wiley-Interscience, New York, N. Y. 1972. x + 222 pp. $12.95.

This book is a practical guide to using the Halford–Hornig factor group method in analyzing the vibrational spectra of crystals. The authors use the term "selection rules" in its narrow sense, *i.e.*, to indicate the presence or absence of infrared and Raman activity; polarization and orientation effects are not considered. The book's principal value lies in its many carefully treated examples, a feature which recommends it especially to students in the field.

The correlation method is described in the first two chapters. Most of this is repeated unchanged from the authors' 1971 paper in *Applied Spectroscopy*, but the addition of a table of Wyckoff site correlations somewhat simplifies its application. Its advantages are illustrated in Chapter 3, where the selection rules for $SrTiO_3$ are rederived using the more laborious method of Bhagavantam and Venkatarayudu for comparison. Chapter 4 applies the method to molecular selection rules and the distribution of vibrational fundamentals. Except for the addition of some point groups of little physical interest, these 50 pages essentially duplicate material presented (much more compactly) in Herzberg's book. The final chapter contains some two dozen worked examples chosen from a variety of systems: ionic and covalent inorganic crystals, plane and helical polymers, and layer structures. Except for polymers, no organic crystals are treated. Three appendices contain site symmetry, character, and correlation tables. These should perhaps be used with some caution: a check of Appendix II showed that no fewer than six of its 44 character tables contained misprints.

Several texts have appeared recently in which selection rules are covered as part of much more general treatments of the vibrational spectroscopy of solids. Anyone newly approaching the field would probably prefer one of these to the present volume. Within its rather narrow scope, however, this book is reasonably clear and well written; any reader who works his way through it should become thoroughly familiar with vibrational selection rules and their derivation.

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