

downfield. The relative shifts are H_1 (10), H_2 (5.0), H_3 (1.4), H_7 (4.0), and H_4-H_6 (<0.5).

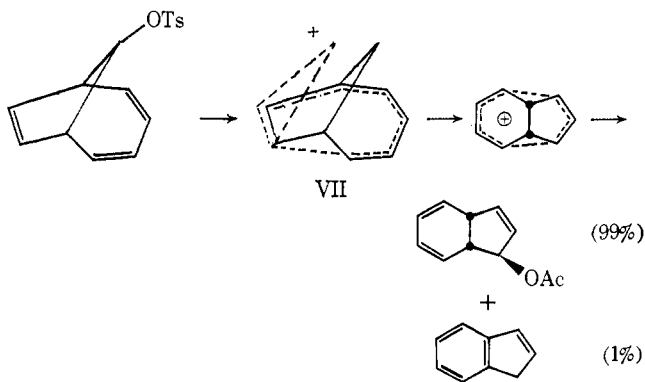
The spectra for VI-OAc-*d* produced in the acetolysis of α -D-I-OTs is identical with the undeuterated material except that the signal at δ 5.83 integrates for one hydrogen. In the presence of $\text{Eu}(\text{fod})_3$ the peak at δ 7.18 disappears, the δ 6.12 doublet collapses to a singlet, and the rest of the spectrum is unchanged.

Therefore, effectively all the deuterium appears at one position, the C_2 position of VI-OAc.¹¹ This result eliminates the possibility of rearrangement occurring *via* a simple shift of the C_1-C_2 bond to the C_3 cationic center of I as observed in the reaction of 9-phenyl-bicyclo[4.2.1]nona-2,4,7-trien-9-ol with SOCl_2 in pyridine¹² and is more in line with reaction of this carbinol with toluenesulfonic acid in HCCl_3 to produce 2-phenylindene.¹² The acetolysis of IV-OTs in NaOAc buffered acetic acid produces IV-OAc, which was recovered in 97% yield, and no other products were observed. Thus, the solvolysis of IV-OTs must proceed *via* a bishomocyclopropenyl cation intermediate. On the other hand the acetolysis of V-OTs produces a four to one mixture of the epimeric *exo*-V-OAc and a rearranged olefin.

The enhanced reactivity of I-OTs in spite of the rate retarding inductive effect of the butadiene moiety is ascribed to a stabilizing interaction by this group with the incipient bishomocyclopropenyl cation (involving carbons 7, 8, and 9) in the rate-determining step to produce a bicycloaromatic cation (VII). The bicycloaromatic character of this cation contributes *ca.* 7.2 kcal of additional stabilization to the transition state from I-OTs (calculated from the relative k 's for I-OTs and IV-OTs), while the stabilization attributed to homo-

aromaticity is a small portion of the total resonance stabilization.¹³ In contrast, for the 7-norbornadienyl cation, 75% of the stability is due to homoaromaticity and only 25% to bicycloaromaticity.⁴

Since the photoelectron spectroscopy data reported by Heilbronner, *et al.*, suggest no interaction between the monoene and the diene in the bicyclo[4.2.1]nonatriene,¹⁴ the interaction upon ionization of I-OTs must occur with a considerable amount of motion of the atoms involved and little or no vertical stabilization. Thus the ionization of I-OTs is consistent with the formation of a bicycloaromatic cation generated by extensive laticyclic interaction between the bishomocyclopropenyl cation and the butadiene moiety (VII).^{15,16} However the stabilization of the initial cation is not large and it efficiently rearranges in a specific and symmetrical way to the more stable bishomotropylium ion which gives chemical capture products primarily.



(13) Analysis of the homoaromaticity and bicycloaromaticity contributions to the stability of this system will be presented in a fuller paper with the necessary definitions of the k 's selected for the various ROTs esters.

(14) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).

(15) Interaction of the olefinic groups with the developing cationic center in solvolysis is consistent with the photoelectron spectra data on the 9-methylenebicyclo[4.2.1]nonatriene¹⁶ which shows a stabilizing interaction between the isolated double bonds when the polarization of the *exo* methylene makes C-9 a positive center (see footnote 8 of ref 16).

(16) M. Reetz, R. W. Hoffmann, W. Schafer, and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **12**, 81 (1973).

(17) Deceased Nov 23, 1969.

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Book Reviews*

Advances in Catalysis. Volume 23. Edited by D. D. ELEY, H. PINES, and P. B. WEISZ. Academic Press, New York, N. Y. 1973. ix + 352 pp. \$19.00.

This volume has contributions on both heterogeneous and homogeneous catalysis. J. R. Anderson writes about skeletal re-

arrangements of hydrocarbons catalyzed by metals, and J. H. Sinvelt discusses metal-catalyzed hydrogenolysis of hydrocarbons. Chemisorption of benzene, hydrogen-deuterium exchange, and hydrogenation of benzene are the subject of a contribution by R. B. Moyes and P. B. Wells. The photocatalytic effect, discussed by Th. Wolkenstein, is less well known; it is defined as the change in catalytic activity of the surface of a semiconductor under illumination and has been applied particularly to hydrogen-deuterium ex-

* Unsigned book reviews are by the Book Review Editor.

change, oxidation of carbon monoxide, and synthesis of hydrogen peroxide. The remarkable selective catalytic activity of cycloamyloses is reviewed by D. W. Griffiths and M. L. Bender. Finally, transition metal-alkyl compounds as catalysts for polymerizations of olefins and vinyl monomers are discussed by D. G. H. Ballard. It is nowhere indicated when the manuscripts were received, or when the literature coverages ended, unfortunately. The book is well indexed.

Aliphatic, Alicyclic, and Saturated Heterocyclic Chemistry. Volume I (in three parts). Edited by W. PARKER (University of Stirling). The Chemical Society, London. 1973. vii + 213, ix + 517, xi + 567 pp. £20 per set.

This is a further representative of the new subdivisions of the Specialist Periodical Reports. It covers a two-year span (1970 and 1971), but future volumes are planned to be annual. Part I is devoted to open-chain compounds in three chapters: Acetylenes, Allenes, and Olefins; Other Functional Groups; Fatty Acids and Related Compounds. Part II covers three- and four-membered rings, with carbocyclic and heterocyclic rings treated separately from each other. Part III covers five- and six-membered rings, medium-sized rings, and bridged and caged systems. The amount of work involved in compiling this series is formidable, and the many contributors are to be commended for their joint service to chemistry.

As is customary in the series, there is no subject index, but each part has an author index, which makes it possible to locate quickly what any author has published on the subject in the period covered, thus serving as a current-awareness aid.

Band Structure Spectroscopy of Metals and Alloys. Edited by D. J. FABIAN and L. M. WATSON (University of Strathclyde). Academic Press, New York, N. Y. 1973. xviii + 753 pp. £11.80.

This is another "Proceedings" volume reproduced from typescript. The conference that generated it was held in September 1971 in Scotland. The term "band structure" used in the title has been adopted to cover "all those solid-state spectroscopies that probe the electron states in the valence or conduction bands of a metal, such as soft X-ray emission and absorption, X-ray photoelectron spectroscopy, ultraviolet photoemission, and isochromat spectroscopy." Original research is included in many of the papers; will it be reported only here, and thus not be abstracted, or has it already been published elsewhere?

Catalysis Reviews. Volume 6. Edited by HEINZ HEINEMANN (Mobil Research and Development Corp.). Marcel Dekker, Inc., New York, N. Y. 1972. vii + 341 pp. \$19.50.

The emphasis is almost exclusively on heterogeneous catalysis in this volume, which includes the P. H. Emmett Award Address by R. K. Kokes and seven other contributed chapters. Topics included are hydroformylation, the oxo reaction, oxygen transfer on zinc oxide, automotive emission control, investigation of surface catalysts by programmed desorption and by X-ray scattering, and study of kinetic structure using marked atoms. A long author index and a quite short subject index conclude the work.

The Characterization of Chemical Purity. Organic Compounds. Edited by L. A. K. STAVELY (University of Oxford). Butterworths, London. 1971. vii + 173 pp. \$15.00.

This is a publication of the IUPAC Commission on Physicochemical Measurements. It consists of twelve chapters contributed by an international group of experts. The chapters deal with criteria for purity, methods used to determine it and their characteristics and applicability, and reference standards. The methods covered are thermal methods, density, vapor pressure and boiling point, refractive index, chromatography, and the various spectroscopic techniques. This is largely a discursive work and does not contain extensive tables (although many examples and figures are shown). There is unfortunately no index.

Chemical Engineers' Handbook. Fifth Edition. Edited by ROBERT H. PERRY and CECIL H. CHILTON. McGraw-Hill, New York, N. Y. 1973. xx + 1958 pp. \$35.00.

This Fifth Edition of the time-tested work has, according to the publishers, been reworked to a major extent, and every one of the twenty-five sections has received attention. The section on mathematics now includes conversion to SI units, and a detailed treatment of optimization techniques, for example. A book of such a size and such varied content cannot be adequately described in a short review, but most potentially interested readers will be familiar with

previous editions, and it is only necessary to state that the book is evolving with the times and should continue to be a valuable aid.

Concise Dictionary of Physics. By J. THEWLIS. Pergamon Press, Elmsford, N. Y. 1973. viii + 366 pp. \$16.50.

This is a useful volume, printed in larger type than the usual dictionary. The definitions are short but adequate, and include a large number of terms of concern to chemists, such as "Bremsstrahlung", "Littrow Mirror", "Compton Effect", etc. A few of the entries seem rather trivial, such as "Compressor" and "Branched-Chain Compound", but on the whole, they are well selected.

The Determination of Sulphur-Containing Groups. Volume 1. By M. R. F. ASHWORTH (University of the Saarland). Academic Press, London. 1972. viii + 149 pp. £3.20.

In this volume, sulfones, sulfoxides, and sulfonyl halides, thiocyanates, isothiocyanates, and, oddly enough, isocyanates are covered. For each functional group, qualitative detection and quantitative determination are described, and both chemical and physical (spectroscopic, chromatographic) methods are considered. The presentation is more encyclopedic than critical, and the reader may often be in doubt about which of several methods may be recommended; references for all methods are given, however, and this book thus serves as a valuable source of information. Much information is given in tables, which make consulting the book easy, in spite of a rather skimpy index. The importance of sulfur-containing organic compounds in medicinal and agricultural chemistry increases the significance of a book such as this.

Enzyme Synthesis and Degradation in Mammalian Tissue. Edited by M. RECHCIGL (U. S. Department of State). University Park Press, Baltimore, Md. 1971. xvi + 477 pp. \$17.50.

This treatise is intended to be "a comprehensive review of the... factors that control enzyme activity as well as the regulatory mechanisms involved in enzyme synthesis and degradation..." This purpose is accomplished with the help of seventeen contributors, two of whom are from Europe. There is also a useful glossary. Extensive lists of references, an author index, and a detailed subject index make this a valuable work of reference.

Fibre Reinforced Materials Technology. By N. J. PARRATT (Ministry of Defence, United Kingdom). Van Nostrand-Reinhold Co., New York, N. Y. 1973. xi + 180 pp. \$21.50.

Although there is much more technology than chemistry in this book, chemists concerned with solid-state science, polymer chemists, and those concerned with carbon, boron, glass, cellulose, and other fibers should find it of interest. The extensive documentation gives it reference value, yet it has a didactic approach and a set of 22 practice problems.

Identification of Organic Compounds with the Aid of Gas Chromatography. By RAYMOND C. CRIPPEN (Northern Kentucky State College). McGraw-Hill Book Co., New York, N. Y. 1973. x + 331 pp. \$19.50.

Identification of organic compounds (qualitative organic analysis) has evolved during the postwar years from the traditional chemical tests and formation of derivatives to an increasing reliance on spectrographic methods. Accordingly, books on the subject have been revised so as to include spectroscopy either as a separate chapter, or as an integral part of the discussion of each functional group. Separate books on spectroscopic identification are often used in college courses to amplify this aspect.

Vapor-phase chromatography has risen to importance over the same period, but its use has been largely limited to detection of the number of components in a mixture. Although the value of specific retention time as an identifying physical characteristic of a substance is well appreciated in research and in forensic chemistry, its potential has been relatively ignored in books and courses on qualitative organic analysis. Dr. Crippen's book appears to be the first to emphasize the usefulness of vpc and to integrate it into an organized approach. This book is essentially a pragmatic text on qualitative organic analysis, with all the conventional chemical tests, but with a heavy emphasis on vpc everywhere superimposed. The author has gathered together a great variety of published information relating structure to retention times and has augmented it with a substantial amount of unpublished information from his own experience. This information appears throughout the book in the form of tables or graphs, the latter usually being plots of retention time against some such property as boiling point or solubility for a homologous series. Vpc traces of mixtures of homologs abound.

This book differs from conventional textbooks in that it does not have the pedagogical appurtenance of sets of problems and exercises, nor does it have extensive tables of melting points of derivatives. It is evidently intended to serve as a handbook or reference work, a purpose that is furthered by the selected list of 199 references primarily to the primary literature to document the information presented. The detailed, 55-page index further enhances its reference value. Dr. Crippen's book is not intended to be a fully rounded treatment of identification, for it does not take up spectroscopic methods at all; its aim is to demonstrate the power inherent in vpc used to its full potential.

Infrared Spectroscopy. By M. AVRAM and GH. MATESCU. Translated by L. BIRLADEANU from the Romanian original. Wiley-Interscience, New York, N. Y. 1972. 527 pp. \$14.95.

This is intended as a textbook for chemists, but the wealth of documented information makes it serve well as a work of reference also. The first fifth of the book, "Introduction to the Theory of Infrared Spectra", takes up the subject from its beginning in 1800 with Herschel's discovery of infrared radiation and moves rapidly through wave mechanics to the fundamentals of vibration and rotation and symmetry in polyatomic systems. The remainder of the book is devoted to the spectrographic characteristics of the principal classes of organic compounds (inorganic compounds are not explicitly considered).

Pragmatic details, presented with many useful tables, are deftly balanced with just sufficient theoretical interpretation to help the organic chemist, who is, after all, primarily interested in infrared spectroscopy as a tool rather than as an end in itself. There are even chapters on carbohydrates and amino acids, peptides, and proteins. The references are carefully selected for usefulness rather than quantity, and include both books and reviews and primary journals. This book is a useful addition to the organic chemist's personal shelf.

5th International Symposium on the Chemistry of Coffee. Association Scientifique Internationale du Café, Paris. 1973. 436 pp. 160 francs.

This volume of proceedings contains papers delivered at the symposium held in 1971 in Lisbon. The papers are reports of original research and are written in English, French, German, or Portuguese. They are divided among the areas Chemical Composition and Methods of Analysis, Chemistry in Relation to Technology, and Organoleptic Character and Physiological Effects, plus two bibliographical review papers. Among the more intriguing subjects is the correlation of the color of raw coffee beans with quality; No. 39 clone coffee from Lyamungu, Tanzania, is said to be outstanding for its production of the highly desirable blue beans. Can we now hope for coffee in a selection of decorator colors?

Nuclear Magnetic Shift Reagents. Edited by R. E. SIEVERS (Wright-Patterson Air Force Base). Academic Press, New York, N. Y. 1973. xii + 410 pp. \$9.50.

A symposium on the title subject was held at the 165th National Meeting of the American Chemical Society in April 1973, and the papers presented there have provided the basis for the present book. There are seventeen contributions, which treat the subject on a broad front, from the nature of the interaction between the reagent and substrate to various applications. Most of the contributions are concerned with proton magnetic resonance, but one is devoted to ^{13}C nmr, and one to secondary deuterium isotope effects. A useful feature is a general bibliography of no less than 53 pages that brings together a large number of publications, organized into nine categories for ease of consulting. Unfortunately, there is no introductory statement to inform the reader whether this bibliography is selective or comprehensive, or what time period it covers. There is also a glossary, which tells you what "focam", "fhd", and "tmhd" mean, and that "pta" does not mean what you might at first think.

The Proton in Chemistry. Second Edition. By R. P. BELL (University of Stirling). Cornell University Press, Ithaca, N. Y. 1973. vii + 310 pp. \$17.50.

Professor Bell's little book "Acids and Bases" and its big brother, "The Proton in Chemistry", published in 1959, have become classics of clear, rational exposition in a subject of fundamental importance to chemists. In the years since Professor Bell presented the material that was to become the first edition of the latter book, during his tenure as George Fisher Baker Lecturer at Cornell, the subject has advanced considerably. Professor Bell's own researches have been a major contribution. It is very timely for a new edition to appear, and particularly appropriate that Professor Bell was able to spare the substantial amount of effort to accomplish this major revision.

New material is especially evident in the treatment of fast proton-transfer reactions and of hydrogen isotope effects. The chapter on concentrated solutions of acids and bases has been omitted, partly because there are now available extensive treatments of the subject by other authors, and partly for the curious circumstance that "the interpretation of reaction velocities in these concentrated solutions has become more rather than less confused with the passage of time" (a refreshingly modest and honest statement!). References have been brought up to date and new data have been infused throughout. This edition is recommended to those who have enjoyed and profited from the first edition as well as to those who have such pleasure to look forward to.

Residue Reviews. Volume 45. Edited by F. A. GUNTHER and J. D. GUNTHER. Springer-Verlag, New York, N. Y. 1973. vii + 186 pp. \$16.20.

This volume contains five contributed chapters on various aspects of residual pesticides in agricultural products and soil. A good subject index increases its usefulness.

Laboratory Methods in Infrared Spectroscopy. Second Edition. Edited by R. G. J. MILLER (Imperial Chemical Industries) and B. C. STACE (University of Surrey). Heyden and Son, London/New York/Rhine. 1972. xxi + 375 pp. \$18.00.

In the preface to this second edition the editors remark that "infrared spectroscopy has moved rather slowly in the last decade and significant advances have been few in number" and then go on to add ten new chapters. The new chapters are Far-Infrared Spectroscopy, Quantitative Infrared Analysis of Polymeric Materials, Fourier Transform Spectroscopy, Techniques for the Measurement of Infrared Spectra under High Pressure, The Examination of Gas Chromatographic Fractions by Infrared Spectroscopy, Practical Approach to Internal Reflection Spectroscopy, Raman Instrumentation and Sampling, Insoluble Polymers and Rubbers, Surface Adsorbed Samples, Matrix Isolation Techniques, and Corrosive, Unstable, and Explosive Samples. Many of these new chapters reflect the natural spread of techniques from the laboratories of specialists to those of nonspecialists. Apparently not far enough along for the present volume are areas such as fast, sensitive semiconductor detectors, rapid-scan infrared spectrometers, and infrared lasers and their applications. Also, low-temperature techniques would seem even more accessible had the use of closed cycle refrigerators been given greater emphasis. In bringing the other eleven chapters up to date, substantial revisions have been made in some, such as the introduction of material on the Raman effect into the Single Crystals chapter. The several additions of material on Raman spectroscopy to an infrared book are a welcome modernization.

On the whole, the many authors have succeeded under the title of "Laboratory Methods." Numerous illustrative spectra as well as diagrams of instruments and sampling devices are given. However, in few instances could a person inexperienced in the practice and theory of vibrational spectroscopy go directly to the laboratory with this book in hand. Such a person could quickly survey the range and performance level of techniques available and find references to greater detail. This second edition is recommended as a useful reference in all laboratories where experimentalists are interested in applying vibrational spectroscopy to a wide range of problems.

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