The structure and stereochemistry of **1a** suggest[8] that it is formed by solvation of a 6-azabicyclohexenyl cation **4**. The formation of a 2,6 bridge in the excited pyridinium ion would yield **4a** and might be regarded as a plausible path, but results obtained in the photolysis of 3,4,5-trideuterio-1-methylpyridinium chloride[14] are not compatible with this simple origin. The observation that proton resonances in the product appear at R_2 and R_4 as well as in the aziridine positions implies that skeletal rearrangement precedes formation of the bicyclic ion. A plausible intermediate is the 1-azoniabenzvalene **3** which can yield **4b** as well as **4a** (eq 1). If all of the ions were formed in this way, and isotope effects were negligible, proton areas at R_2 and R_4 would each equal one-third that at each aziridine position. The observed ratio of 1:7 indicates that half the ions result from 2,6 bridging.

Products obtained from photolysis of picoline methochlorides provide further support for the intermediacy of **3** and indicate that methyl groups can exert a strong directive influence on its formation and fate. Photolysis of the 1,4-dimethyl isomer yields **1b**, **1c**, and **1d** in the ratio 1:1:2, whereas only **1d** would be expected from a 2,6-bridged intermediate; the observed result is in accord with statistical opening of its 1-azoniabenzvalene[15] (4-methyl-**3**) by paths a and b and statistical hydration at positions 2 and 4 in the ion corresponding to **4b**. Photolysis of the 1,2 isomer yields only **1b** and **1c**, in approximately equal amounts. The absence of products derived from a 2,6-bridged ion indicates that 2-methyl-**3** is formed to the exclusion of 6-methyl-**3**, and opens only by path b. The 1,3 isomer similarly yields only **1b** and **1c**. Although these products might involve the intermediacy of 2-methyl-**3** or 4-methyl-**3**, they might equally well result from 2,6 bridging. Similar effects are noted in the photolysis of the methochlorides of the lutidines. **1e** is the sole product from the 1,3,5 isomer and the highly predominant product from the 1,2,4 isomer. In the latter case it must be formed by selective ring opening in 2,4-dimethyl-**3**.

In the absence of added base the photohydrations occur with comparable (initial) quantum yield, but as the solution becomes acidic the products slowly re-form pyridinium ions. Nmr studies of the aromatization of isolated **1a–e** in D_2O indicate that both rearrangement and hydrogen exchange occur during the process: R_2, R_3, and R_4 appear at α, β, and γ positions, respectively, in the ions, and resonances for β protons are absent. In the case of **1d**, where aromatization occurs even at pH 7, the accompanying formation and disappearance of 370-nm absorption suggests the intermediacy of an open-chain aminoaldehyde. In the case of **1e**, where a lower pH is required, the intermediacy of a 1,2-dihydropyridin-2-ol is suggested by the formation and disappearance of 240-nm absorption.

A corresponding photohydration of protonated pyridines is suggested by the observation that 3,5-lutidine irradiated in acidic D_2O disappears with $\Phi \sim 0.1$, and that 2,4-lutidine-d_2 is subsequently formed.

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(14) Prepared by exchange of methylpyridinium-d_5 chloride with aqueous NaOH.

(15) Formation of **1d** *via* a simple 2,6-bridged intermediate is not precluded if ring opening of the azoniabenzvalene occurs preferentially by path b. Formation of **1b** and **1c** did not involve prior formation of 1,3-dimethylpyridinium ion, either by rearrangement of the 1,4 isomer or by dehydration of **1d**, since its characteristic uv absorption was not observed during photolysis.

(16) University of Wisconsin—River Falls, River Falls, Wis., Faculty Research Participant, Summer 1971.

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*Book Reviews**

Mechanisms of Molecular Migrations. Volume 4. Edited by B. S. Thyagarajan (University of Idaho). Wiley-Interscience, New York, N. Y. 1971. xv + 326 pp. $22.50.

The latest volume in this continuing series contains four chapters, the first two of which are much concerned with orbital symmetry considerations. Joseph J. Gajewski discusses *thermal degenerate rearrangements of hydrocarbons*, a subject that embraces those transformations in which the product has the same structure as the reactant (for example, the rearrangements of bullvalene to itself, and 1,3-hydrogen shift in propene). M. J. Perkins and P. Ward write about *dienyl rearrangements:* electrocyclic and sigmatropic rearrangements of dienyl cations, anions, and radicals. The growth of this new field is indicated by the fact that although the references are drawn almost entirely from the last ten years, there are 137 of them. A. Fry writes about *acid-catalyzed rearrangements of ketones*, a field whose long history begins with the conversion of camphor to carvenone in hot sulfuric acid by Delalande in 1839. Finally, R. T. Conley and S. Ghosh discuss *abnormal Beckmann rearrangements:* the Beckmann fragmentation, the Semmler–Wolff aromatization, and the Neber rearrangement.

The chapters give thorough treatments to the subjects, and cover both mechanism and applications but do not include comprehensive tables of reported examples. Coverage of the literature appears to extend well into 1970. Besides author and subject indexes, this volume includes a cumulative index to the chapter titles in Volumes 1 to 4.

Fused Pyrimidines. Edited by D. J. Brown. **Part II. Purines.** By J. H. Lister, R. L. Jones, and P. D. Lawley (Chester Beatty Research Institute, London) and G. H. Hitchings and G. B. Elion (Wellcome Research Laboratories). Wiley-Interscience, New York, N. Y. 1971. xxiv + 655 pp. $49.50.

This book constitutes Volume 24, Part 2, of the series "The Chemistry of Heterocyclic Compounds," under the general editorship of A. Weissberger and E. C. Taylor. The chemistry of pyrimidines has become so extensive that the subject is now separated into four volumes, of which two are yet to come. The authors follow the customary emphasis of this series on a critical, yet exhaustive treatment of the practical aspects, with theoretical aspects being treated in outline. There must be several thousand references. An 81-page appendix lists nearly 3000 purine derivatives in tabular form with melting points and references. The literature has been

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* Unsigned book reviews are by the Book Review Editor.

surveyed through 1969, with some references to 1970 publications. There is a good subject index (to this part only).

Applications of Infrared Spectroscopy in Biochemistry, Biology, and Medicine. By F. S. Parker (New York Medical College). Plenum Press, New York, N. Y. 1971. xiv + 601 pp. $25.00.

This is a book intended for those in fields marginal to chemistry who wish to use infrared spectroscopy as a tool. It is intended for research workers in various biological fields and for graduate students and advanced undergraduates. There is a brief introductory chapter for those who know nothing about infrared spectroscopy, and a longer chapter on techniques and sampling. A useful feature is a table of spurious bands—those that might arise from unsuspected artifacts such as plasticizers from tubing, inorganic contaminants in sodium chloride plates or potassium bromide pellets, stopcock grease, etc.

The bulk of the book is concerned with applications to identification and analysis of carbohydrates, lipids, proteins and polypeptides, nucleic acids, steroids, pharmaceuticals, etc., with sections on enzymology, microbiology, medical analysis, pesticides, etc. The book concludes with a good guide to sources of information concerning infrared spectra and an appendix summarizing fractionation methods commonly used to prepare samples of biological origin. There is much information in tables throughout and a large number of illustrated spectra. Each chapter has an extensive list of references. There is both a general subject index and an index of compounds.

Impingement of Man on the Oceans. Edited by D. W. Hood (University of Alaska). Wiley-Interscience, New York, N. Y. 1971. x + 738 pp.

Organic Compounds in Aquatic Environments. Edited by S. D. Faust and J. V. Hunter (Rutgers University). Marcel Dekker, Inc., New York, N. Y. 1971. xxii + 638 pp. $20.75.

These two books are both concerned with pollution of natural waters, and both are composed of chapters contributed by a variety of authors. The "Oceans" book, although concerned only with salt waters, has otherwise a broader scope and includes oceanographic, meteorologic, engineering, and social subjects, and covers inorganic (*e.g.*, lead) as well as organic pollutants. Chemistry, although of major importance in certain chapters, is on the whole a lesser part of the book.

The "Aquatic" book deals with the sources and mechanism of formation of organic constituents of natural waters and their transformation by photochemical, bacterial, and atmospheric processes. The emphasis on thermodynamics and kinetics is substantial.

Both books have extensive lists of references in every chapter; the subject index (26 pp) of the "Oceans" book is excellent, but that of the "Aquatic" book is hardly adequate (7$^1/_2$ pp in large print).

Advances in Environmental Science and Technology. Volume 2. Edited by J. N. Pitts, Jr. (University of California, Riverside), and R. L. Metcalf (University of Illinois). Wiley-Interscience, New York, N. Y. 1971. vii + 354 pp. $17.95.

The following topics are treated in eight contributed chapters: air pollution; pollution by mercury; motor vehicle emissions; spectroscopic methods and remote sensing; agricultural wastes; antibacterial drugs as contaminants; toxicity of aflatoxins. Much of the material is, of course, more concerned with technology than chemistry. In one chapter there is a total of eight structural formulas of significant organic contaminants, but not one of them is correct; it is to be hoped that this is not indicative of the overall reliability.

Encyclopedia of Industrial Chemical Analysis. Volume 14. Edited by F. D. Snell and L. S. Ettre. Wiley-Interscience, New York, N. Y. 1971. xiv + 616 pp. $45.00 ($35.00 by subscription).

This volume contains twenty-one entries from Gold through Iodine, including such important subjects as Hormones (53 pp), Hydrazine (10 pp), Hydrocarbons (56 pp), and Hydrogen Chloride (13 pp). As usual, short but adequate sections on properties, toxicity and handling, and manufacture precede the detailed discussions of analysis and identification, and there are extensive lists of references.

Analysis of Biogenic Amines and Their Related Enzymes. Edited by D. Glick. John Wiley & Sons, Inc., New York, N. Y. 1971. 350 pp. $17.50.

This volume of the series "Methods in Biochemical Analysis" comes quite close to fulfilling the aim expressed by the editor in the book's preface, "... advances in methods have been so rapid that it is essential to provide critical evaluations ... and to present selected procedures of special value." I must say at the outset that when a given chapter of the book falls short of this aim, this may not be held against the author's diligence but instead reflects the rapid evolution of the field. By consulting the references of each chapter one can infer that the authors must have presented their manuscripts early in 1970 because the accurate bibliographic documentation included covers most of the papers published in 1969 and some papers published in the beginning of 1970; no papers published in 1971 are quoted. I am reviewing the book in 1972 and already too much time has elapsed. In the last two years, many methodological innovations have occurred: gas chromatography (GC) and gas chromatography combined with mass spectrometry (mass fragmentography (MF)) are becoming powerful and specific tools for quantitative analysis of biogenic amines. Only the excellent chapter concerning the choline esters refers with great detail to GC and MF methods. The methods for analysis of catecholamines, indolealkylamines, and histamine refer almost exclusively to fluorescence spectrometry and enzymatic methods; the reason for this ostracism against GC is not clearly stated in any chapter. Probably a chapter on the GC as it applies to the analysis of biogenic amines and its metabolites might have been in order.

Another obvious inadequacy can be found in the reports on the methods for measuring enzyme activities related to biogenic amines metabolism. This is particularly evident in the chapters on dopamine β-hydroxylase (DβH) and monoamine oxidase. The former enzyme can now be assayed quantitatively in plasma of animals and man. The assay of this enzyme activity has been proposed as a convenient tool to estimate sympathetic tone in the clinic and obviously may be of great interest to the readers of this volume who, unfortunately, will be left with the statement on page 164, "Further investigations are obviously necessary before DβH activity can be measured in crude tissue preparations with any degree of reliability." In the last two years, the field of monoamine oxidase has been the object of intense investigations after it was shown that multiple forms of the enzyme are present in various tissues. Hence, the trend of present research is not only that of establishing how much monoamine oxidase activity is present in a tissue sample but whether this activity belongs to the type A or type B enzyme. Techniques are presently available to help an investigator to decide on the form of MAO he is measuring, but this information will not be found in the present volume. Incidentally it is currently believed that sympathetic nerves contain almost exclusively type A enzyme.

My critical appraisal of this volume can be certainly disregarded by the reader who is looking for a fast reference to established methods and who seeks information on the historical background of these methods. From this standpoint most of the chapters are easy to read and extremely informative, and the subject matter is exposed in excellent perspective. Since many of the authors were instrumental in developing the methods they describe, frequently they give tips for the practical use of the various methods.

E. Costa, *National Institute of Mental Health*

Analytical Metabolic Chemistry of Drugs. Volume 4 (Medical Research Series). By J. L. Hirtz (Ciba-Geigy). Marcel Dekker, Inc., New York, N. Y. 1971. xvii + 395 pp. $24.50.

This is the English translation of a text published in France in 1968 under the title "Les Methodes Analytiques dans les Recherches sur le Metabolism des Medicaments." It is basically a review of the literature in the style of the Analytical Chemistry Annual Review Series. The emphasis is on analysis of metabolites of compounds used in therapeutics, rather than those from endogeneous sources. There are no detailed instructions nor critical evaluation for any method. The material is divided into 20 chapters grouped according to chemical rather than pharmocologic similarity. The areas covered include phenolic acids, amines, aminophenols and catecholamines, phenothiazines, dibenzazepines and benzodiazepines, carbamates, anilides, barbiturates, urea and guanidine derivatives, sulfonamides, imides, hydrazides and hydrazines, heterocycles with and without nitrogen, alkaloids, a variety of antibiotics, glycosides, and sulfur-, metal- or halogen-containing drugs. It is unfortunate that a book published in 1971 contains reference material only through the end of 1966. However, up to that date it is a remarkably complete survey including almost 1100 references. The methodological emphasis is chromatography, and R_f values of hundreds of compounds are listed, as are the structural formulas of the major compounds. The value of this collection of references is to the investigator who wants a starting place for information concerning metabolites of therapeutically useful compounds and methods that have been used for analysis.

Morton K. Schwartz, *Memorial Hospital for Cancer and Allied Diseases*

Application of the Mössbauer Effect. Edited by I. Dézsi (Central Research Institute for Physics, Budapest). Akadémiai Kiadó, Budapest, Hungary. 1971. 808 pp. $26.40.

This volume is a compilation of the proceedings of a conference on the applications of the Mössbauer effect held in Tihany, Hungary, in June 1969. It contains a comprehensive number of rather short papers dealing with most of the current areas of interest and activity in Mössbauer spectroscopy. It includes papers on the theoretical aspects of the Mössbauer effect as well as those dealing with practical applications in chemistry, biology, and metallurgy. Most of the contributions are necessarily abbreviated, and some frustration is caused the reader by the inclusion of a number of papers by short abstract or title only.

The nature of the material presented in this book does not lend itself to the novice in Mössbauer spectroscopy. However, it is obviously a volume aimed at the whole range of working Mössbauer spectroscopists, from those dealing entirely with the theoretical aspects to those devising analytical applications of the Mössbauer effect. The Table of Contents is well arranged and the list of participants and the author index are helpful. There is no subject index. The major contribution of the volume may well be the large number of articles by Eastern European and Russian scientists whose work may not be that familiar to American and Western European workers.

This large volume can be recommended as a reference work for all serious Mössbauer spectroscopists and should certainly be included in the library holdings of any institution which has an active Mössbauer research group.

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The Analytical Chemistry of Sulfur and Its Compounds. Part III. Edited by J. H. Karchmer. **Nuclear-Magnetic-Resonance Data of Sulfur Compounds.** By N. F. Chamberlain and J. J. R. Reed (Esso Research & Engineering Co.). Wiley-Interscience, New York, N.Y. 1971. xii + 388 pp.

This volume consists largely of a table, produced by photo-offset of computer output, which lists the chemical shifts and coupling constants of 1393 sulfur-containing compounds. The computerization of nmr data required the use of line structural diagrams and multitudinous symbols and abbreviations. The sources of the data are other published computations of nmr spectral data, the spectral files of the Esso Research and Engineering Company, and original literature. In the latter case, references are not provided. In general, the book can be recommended only for very specialized library collections.

Carl R. Johnson, *Wayne State University*

XXIIIrd International Congress of Pure and Applied Chemistry. Special Lectures Presented at Boston, 1971. Butterworths, London. 1971. Volume 5: 128 pp. $7.50. Volume 6: 296 pp. $12.00. Volume 7: 279 pp. $12.00. Volume 8: 317 pp. $12.00.

These volumes contain the full texts of the special lectures reproduced directly from the typescripts submitted by the lecturers. The lectures also include an abstract, illustrations, and references. Volume 5 consists of four lectures in the area of Biosynthesis, and one on Mechanism of Enzyme Action. Volume 6 contains six lectures on Organotransition Metal Chemistry and four on Homogeneous Catalysis. Volume 7 contains nine lectures on Spectroscopy in Structural Determination, ranging from ion cyclotron resonance to laser-Raman spectroscopy, four lectures on Advances in Conformational Analysis, and three on Synthesis and Conformation of Biopolymers. Volume 8 is devoted to the polymer field, and contains four lectures on Photochemistry of Macromolecules, one each on New Developments in Ionic Polymerization and in Free-Radical Polymerization, four lectures on Reactions and Modifications of Polymers, one each on Heterophase Polymer Systems and Olefin Copolymers, and four on Interface and Adhesion Problems in Polymer Composites.

There are no indexes, a circumstance that is presumably part of the sacrifices required in order to gain maximum promptness in publication. The publishers and the anonymous editor are to be congratulated for making these lectures available so soon after the Congress.

Beta-Lactams. Part 1. By M. S. Manhas and A. K. Bose (Stevens Institute of Technology). Wiley-Interscience, New York, N. Y. 1971. xiii + 233 pp. $11.95.

The reactions of β-lactams are covered in four chapters in this volume; a second volume is planned to cover synthesis. The first chapter is more or less a historical summary of the subject from the nineteenth century to the post-World War II work on cephalosporins. It includes a brief glance at the wartime program to synthesize penicillin, which was a remarkable cooperative effort involving academic and industrial laboratories on both sides of the Atlantic, and whose failure to generate a practical synthesis was more than made up for by the fact that it effectively introduced infrared spectroscopy to organic chemistry. The remaining chapters are devoted to molecular rearrangements and physiological activity.

The literature is covered through the first half of 1971, and such prompt publication is a commendable achievement. The references appear to be comprehensive. There is an author index and a subject index; the latter is so short that it would have been better to have withheld it until Part 2.

Indoles. Parts I and II (Volume 25 of the Chemistry of Heterocyclic Compounds). Edited by W. J. Houlihan (Sandoz-Wander, Inc.). Wiley-Interscience, New York, N. Y. 1972. 587 and 616 pp. $48.00 each.

These are the first two of a planned three-part coverage of indoles; carbazoles and other condensed indole derivatives are scheduled for still further volumes. The scope of the literature surveyed goes back to the nineteenth century, but the tremendous amount of material published since the original edition of this series, which covered the literature through 1952, dominates the presentation. Unfortunately, the terminal date of the literature search for this edition is not stated, although a quick scan of the references did not reveal any dates later than 1969. A three-year lapse between completion of writing and final publication is undesirable, but understandable in works of this magnitude; failure to inform the reader of the status, however, is simply irresponsible.

Part I contains a basic survey of indole chemistry in two chapters: Properties and Reactions of Indoles, by W. A. Remers, and Synthesis of the Indole Nucleus, by R. K. Brown. Even though the authors disclaim any attempt to be encyclopedic, the fact that these chapters contain 587 and 810 references, respectively, demonstrates the thoroughness of the treatment, which is also thoroughly modern in outlook. There is relatively little tabular information in Part I, however. Part II consists of a more detailed treatment of various kinds of compounds containing the indole nucleus, and accordingly has extensive tables. Its five chapters are devoted to biosynthesis (R. J. Parry), alkyl, alkenyl, and alkynyl indoles (L. R. Smith), halo and organometallic derivatives (J. C. Powers), indoles bearing basic nitrogenous functions (F. Troxler), and indoles bearing other nitrogenous groups, from imino to nitro. Each volume has an independent index although that for Part II is decidedly short (10 pp) for a book that is certain to be an indispensable reference work.