

distribution of the tritium label between C-2 and C-3 in **12** and **13** was determined by ozonolysis of the labeled olefins to give acetaldehyde and the ethylene glycol ester¹² of 6-formylhexanoic acid. The two labeled aldehydes obtained from each olefin were derivatized as thiosemicarbazones and recrystallized to constant specific activity. In this way, it was established that the labeled olefin **12** carried 17% of the tritium label at C-2 and 83% at C-3 while the labeled olefin **13** carried 58% of its tritium at C-2 and 42% at C-3. The labeling pattern in **12** and **13** having been defined, each of the labeled olefins was converted into the corresponding labeled form of (±)-dethiobiotin by established methods.⁵

The synthesis of [4(*RS*)-³H]-(±)-dethiobiotin was accomplished as outlined in Scheme I. The known⁵ acetal alcohol **14** was oxidized to the corresponding aldehyde using Collins reagent, and the aldehyde was then reduced with tritiated potassium borohydride to the 1-³H acetal alcohol **15**. The labeled bromide **16** obtained from the labeled alcohol **15** by treatment with triphenylphosphine and carbon tetrabromide⁵ was converted into [4(*RS*)-³H]-(±)-dethiobiotin via the trans-allylic alcohol **17** and the trans-acetal olefin **18**.

The samples of tritiated (±)-dethiobiotin prepared as described were each mixed with [10-¹⁴C]-(±)-**2** and the doubly labeled precursors were then administered to cultures of *A. niger* (ATCC 1004) using previously reported methods.³ The precursors were not resolved since only (+)-dethiobiotin appears to serve as a biotin precursor.¹³ After an incubation period of 5 or 6 days, the biotin produced from each doubly labeled precursor was isolated as (+)-biotin sulfone,³ and converted to biotin sulfone methyl ester. The methyl esters were purified by chromatography and then recrystallized to constant activity and constant tritium to carbon-14 ratio. The results of these experiments are summarized in Table I.

A number of conclusions can be drawn from the data in Table I. Experiments 1 and 2 clearly demonstrate that the introduction of sulfur at C-1 and C-4 of (+)-dethiobiotin takes place without the loss of hydrogen from C-2 or C-3. It therefore seems unlikely that unsaturation is introduced at C-2 or C-3 during the biosynthesis of (+)-biotin from (+)-dethiobiotin; however, the possibility of enzymatic removal of hydrogen from C-2 or C-3 followed by replacement of the hydrogen without exchange cannot be excluded. Experiment 3 shows that the incorporation of [1-³H]-(±)-**2** into biotin proceeds with about 30% tritium loss. The nature of the reaction associated with the oxidation of the methyl group of (+)-dethiobiotin is un-

known, but the tritium loss observed in experiment 3 is consistent with the removal of one hydrogen atom from the methyl group of **2** by a process which exhibits little or no isotope effect. Experiment 4 reveals that [4(*RS*)-³H]-(±)-dethiobiotin is incorporated into (+)-biotin with about 47% tritium loss. This figure is within experimental error of that expected (50%) for the stereospecific removal of one hydrogen atom from C-4 of **2** during the formation of biotin. Thus, it appears that two hydrogen atoms are removed from (+)-dethiobiotin (**2**) as the result of its conversion to (+)-biotin (**1**). Work is now in progress to determine the stereochemistry of hydrogen loss from C-4 of **2** and to ascertain the order of functionalization of C-1 and C-4 in this precursor.

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Book Reviews

Ion-Selective Electrodes. By JIRI KORYTA (Charles University, Prague). Cambridge University Press, New York, N.Y. 1975. 206 pp. \$29.95.

This small volume (number two in Cambridge Monographs in Physical Chemistry series) is a survey of the field of ion-selective electrodes up to the beginning of 1973, based on published literature. There are eight chapters. The first is a brief history of the concepts leading to the theoretical basis of ion-selective electrodes. This is followed by chapters on the theory of membrane potentials, basic properties of ion-selective electrodes, analytical applications, electrodes with fixed membrane sites, electrodes with liquid membranes, electrodes with electroneutral macrocyclic ion-carriers, and the relatively new field of enzyme electrodes. There is an extensive list of references (over 1150) and a short index of subject matter.

An informative section on the construction of various types of ion-selective electrodes and several tables showing the applications of certain ion-selective electrodes to various types of analysis make

the book useful for the practicing chemist.

This book contains a wealth of information and is recommended for all professional analytical and clinical chemists.

R. H. Lansing, *Eastman Kodak Company*

Topics in Current Chemistry, Volume 52, Medicinal Chemistry. Edited by F. BOSCHKE. Springer-Verlag, Berlin—Heidelberg—New York. 1974. 233 pp. \$25.50.

This volume of "Topics in Current Chemistry" contains five chapters that range from general approaches in the design of active compounds to very specific and limited topics. Taken separately, the chapters are well written and clearly of importance to their specific area. However, the lack of a general theme or direction throughout the entire volume is distracting.

The first chapter, by E. J. Ariens and A. M. Simonis, deals with the design of bioactive compounds with emphasis on a rational and

planned approach. The chapter is explicit in purpose and is balanced with examples from the recent literature which strengthen the authors premise that there is a rational approach. A chapter by T. J. Bardos reaffirms the antimetabolite approach to drug design and is complemented by a chapter entitled "Molecular Approaches for Designing Antiviral and Antitumor Agents" by P. Chandra. The latter concentrates on Distamycin antibiotics, Daunomycin, and Tilorone with literature coverage through early 1972.

Chapters on Alkylating Agents (T. A. Connors) and Synthetic Interferon Inducers (E. De Clercq) place emphasis on the chemistry and structural features important to the biological action. The last chapter, "Synthesis and Properties of Some New NAD Analogs", by C. Woenckhaus analyzes the structural properties that contribute to binding and coenzyme action.

The book will be useful to investigators working in these research areas and should serve as a good introduction to those beginning research in these areas.

M. P. Mertes, *University of Kansas*

Anodic Oxidation. By SIDNEY D. ROSS (Sprague Electric Company), MANUEL FINKELSTEIN (Sprague Electric Co.), and ERIC J. RUDD (Hooker Chemical & Plastic Corp.). Academic Press, New York, N.Y. 1975. 339 pp. \$37.00.

This book is another in the series of monographs entitled "Organic Chemistry". The first part of the book is an introduction to the principles and methods of electrochemistry. These four chapters present a discussion of electrochemical theory including double layer effects and adsorption phenomena, followed by practical aspects including a description of electrodes and cells. A useful list is given of the accessible potential ranges for various solvents with different electrolytes and working electrodes. The main portion of the book, Chapters Five through Twelve, is a survey of anodic reactions, including the oxidation of hydrocarbons, acids, amines, amides, hydrazines, alcohols and phenols, and ethers. In this section emphasis is placed on anodic reaction intermediates and mechanisms.

This book would probably be quite useful to the chemist who wishes to carry out electrochemical synthesis of organic compounds or study anodic reaction mechanisms. Unfortunately, only a small section is dedicated to coulometric studies and preparative methods. As an aid to the analytical chemist this book might be helpful in designing an analytical method; however, it would be of limited value as a source of oxidation potential data.

Karen K. Lovecchio, *Eastman Kodak Company*

Rheometry. By K. WALTERS (University College of Wales). Chapman and Hall Publishers, London. 1975. x + 278 pp. \$32.

Rheology has come a long way since it was established as a science in 1929, at which time it was confined to the flow properties of matter under conditions of steady shear. As the name implies, rheometry should refer to the same genre of properties under different modes of shear, but the practice of rheology has expanded so significantly that no word stemming from classical origins can cover its range. Rheometry should be as good a coinage as any.

This monograph is devoted to those equations of state which govern the response of liquids to applied stress. Except for the curious labeling of the very first section as viscoelasticity (instead of elastoviscosity), the author carefully restricts his coverage to materials and situations that emphasize flow rather than recoverable deformation, reliance being placed on dynamic viscosity as the prime measure of the response. Viscometers are replaced by rheometers and constant unidirectional shear is replaced by inconstant, generally oscillating, shear in which fragile structures are not broken down during the measurement.

The book is competently done. It is highly mathematical, requiring one to have mastered the theory of functions of the complex variable and tensor notation, along with quite a few abstractions. By dealing with liquids that are isotropic and incompressible, the author succeeds in complicating the mathematics no more than the subject demands; however, he communicates only to those who are already dedicated to a rigorous treatment. He starts in Chapter 1 with the assumption that the reader already is conversant with normal stress; in beginning with the equations of motion he does not bother to define τ (the absence of a glossary, with all quantities expressed with their dimensions, is downright inexcusable); he assumes the level of the reader's knowledge is such that he can start with the Navier-Stokes equations for Newtonian liquids and proceed from there.

Because the intended audience is not revealed explicitly in the monograph, one must assume it is slanted toward the author's peers. This pitch is, of course, proper in a research paper; but if the secondary literature is to be of value, it should reach those who are not the peer of the author in his specialty, which is applied mathematics. In Chapter 2 he wades into convected coordinate notation (and explains why) without empathy for those readers who are beyond their depth in the first step; fortunately these early sections are well documented so that the serious student can scurry back to high ground for a breather. Mastery of the rest of the chapters depends on survival at this stage, for references are sparse in Chapter 3 (18), in which the basic rheometrical concepts are presented (cf. 55 references in Chapter 4 on Rheogoniometer Measurements, 44 in a short Chapter 5 on Capillary Measurements, 61 in his tour de force chapter on Complex Dynamic Viscosity). This emphasis does not necessarily imply uneven coverage as much as it reflects the author's area of greatest competence.

The writing is fluid (no pun intended) and lucid. Few grammatical errors were noted, except for using the singular verb after data; and the mathematical layout is done with a minimum of confusion, again with a notable exception where an equation is wrongly referenced and superscripts are used in place of subscripts in a manner which confounds the operations of squaring and cubing a term.

Legends are missing from certain figures, which appear to have been judiciously selected. Concluding summaries at the end of about half of the chapters are helpful. A chapter on novel experimental methods is particularly interesting, for it seems to have been written with particular relish, covering the author's strong attachment to delineating secondary flows. The few applications interspersed throughout the book could have used some company, particularly in justifying the novel approaches.

This is an uplifting book. It does a creditable job of elevating rheology, and one can only hope that it will take a few more neophytes along with it.

Raymond R. Myers, *Kent State University*

Progress in the Chemistry of Organic Natural Products. Volume 32. Edited by W. HERZ (Florida State University), H. GRISEBACH (University of Freiburg), and G. W. KIRBY (University of Glasgow) Springer-Verlag, Vienna and New York. 1975. viii + 560 pp. \$94.60.

The latest volume in this famous series contains six reviews on vastly differing topics. The chapters are well written (in English) by authorities in the various fields. The literature coverage is through 1973 except as noted. Quite thorough subject and author indexes are provided for the volume.

W. K. Seifert's contribution, "Carboxylic Acids in Petroleum and Sediments", is a timely discussion of the complex mixtures of acidic substances found in crude oils. Included is a presentation of combined gas chromatography-mass spectrometry applications which should be useful in other natural product areas. The 2,5-dioxopiperazines constitute a class of natural products, commonly derived from peptides, which includes many powerful and interesting medicinals (e.g., gliotoxin). P. G. Sammes reviews the synthesis as well as the isolation and structure determinations of members of this class. A chapter on the "Chemistry and Biosynthesis of Plant Galactolipids" (H. C. van Hummel) is also included.

The two chapters on the use of physico-chemical techniques in the study of natural products are unusual for this series, but certainly not inappropriate. R. J. Highet and E. A. Sokoloski, in "Structural Investigations of Natural Products by Newer Methods of NMR Spectroscopy", present some theoretical background on shift reagents, INDOR, NOE, FT, and ^{13}C techniques, then proceed to demonstrate the use of these techniques in solving structural problems of natural products. While certainly not complete, the review does pique one's interest in the methods. "Applications of the Chiroptical Techniques to the Study of Natural Products" (P. M. Scopes) contains no consideration of theory, but is fairly exhaustive of the ORD and CD applications literature from 1966 to 1972.

By far the longest review (210 pages) is that by H. Kössel and H. Seliger on "Recent Advances in Polynucleotide Synthesis". To review such a vast and fast-moving field is a momentous undertaking. Although the authors have achieved considerable success in the review, parts of the discussion suffer from a slight lack of clarity. Lengthy tables of blocking groups, phosphorylating agents, and polymeric supports are included for quick reference.

This volume will be very useful, but the price makes one glad to have

access to a well-funded library. The publisher would do well to find ways in which to lower the cost and thus increase the accessibility of the series.

James Quick, *Northeastern University*

Ion Implantation in Semiconductors, Science and Technology. Edited by SUSUMU NAMBA (Osaka University). Plenum Press, New York, N.Y. 1975. xv + 742 pp. \$49.50.

This book is a record of the papers presented at the Fourth International Conference on Ion Implantation in Semiconductors and Other Materials held at the Osaka Chamber of Commerce and Industry, August 1974. There are 93 papers spread over 237 authors. Papers are grouped under the headings III-V Compound Semiconductors (136 pp), Profiles (82 pp), II-VI Compound Semiconductors and Other Materials (69 pp), Metals (80 pp), Radiation Damage (167 pp), High Dose Implantation (41 pp), and Devices (129 pp). None of the papers is truly a review paper, which is unfortunate since critical reviews would have been extremely useful in each of these rapidly expanding topical areas. Most of the present contributions are specialist, current-research reports. Their quality is uneven; the whole collection would have benefited from vigorous refereeing.

Ion implantation is a relatively new but fast-growing technique, applied for the most part to device fabrication, for which purpose its reliability factor has recently increased enormously. Although there are claims for important application to fundamental studies of the properties of materials, such applications are relatively rare. Chemical applications are rarer still. Increasing availability of ion implanters and associated mass analysis facilities as well as recently announced commercial ion implantation services should encourage chemists to adapt the technique as a possible unconventional solution to difficult synthesis problems. Scattered hints of what may come, e.g., reported formation of heteronuclear metal carbonyls by ion implantation, are found in this volume. The yield of such hints, unfortunately, is too low to justify more than passing study of the papers by chemists. The volume will be of principal use to device designers and applied solid-state physicists.

M. J. Sienko, *Cornell University*

Alicyclic Chemistry, Volume 3. Edited by W. PARKER (University of Stirling). The Chemical Society, London. 1975. viii + 581 pp.

This comprehensive review of the 1973 literature reflects the sustained interest of organic chemists in alicyclic chemistry. The book is divided into four chapters: Chapter 1 (S. A. Matlin) "Three and Four-membered Rings"; Chapter 2 (D. G. Morris) "Five- and Six-membered Rings and Related Systems"; Chapter 3 (M. S. Baird) "Medium and Large-Ring Compounds"; and Chapter 4 (J. M. Mellor) "Bridged Carbocyclics". All of the chapters give concise, well-written summaries of the syntheses and reactions within these areas including selected but pertinent discussions of mechanisms. Like other volumes in this series, the book should find a welcome place in most libraries. The considerable effort which the authors have invested in this volume will benefit all organic chemists. It is regrettable only that the price of such compilations will preclude many chemists from adding this volume to their personal libraries. Although the book contains a fairly detailed Table of Contents, I would suggest that the inclusion of a Subject Index would assist readers considerably in locating specific details.

David S. Watt, *University of Colorado*

Basic Inorganic Chemistry. By F. A. COTTON (Texas A&M) and G. WILKINSON (Imperial College). John Wiley & Sons, New York, N.Y. 1976. viii + 479 pp. \$14.95.

The level and scope of this inorganic chemistry text are appropriate to a one- or two-semester course for undergraduates who preferably have had physical chemistry. A bit over 40% of the text is devoted to principles, such as thermodynamics, kinetics, atomic structure, ligand field theory, coordination chemistry, and the like. These are coherent, well-written chapters reviewing only the essential physical concepts and in some cases presenting considerable descriptive material. The remainder of the book is devoted to descriptive chemistry, which in large part is covered group by group. The quality of these chapters is somewhat variable. For example, the chapters on oxygen and nitrogen provide brief and clear summaries of the highlights of the chemistry of these elements, but in some other chapters one finds a high density of facts without sufficient discussion to put these facts into perspective. Descriptive material also is presented in an attractive final section of

special topics which covers organometallic chemistry, homogeneous catalysis, and metal atoms in biochemistry. In all, the authors have done an amazingly good job of presenting the important aspects of inorganic chemistry in relatively few pages. The only neglected area is solid-state chemistry.

The text contains many aids to the student, such as the presentation of two sets of problems, one being of a straightforward review type, and the other requiring some imagination and thought. References to the primary literature are not given, but most chapters contain a supplementary reading list of review articles. In some cases this reading list directs the student to the corresponding chapters of the authors' excellent "Advanced Inorganic Chemistry". The availability of this larger book, which is parallel in organization, should be helpful to instructors and superior students. The text is amply illustrated with well-executed figures and structural formulas.

This book has the great virtue of providing general coverage of descriptive inorganic chemistry in a compact format which is suitable for undergraduates. I expect that it will receive wide adoption.

D. F. Shriver, *Northwestern University*

Photochemistry, Volume 6. Edited by D. BRYCE-SMITH (The University of Reading). The Chemical Society, London. 1975. xxiii + 796 pp. £27.50.

The latest volume of the Specialist Periodical Reports on photochemistry maintains the high standards of the preceding volumes. Volume 6 reviews the literature published between June 1973 and June 1974. The organization has not been altered from previous years except for the addition of a new chapter, "Photochemical Aspects of Solar Energy Conversion". This is a welcome addition, and, since the contents of this review are not limited to the yearly literature, it is a useful introduction to this interesting area.

It is indeed regrettable that the price of this volume (almost 8¢ per page) is so great. A major attraction of this series was its relatively low price and therefore availability to those with a peripheral or budding interest in photochemistry. Unfortunately, at the present price, few will consider personal purchase and fewer still will find it affordable.

David S. Weiss, *University of Michigan*

Analytical Chemistry of Radium. By V. M. VDOVENKO and YU. V. DUBASOV (Vernadskii Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences). John Wiley & Sons, New York, N.Y. 1975. viii + 198 pp. \$30.00.

This is a highly comprehensive treatise on the chemistry of radium which provides a wealth of useful information to researchers and students. The historical discovery of radium is briefly described together with an accounting of many of the early chemical experiments employed for its isolation, purification, and the determination of many of its physical properties. The text is divided into six chapters which include the subjects of: general information, analytical characteristics of radium and compounds, isotopic and qualitative determination, quantitative determination, separation from impurities, and determination in natural and industrial materials.

The section on the Quantitative Determination of Radium includes a brief discussion of standard gravimetric procedures. Since samples suitable for gravimetric analysis are so seldom encountered, an extensive discussion of radiometric procedures is included, with specific reference to γ -radiation or α -radiation detection. However, there is no mention of the application of solid-state detectors for the assay of these radiations, which, if employed, would lead to an enhancement in specificity. An extensive discussion of the older radiometric procedures, as applied to radium determination, is included, often together with many of the pitfalls. Nevertheless, for the uninitiated or the student there is insufficient detail presented to enable the reader to apply these techniques directly in the laboratory. The text is well referenced, however, to a number of both standard and specific sources of information on procedural technique.

There is an overall historical flavor to this work. Referencing to the literature ends with mid-1970. Out of 519 cited references, 360 are of literature published before 1960. This would be expected in view of the extensive research on radium undertaken at and shortly after the turn of the century. Many of these pioneering techniques are described. To the researcher the text is a convenient extensive source of literature references which can be useful in adapting today's techniques to the analytical determination of radium.

Albert A. Caretto, *Carnegie-Mellon University*