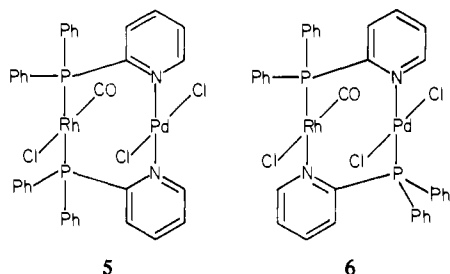


terminal chloride ligands, a carbonyl ligand and bonds to each of the bridging  $\text{Ph}_2\text{Ppy}$  ligands. The second metal possesses nearly square coordination. The metal-metal separation [2.594 (1) Å] is indicative of the presence of a direct bond between the metals. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum allows the location of the two metals to be specified and indicates that each particular metal occupies a unique site in the molecule. The spectrum consists of two groups of four equally intense lines and has been analyzed in terms of the following parameters:  $\delta_1$  21.89;  $\delta_2$  16.15 ( $^1J_{\text{Rh-P}} = 112.7$  Hz,  $^3J_{\text{P-P}} = 17.4$  Hz,  $^2J_{\text{Rh-P}} = 2.3$  Hz). The values of  $^3J_{\text{P-P}}$  and  $^2J_{\text{Rh-P}}$  are consistent with the parameters observed for other binuclear complexes. The value of  $^1J_{\text{Rh-P}}$  is sensitive to metal oxidation state/coordination geometry. In the present case, this value, which has decreased from the value found for  $\text{Rh}(\text{CO})\text{Cl}(\text{Ph}_2\text{Ppy})_2$ , is consistent with placing the rhodium ion at the 6-coordinate site in the molecule.<sup>10</sup>

The formation of **4** involves the oxidative addition of a  $d^8$  Pd(II) complex to an isoelectronic,  $d^8$  Rh(I) complex, a reaction which is otherwise unknown. It must occur because the bridging  $\text{Ph}_2\text{Ppy}$



ligands bring the two metals into close proximity. Face-to-face dimers such as **5**, with a head-to-head orientation of the bridging

ligands, or **6**, with a head-to-tail arrangement of the  $\text{Ph}_2\text{Ppy}$  ligands, may be intermediates in the formation of **4**. Several such face-to-face dimers, which involve  $d^8$  metal ions but which lack direct metal-metal bonds, are known.<sup>11,12</sup> Both **3** and **4** deviate from the expected product of reaction 1 in that the ligands are found in the head-to-tail arrangement. This reorientation emphasizes the mobility of phosphine ligands in binuclear species.

We are continuing to explore the ability of  $\text{Ph}_2\text{Ppy}$  to act as a bridging ligand in constructing polynuclear complexes and in promoting the transfer of ligands between metal centers.

**Acknowledgment.** We thank the National Science Foundation and the U.C.D. NMR Facility for support, Matthey Bishop for a loan of precious metal salts, and C. H. Lindsay for experimental assistance. Acquisition of the X-ray diffractometer and NMR spectrometer used in this study was made possible through NSF instrument grants.

**Supplementary Material Available:** A list of atomic fractional coordinates and temperature factors for  $\text{Rh}_2(\text{Ph}_2\text{Ppy})_2(\mu\text{-CO})\text{Cl}_2$  and  $\text{RhPd}(\text{Rh}_2\text{Ppy})_2(\text{CO})\text{Cl}_3$  (2 pages). Ordering information is given on any current masthead page.

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## Book Reviews

**Photometric and Fluorometric Methods of Analysis, Metals.** By Foster Dee Snell. Wiley-Interscience, New York. 1978. In two parts: xi + 1003 pp; xi + (1005 to) 2167 pp. \$160/set.

Many practicing analytical chemists have long been familiar with the much earlier forerunner of this work. The present, totally new, treatment employs two volumes to embrace the content of 8700 relevant references spanning the past 20-year period. The emphasis is on typical colorimetric and spectrophotometric procedures; a very few involve colloidal systems, and there remains little explicit reference to turbidimetric or nephelometric methodology. A fair number of fluorometric methods are included, and some flame photometric procedures. There is virtually no reference to atomic absorption methods.

While the treatment is necessarily abbreviated, most of the methods indicate a suitable dissolution procedure, desirable preliminary separations, the method of color formation, and a suitable wavelength for reading. Prominent interferences may be noted and the sensitivity is often implied, indirectly, by some of the given data or modulus operandi. Few fundamentals are given such as full absorption curves, molar absorptivities, or partition coefficients for L-L extractions, etc. There are no critical evaluations of methods or comparisons of their relative merits. Sometimes, but not always, the procedural descriptions are adequately full for application of the method without consulting the original references.

A very helpful feature is the 204-pp Index, in which a given metal may be listed in three different respects. The determination of other components in the metal as matrix will be listed. The determination of the metal in various kinds of samples is listed. Finally, the various reagents or color-forming reactions of the metal are tabulated.

Any criticism of this compilation would probably relate to its relatively indiscriminate approach to complete coverage and the resulting brief, almost cryptic, outlines of some of the procedures. There are 134 pp, each, of Cu and Fe methods, while treatments of 36 elements in Part 2 average 27 pp, each. Concise exposition sometimes leads the author into

sentences which are four to five lines in length, or into the use of short verbless phrases. A typical sentence, "Reading is against a sample reverted with sulfuric acid in addition to subtraction of a blank", is clear enough within its context, yet illustrative of some sacrifices on the altar of compactness. The journal name, *Talanta*, is misspelled, *Talanta*, in all citations.

Despite some flaws inherent in such an ambitious coverage, the practicing analyst will find in this work a broad selection of methods, some more useful than others, for photometric measurements of metals.

Charles L. Rulfs, *University of Michigan*

**Liquid Chromatographic Analysis of Food and Beverages.** Edited by G. Charalambous. Academic Press, New York. 1979. xii + 326 pp. \$25.00.

This book on the use of HPLC in food analysis joins Volume 1 on the same topic. The book consists of 14 chapters contributed by 32 authors on a wide range of HPLC methods dealing with the analysis of foods and beverages. Included are HPLC applications to beer, wine, carbohydrate products, cough remedies, and fruit juices. Constituents for which detailed experimental analytical procedures are provided include carbohydrates, gluconic acids, flavor constituents, hop compounds, vitamins, polymers, and flavones. There are two chapters which are particularly useful for those who wish to consider using HPLC for food analysis, but who have had no previous experience. One of these chapters is by Howard and Hodgkin and deals with instrument selection for HPLC. These authors have provided extensive coverage of HPLC instrumentation and component systems and they have included very useful information for potential purchasers of HPLC equipment from the standpoint of cost, efficiency, overall performance, and utility. The chapter by Popovich and Southern on the advantages of HPLC for the analysis of foods and beverages provides a very valuable overview of HPLC and includes a wide range of useful applications to food chemistry. An incorrect use of terminology, which appears throughout the book, is the

phrase "analysis of (component to be determined) in". The correct phrase should be "determination of ...". Mixtures are "analyzed", whereas compounds in mixtures are "determined".

This text is essentially a collection of contributed research articles written by many authors. As such it suffers from a lack of continuity in that each chapter stands apart as an independent unit. The book does, however, provide both general as well as very specific coverage of the subject with the latter predominating. Both newcomers to the field and advanced workers should find this book useful.

Hans Veening, *Bucknell University*

**Electric Energy: Policy Issues.** By Terry A. Ferrar, Frank Clemente, and Robert G. Uhler. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. 1979. xii + 135 pp. \$27.00.

This volume treats some policy issues of the electric utility industry, said to be the largest industry in the U.S.A. in terms of both capital assets and its interaction with the financial markets. The book's 135 pages can be read in a Sunday afternoon, making it an expensive afternoon at \$27.00 for the volume.

I found the chapter entitled "The Role of Government" the most stimulating. It argues that if nonexclusionary (environmental) goods exist, there is a meaningful role for the public sector to assure that the allocation of these nonexclusionary goods be not inappropriately usurped by particular user classes. It must be decided by what means the "public sector" assumes this meaningful role. Is the "public sector" to be a federal government agency, a local government, or a voluntarily subscribed public morality? Is the mechanism by which the "public sector" performs its role to be to convert these nonexclusionary goods into exclusionary goods by imposition of user charges? Some of these possibilities are quite well treated.

A good chapter outlines the jurisdictions and the roles of public governmental bodies in the siting of electric utility generating facilities. Another treats four key socio-economic issues: power plants vis-à-vis industry, taxation policy, the boom-bust issue, and the quality of life. The chapter on "Load Management Strategies for the 1980's" is a useful introduction to the new policies that will have to be developed under the Public Utilities Regulatory Policies Act of 1978.

The chapter giving the overview and the technical background is replete with misapplied sesquipedalia. It is poorly organized, often giving laundry lists of points rather than evaluations according to relative importance and priority. It lacks the quantitative information that instills in the reader a sense of confidence. In discussing hydropower, the fact that it comprises about 10% of the electric utility capacity in the United States and that it is almost entirely saturated except for some small low-head hydro installations is not mentioned. In discussing nuclear generating facilities, thermal pollution is mentioned, but concerns for waste fuel disposal or safety are not mentioned. The tremendous economic burden that has been laid upon coal-burning facilities to remove SO<sub>2</sub> is not mentioned. Overhead transmission is said to be the most popular form, whereas it is probably the most unpopular form. It is the lowest cost and most widely used form of electrical power transmission.

The discussion does not take into account experiences from any country other than the United States, and it fails to provide to the reader a perspective on how the policies and issues have been handled in other advanced societies.

A number of the figures are poorly drawn, and some items referred to in the text are either absent or have different symbols.

In one chapter, "reserves" are not properly distinguished from "reliability". The authors falsely imply that the flight of industry from the northeast to the sunbelt is connected with electric system reliability.

This volume does not treat some of the core issues of electric energy policy. For example, in an industry that was doubling every 8 years, reserves were inevitably present to sustain the growth. Reliability arose naturally from the presence of these reserves. We are now in a situation of much slower growth owing to increases in the price of electricity and as a consequence of price elasticity. The role of reserves in providing reliability has to be reevaluated. What growth should we anticipate in the future and why? In the study of the design of rates, the text offers inadequate insight into the bases of electrical rates.

Lennard Wharton, *McGraw-Edison Company*

**Dietary Fibers: Chemistry and Nutrition.** Edited by George E. Inglett and S. Ingemar Falkehaug. Academic Press, New York. 1979. xiii + 285 pp. \$17.00.

The influence of dietary fiber on human nutrition and health has recently become the subject of renewed investigative and clinical interest. This new concern has been sparked by the possible inverse relationships between the levels of dietary fiber, on the one hand, and intestinal disease and serum levels of cholesterol on the other. This book represents another title in the growing literature that deals with the composition and physical

chemical behavior of dietary fibers in vitro as well as in the gastrointestinal tract. The nutritional role of these materials also receives attention. Theoretical and practical considerations are discussed. The 18 papers in the book were presented at a symposium held in September 1978 at a meeting of the American Chemical Society. Many of the reports focus on the characterization of various types of fibers, which is important because, as noted in other papers, fibers of different compositions show differences in behavior. Several papers discuss interactions which could take place in the intestine between dietary fibers and nutritional as well as toxic substances. The information conveyed by the various authors is easily assimilable and appears to be authoritative. The book provides a good introduction to the field of dietary fibers for anyone whose investigative or academic interests impinge on this subject.

I. A. Bernstein, *The University of Michigan*

**Oil Shale and Tar Sands Technology. Recent Developments. Energy Technology Review No. 49. Chemical Technology Review No. 137.** By M. W. Ranney. Noyes Data Corp., Park Ridge, N.J. 1979. xii + 430 pp. \$48.00.

This is a compendium of the U.S. patent literature dealing with oil shale and tar sands since March 1975, the date of the previous technology review on this subject. Each of the 279 patents covered in this volume is presented in much greater technical detail than in patent abstracts, but with more clarity than in the full patent. Flow sheets, tables, graphs, and experimental data as well as verbal technical descriptions from the original patents are included. According to the author, "these patents include practically all those issued on the subject in the United States during the period under review". This has the advantage of presenting a broad spectrum of topics related to each area, from basic recovery techniques to environmental control methods for process effluents. However, the disadvantage of this lack of selectivity is that the feasibility of some of the processes described could at best be characterized as dubious.

The book also contains an informative and concise overview of background material including reserves and availability, as well as individual introductions to the state of the art and outstanding problems in each of the five major subject areas: oil-shale retorting, in situ processing of oil shale, shale oil refining and purification processes, in situ processing of tar sands, and tar-sands separation processes. The three indexes, by company, by inventor, and by number, and the table of contents, which is detailed enough to serve as a subject index, greatly augment the utility of the book as a quick and comprehensive reference for the engineer or applied chemist working in the field.

J. I. Brand, *Oak Ridge National Laboratory*

**The Alkaloids. Volume XVII.** Edited by R. H. F. Manske and R. G. A. Rodrigo. Academic Press, New York. 1979. xx + 611 pp. \$55.00.

Volume XVII of Manske's "The Alkaloids" is, like its predecessors, a series of fine in-depth reviews for the specialist. Dr. R. G. A. Rodrigo has taken over the editorial duties on this, the first volume since R. H. F. Manske's death in 1977. Manske's obituary is included in this volume.

The five chapters vary in length from 43 to 185 pages. In Chapter 1, S. W. Pelletier and N. V. Mody discuss the literature, appearing since mid-1968, on "C<sub>19</sub>-Diterpenoid Alkaloids". They have divided it into three parts describing the aconitine-, lycocotine-, and heteratisine-type alkaloids and have brought together in tabular form a large quantity of widely dispersed information on the correct or corrected structures, the physical properties, and the plant sources of these alkaloids.

Chapter 2 is an exhaustive compilation by M. F. Grunton of the chemistry of the "Quinoline Alkaloids related to Anthranilic Acid". This review is well documented and referenced and covers the period from 1966 to mid-1976.

The "Aspidosperma Alkaloids" are reviewed by Geoffrey A. Cordell in Chapter 3, which is the longest at 185 pages despite an attempt to keep the length down by excluding the dimeric alkaloids of this family. It is divided into three parts which discuss (1) isolation and structure determination of newly discovered alkaloids, (2) chemical and synthetic investigations of this family, and (3) the application of <sup>13</sup>C NMR and X-ray crystallography to this class of compounds. Tables of isolation data on new and established alkaloids appear along with detailed information on synthetic routes to the alkaloids.

In Chapter 4, F. Šantavy updates the isolation and chemistry of the "Papaveraceae Alkaloids". Once more the expert is presented with the recent developments in the field since around 1970.

R. S. Kapil and R. T. Brown have reviewed the "Monoterpene Alkaloid Glycosides" in Chapter 5 by discussing separately the dopamine, tryptamine, and tryptophan derivatives and then considering their biosynthesis and their biosynthetic roles.

These reviews, which were commissioned by Manske before his death, maintain the high quality of this series. Consequently, this volume will

probably be added to an already established collection of "The Alkaloids" and will certainly appeal to the specialist in any of the areas which were reviewed.

Leslie J. Browne, *Pharmaceuticals Division, CIBA-GEIGY Corporation*

**The Alkaloids: The Fundamental Chemistry. A Biogenetic Approach. (Studies in Organic Chemistry Series. Volume 7).** By David R. Dalton. Marcel Dekker, New York. 1979. x + 789 pp. \$49.50.

Volume 7 in "Studies in Organic Chemistry" is a good-humored review of the fundamental chemistry of the many alkaloid families. The author has taken a biogenetic approach and has provided detailed information on the source, isolation, and structure determination of the natural products which are included in the text. In certain cases, notably dendrobine and some of its derivatives, this includes extensive spectroscopic data where such information is important. In addition, the syntheses of representative examples are briefly described with adequate reference to the reagents which were employed.

The chemistry of the alkaloids is a large and complex subject. Since the text is designed to provide the chemically experienced beginning student with a foundation on which to build, this has necessitated the omission of numerous examples to ensure clarity for the reader who is less experienced in the alkaloid field. Conformational representations of the structures are used throughout. The more important examples are frequently illustrated side by side in conventional and conformational notation. This also adds to the overall presentation.

The first two chapters, which together comprise Part 1, are devoted to the reactions and the reactants commonly encountered in biosynthetic pathways. This helps to simplify the large volume of material which follows but also underlines by its brevity the reader's need for an extensive background in organic chemistry. There are an additional six parts, a prologue, and an epilogue. Parts 2 to 6 discuss the chemistry of the alkaloids derived from ornithine, lysine, nicotinic acid, tyrosine, and tryptophan, respectively, and Part 7 outlines the "Alkaloids Derived from the Introduction of Nitrogen into a Terpenoid Skeleton".

The volume is well referenced and indexed and is a valuable addition to any library. It should prove particularly useful to the novice as a learning text but less useful to the experienced alkaloid chemist as a reference.

Leslie J. Browne, *Pharmaceuticals Division, CIBA-GEIGY Corporation*

**The Molecular Basis of Optical Activity. Optical Rotatory Dispersion and Circular Dichroism.** By Elliot Charney. John Wiley & Sons, New York. 1979. xxi + 364 pp. \$27.50.

This is a good and even an important book. The author has a pleasant, almost chatty style with flashes of humor, which is not easy when dealing with the theory of optical activity. Yet I am uncertain of the precise readership that it will attract. Organic and biological chemists—the largest community of users of chiroptical methods and hence of potential readers of books on such a topic—will at best consult it on occasion, provided they are interested in theory and have a good mathematical background. Eight of the ten chapters deal with theory (sample headings: Models of Optical Activity; The Application of Group Representations to Chiral Activity), one with history and one (the longest) with chromophoric systems, which is precisely the area of organic chemical applications and hence of greatest interest to practicing organic chemists. Except for a thorough coverage of the octant rule, I find this to be the least satisfactory chapter (not counting the very brief and purposely superficial last chapter dealing with vibrational and magnetically induced chiral activity). Thus, given Charney's interest in history, it is somewhat surprising to read, "In the decade beginning about 1955, Carl Djerassi and his students and colleagues, and also W. Klyne and his students, began an extensive series of investigations of the optical rotatory dispersion of ketones." After citing some 1956 JACS papers of ours (our first three papers were actually published in 1955), he refers to some 1952 and 1953 articles by Klyne. Distinguished as the latter's contributions have been, Klyne's first paper in the field did not appear until 1960 (*J. Chem. Soc.*, p 871), the 1952 and 1953 articles dealing only with molecular rotation differences at the sodium D line and not having any connection with ORD or CD.

The proof reading is so sloppy as to be not only annoying but downright confusing. For instance, in a figure (7.06) illustrating the effect of a cyclopropyl substituent, the cyclopropyl group (as well as an angular methyl group) is missing. Similarly, in a discussion of the ORD behavior of homoannular dienes, all the double bonds in the three examples are

missing. The best that can be said about the organic nomenclature is that it is inconsistent (e.g., 5-methylcyclohexanone on p 100 vs. 3-methylcyclohexanone on p 176; *trans*- $\beta$ -hydroindan-2-one on p 181 vs. other names on p 185, etc.); some of the figure legends are almost incomprehensible (Fig. 8.07 refers to the CD spectrum of "single-stranded poly (A)"; only a very careful reader would have noted three pages earlier that poly (A) is poly(adenylic acid)); and some unqualified statements would be puzzling to the laboratory chemist (p 168: "3-methylcyclopentanone may exist in one of four optically isomeric forms") who has never isolated more than two optical antipodes of this ketone.

In summary, as an up-to-date (1976) and detailed coverage of theory, it is definitely a useful book, especially because it collects all relevant material on the theory of chiroptical phenomena in one place—something that no other book or review has accomplished recently. However, I doubt that it will be used widely as a text and except for the relatively few experts working on the theory of chiroptical phenomena, it is likely to be purchased primarily by libraries as a reference volume. In this respect, it is a good buy because it is unlikely to be replaced by a similar book for a long time.

Carl Djerassi, *Stanford University*

**Developments in Polyurethane-1.** Edited by J. M. Buist. Applied Science Publishers, Ltd., London. 1978. ix + 280 pp. \$32.00.

Consistent with its title, this book does a commendable job of pointing out major new developments in PU technology, chemistry, processing, applications, and problems. The choice of topics is quite good and the lack of extensive overlap (quite common in a book of this nature with each chapter being written by a different author) is worth noting and of credit to the editor. But, although the choice of topics is good, the extent and method of coverage of each of the areas range from excellent to poor, exciting to boring, and inadequate to excessive. The book is meant primarily as a presentation and brief discussion of the areas covered and not meant as a technical handbook; i.e., it will not serve as a critical source of information to an expert in the field. It is more a concentrated source of information about many relevant topics and might be read by a knowledgeable individual, yet nonexpert, requiring a rapid yet complete introduction into the field, or by an individual who is directly involved in one aspect of the urethane industry and is looking for more breadth in the field of a concentrated text.

Some chapters are excellent in that they clarify and simplify points by the use of illustrations, practical examples, and tables, and give adequate or equal coverage to all aspects of the area which they are covering. Other chapters, although not lacking in information, lack illustrations, tables, examples, and adequate referencing, and the authors get bogged down discussing their own area of interest in great detail, while just skimming over others. Thus, a major criticism concerns the wide variation in the quality of writing and presentation in the various chapters. I think Chapter 3 is excellent, well balanced in its content and in the coverage of each area.

The areas which are well covered include morphology, flammability, toxicity of isocyanates, new or novel synthetic route, relationships between basic reactants and mechanical and physical properties, applications of flexible and rigid foams in transportation and construction industry, and processing machinery.

I would recommend this book for a concentrated yet complete coverage of the current state of the urethane industry.

Frank E. Filisko, *The University of Michigan*

**CH-Acids.** By O. A. Reutov, I. P. Beletskaya, and K. P. Butin. Translation Editor: T. R. Crompton. Pergamon Press, New York. 1978. viii + 228 pp. \$30.00

This is the most comprehensive review available on the ionization of carbon acids. It covers all of the major equilibrium and kinetic methods of measuring CH ionization, including the polarographic method developed in the authors' laboratory. The treatments of structural effects on equilibrium acidity and stereochemistry of proton transfer are thorough, and they bring the earlier discussions in D. J. Cram's "Fundamentals of Carbanion Chemistry" up to 1974. The one major omission is the largest reliable set of equilibrium CH acidity measurements available, those in DMSO by F. G. Bordwell and coworkers. The text of the present volume covers the literature only through mid-1974. In an appendix there is a list of references through 1977 that includes Bordwell's work, but a reference list is a poor substitute for a review. It is regrettable that the authors did not bring their book up to date before publication of the English edition.

Warren T. Ford, *Oklahoma State University*