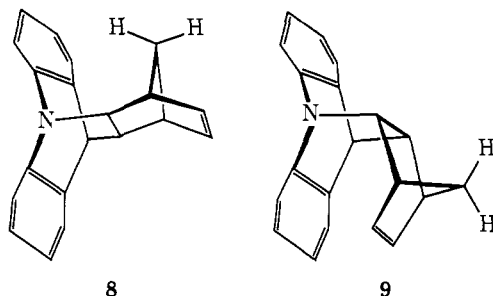


that the reactivity of excited naphthalene is much less than that of excited anthracene. Since the anthracene has a higher electron affinity than the naphthalene,<sup>11</sup> there is a difference in the charge-transfer character of the excited intermediates. Although a number of explanations are possible for the results, the reasons underlying these differences are not yet resolved at the present stage.

Similarly, the irradiation of acridine (7) and quadricyclane (2) in benzene afforded an isomeric mixture of 1:1 adducts 8 and 9 in a moderate yield. The NMR of the reaction mixture showed the ratio of 5:2. A pure sample of 8 was isolated by chromatography on alumina followed by recrystallization: colorless prisms, mp 135°. On the other hand, the isomer 9 decomposed slowly upon chromatography or the attempted purification. A crystalline material of about 95% purity was, however, obtained by crystallizing the crude reaction mixture: pale yellow prisms, mp 115–120°. The structures of the isomers were determined by the NMR data; a significant shielding effect by the anisotropy of the benzene moiety for the methylene bridge protons in 8 is observed at  $\delta$  -0.08 (1 H, d,  $J$  = 9.0 Hz) and 0.90 (1 H, d,  $J$  = 9.0 Hz). By contrast, compound 9 showed methylene protons at  $\delta$  1.2–1.3 (2 H, multiplet). Thus, structures 8 and 9 were assigned to be exo and endo 1:1 adducts, respectively.

Chart I



The formation of the photoadducts might proceed via diradical intermediates, by the stabilization of a polar contributing structure by the electronegative nitrogen of an excited acridine molecule, rather than in a stereoselective concerted fashion, since quadricyclane does not quench appreciably the fluorescence of acridine by the fluorescence quenching experiments. Furthermore, the total yields of the 1:1 adducts of 8 and 9 are considerably decreased for the photoaddition re-

action in the presence of biacetyl which is known to a sensitizer of acridine.<sup>12</sup> In addition, the photoproduct formations are affected by the polarity of a solvent; upon irradiation with 2 in a protic solvent such as methanol and ethanol, acridine gave only the photoreductive products (acridan and biacridan)<sup>12</sup> and no 1:1 adducts were detected.<sup>13,14</sup>

**Acknowledgment.** The authors wish to thank Dr. Keizo Aoki of the Department of General Education, Nagoya University, for measurement of fluorescence spectroscopy.

## References and Notes

- (1) *Molecular Design by Cycloaddition Reactions*, 27. Part 26 of this series: T. Sasaki, K. Kanematsu, A. Kondo, and K. Okada, *J. Org. Chem.*, in press.
- (2) (a) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965); (b) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1971.
- (3) G. B. Gill and M. R. Willis, "Pericyclic Reactions", Chapman and Hill, London, 1974.
- (4) A referee has commented that  $[4\pi + 2\pi + 2\pi]$  photocycloaddition is known to addition of acetylenes to naphthalenes. However, it undergoes the  $[2\pi + 2\pi + 2\pi + 2\pi]$  addition; see G. Sugowdz, P. J. Collin, and W. H. F. Sasse, *Aust. J. Chem.*, **26**, 147 (1973), and references cited therein.
- (5) Regio- and stereospecific thermal  $[2\pi + 2\sigma + 2\sigma]$  cycloaddition reaction and metal-catalyzed  $[2\pi + 2\sigma]$  cycloaddition reaction of quadricyclane are well known; see (a) I. Tabushi, K. Yamamura, and Z. Yoshida, *J. Am. Chem. Soc.*, **94**, 787 (1972); (b) R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, *ibid.*, **97**, 812 (1975). However, it is to be noted that no photochemical cycloaddition reaction of quadricyclane is reported as yet.
- (6) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).
- (7) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).
- (8) (a) N. C. Yang and J. Libman, *J. Am. Chem. Soc.*, **94**, 1405 (1972); (b) N. C. Yang, D. M. Shold, and J. K. McVey, *ibid.*, **97**, 5004 (1975); (c) N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *ibid.*, **97**, 5006 (1975).
- (9) (a) T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Am. Chem. Soc.*, **95**, 5632 (1973); (b) T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Sugiura, *ibid.*, **97**, 355 (1975).
- (10) This observation was agreeable to the result of experiments by Murov and Hammond on the basis of their views of the quenching of fluorescence of naphthalene by quadricyclane; see ref 6.
- (11) See ref 8a.
- (12) M. Hoshino and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **46**, 745 (1973), and references cited therein.
- (13) During preparation of this paper, interesting photoadditions of 1,3-dienes to acridine were reported; see ref 8c.
- (14) The limitation of the photoreaction was that phenazine was inert to the photoaddition of quadricyclane.

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## Book Reviews

**Molecular Oxygen in Biology.** Edited by O. HAYAISHI (Kyoto University). North-Holland Publishing Co., Amsterdam, and American Elsevier Publishing Co., Inc., New York, N.Y. 1974. xiii + 367 pp. \$36.50.

This book represents an ambitious undertaking designed to survey "neglected" aspects of the role of oxygen in biology. The editor has succeeded in assembling a diverse collection of reviews which include unusual topics such as "Molecular Oxygen and Evolution" as well as traditional topics such as the "Structure and Function of Hemoglobins". The references indicate literature coverage through 1973.

Chapter 1 ("The Physico-chemical Properties of Molecular Oxygen") summarizes the physical and chemical properties of oxygen but suffers under the burden of surveying too large an area of

research. It is doubtful whether there is sufficient detail for this summary to serve as an authoritative reference. It is certain that the reader will rarely refer to this chapter while reading later chapters. Chapter 2 ("The Electronic Structure of Coordinated Oxygen") covers a fascinating area of bioinorganic chemistry but contains an array of amusing as well as confusing errors. For example, a molecular orbital diagram (p 40) meant to illustrate the  $^3\Sigma$  state of  $O_2$  results from combining one oxygen atom possessing six electrons with another oxygen atom possessing seven electrons. Chapter 3 ("Molecular Oxygen and Evolution") is a fascinating account of evolution as a function of atmospheric composition. Hypotheses concerning the effect of oxygen pressure variation on evolution are well described and critically evaluated. Chapter 4 ("Oxygen Effects in Radiobiology") is a brief account of the effects of oxygen

on the x-ray irradiation of various targets (water, DNA, mammalian cells). The authors' disclaimer that this article is "not meant to be a scholarly appraisal for the eyes of other radiobiologists" hardly forgives the casual style of this chapter which detracts from the caliber of other chapters. Chapters 5, 8, 9, and 10 discuss four topics of particular interest to biochemists: the effects of hyperbaric and hypobaric oxygen on metabolism, the reduction of oxygen to water by cytochrome oxidase, the biological reduction of oxygen to hydrogen peroxide, and oxidative phosphorylation. These chapters are uniformly excellent. Chapters 6 and 7 focus on the transport of oxygen by respiratory proteins including hemoglobin, hemocyanin, and hemerythrin. Although there is some overlap in coverage in the two chapters, both are well-written accounts in which the authors have made particularly effective use of illustrations.

This book will undoubtedly be useful to the specialist in the aforementioned research areas and to the nonspecialist interested in broadening their understanding of a particular field. To the extent that the articles range over wide areas of biology and chemistry, the book often relies on jargon unfamiliar to most students. In the reviewer's opinion, the book will be of interest principally to biochemists.

David Watt, *University of Colorado*

**Biopharmaceutics and Pharmacokinetics: An Introduction. Second Edition.** By ROBERT E. NOTARI (Ohio State University). Marcel Dekker, New York, N.Y. 1975. x + 285 pp. \$13.75.

The book is intended as a text for an introductory course in the title subject. The presentation is designed as a workbook, using numerous examples to illustrate concepts and encouraging the reader to work as many problems as possible. Although the material can be grasped without following the author's recommendation of active participation, maximum benefit will be gained by solving practice problems as they are presented.

Of the five chapters in the first edition, two have been drastically revised and rewritten, one has been expanded, and a completely new chapter has been added. The modifications represent a significant improvement in clarity, particularly Chapters 2 and 3, which contain a large amount of kinetic and algebraic manipulations. The new chapter on pharmacokinetic aspects of structural modifications in drug design is particularly welcome, as it introduces the significant problems facing the clinical or research pharmacologist.

Considering the author's intention of providing an introductory text with numerous illustrative problems and examples, the book is a useful addition to one's library. Potential readers should be warned that it does not provide information related to active research areas in pharmacology. Particularly lacking are examples of applications of the pharmacokinetic principles discussed to important practical applications. One is left with a perhaps simplified picture of pharmacokinetics, without an appreciation for the complexity of drug transport, absorption, etc. Even at the basic level for which the text was written, some "words of warning" about data interpretation may be appropriate.

The text has greatest value for the beginning student in pharmacology and related fields, and for a researcher from another field who wishes to become familiarized with the topics discussed. The problem-oriented approach is useful for obtaining a good grasp of the material, and coverage of the field appears adequate. The book was found to be very readable and well organized.

Richard L. McCreery, *Ohio State University*

**Water. Volume 3. Aqueous Solutions of Simple Electrolytes.** Edited by FELIX FRANKS. Plenum Press, New York, N.Y. 1973. xvii + 472 pp. \$37.50.

This, the third volume of Franks' treatise on water is divided about equally between theoretical and experimental aspects of the structure and properties of electrolyte solutions. Each of the eight chapters contains an introduction to the theory and/or experimental techniques involved in the specific area, followed by a more detailed discussion.

Chapter 1, "Thermodynamics of Ion Hydration" (H. L. Friedman and C. V. Krishnan), is an extensive review of various electrolyte solution models and the measured thermodynamic properties to be matched. Chapter 2 on the "Thermodynamics of Aqueous Mixed Electrolytes" (H. L. Anderson and R. H. Wood) is a review of this more specialized theoretical area. Chapter 3 discusses "Hy-

dration Effects and Acid-Base Equilibria" (L. G. Hepler and E. M. Woolley). Chapter 4, "Ionic Transport in Water and Mixed Aqueous Solvents" (R. L. Kay), has information on the methods used in obtaining ion conductances and the parameterization of their variation with temperature, pressure, etc. Chapter 5, "Infrared Spectroscopy of Aqueous Electrolyte Solutions" (R. E. Ver-rall), contains a critical review of the available infrared data. "Raman Spectroscopy of Aqueous Electrolyte Solutions" (T. H. Lilley) follows. The next chapter, titled "Nuclear Magnetic Relaxation Spectroscopy" (H. G. Hertz), gives the principles, experimental data, and models involved in the area. With similar divisions, the last chapter discusses "Dielectric Properties" (R. Pottel).

The book has a complete table of contents in outline form, a single bibliography for the whole book, as well as subject, compound, and formula indexes facilitating access to specific points. As in the previous volumes, all technical facets are of high quality.

In the introductory material in each chapter, many parts of the articles in Volume 3 overlap with those in the previous volumes. For instance, chapters on thermodynamics—1, 2, and 3—have similarities with Volume 2, "Thermodynamic Properties", and each uses slightly different notation. In certain areas such as infrared and Raman spectroscopies of electrolyte solutions, the chapters by necessity overlap in large part with Volume 1 of the series since reference is needed to the pure water spectra. The chapter in Volume 1 by G. E. Walrafen is superior and should probably be read first, regarding the chapters in Volume 3 as excellent extensions and keys to the current literature. Similarly, there are chapters on NMR and dielectric properties in all three volumes, each with its own emphasis (1, pure water; 2, nonelectrolyte solutions; and 3, electrolyte solutions). Given these interactions, libraries with the previous volumes should probably obtain a copy of this book. Specialists in the field may find the book somewhat dated while neophytes should probably read Robinson and Stokes' "Electrolyte Solutions" beforehand.

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**Organoborane Chemistry.** By THOMAS ONAK (California State University). Academic Press Inc., New York, N.Y. 1975. x + 360 pp. \$38.00.

This monograph attempts to provide a comprehensive treatment of the structure, physical properties, synthesis, and reactions of organoboranes. To cover every aspect of organoborane chemistry in a 360-page monograph is impossible, as the author acknowledges. Instead, the author provides copious tables containing references to the synthesis of most of the known organoboranes. A section on supplementary sources of information listing most of the reviews on organoborane chemistry written in the past 20 years is a welcome addition.

The book is divided into seven chapters. The first two describe the nomenclature, structure, and physical properties of organoboranes. The remaining five chapters cover: Three-Coordinate Organoboranes, Four-Coordinate Organoboranes, Organodiboranes, Other Organopolyboranes, and Supplementary Chemistry.

In my opinion, the book has two shortcomings. There is little correlation of mechanism with chemical behavior. The viewpoint presented is synthetic chemistry at a descriptive level. For example, it is increasingly clear that the reactivity of tricoordinate organoboranes depends on the intermediacy of tetracoordinate organoboranes. The arbitrary division of these derivatives into two chapters not only will confuse the novice, but forces the reader to look in two places for similar reactions.

Unfortunately, in at least one case, the author has also failed to extrapolate recent evidence to correct the discussions in older literature. Thus in one section he discusses the intermediacy of  $\alpha$ -boraketones and their ease of protonolysis. In a later section, he briefly mentions the rearrangement of these compounds to enolborinates. The novice might never realize that  $\alpha$ -boraketones probably exist only briefly as intermediates and that hydrolysis is probably due to the intermediacy of the enolborinate, unless he reads two well-separated sections of the book.

In spite of the criticisms mentioned above, the author has provided a comprehensive review of the literature. This monograph should be especially useful to those working in organoborane chemistry and related fields.

Alan B. Levy, *State University of New York at Stony Brook*