

was photolyzed under identical conditions, the products were isolated by glpc, and the location of the deuterium atoms was ascertained by nmr (see Scheme II).¹⁶

It has already been noted that 2-MBN can be viewed as a di- π -methane system and the formation of I and II is explicable when approached in this manner. A plausible mechanistic scheme is presented below. Aryl olefin bonding (to give IV) and rearomatization (to give V), is unextraordinary and a typical di- π -methane sequence. However, because the normal di- π -methane product VII is so highly strained, formation of the carbene VI and its rearrangement to 1-methylene-3-vinylindan (I) is preferred. We propose that VII is formed in small amounts, either from V and/or VI, but reopens to VIII which gives, *via* a 1,2-hydrogen shift, the observed minor product II. Support for Scheme II comes from studies¹⁷ of dibenznorborna-

(16) (a) The dideuterated analog of I showed the triplets due to H₇ (δ 5.04) and H₈ (δ 5.45) to be absent. (b) A_N analysis of the nmr spectrum of II follows from the discussion of H. Tanida, K. Tori, and K. Kitahonoki (*J. Amer. Chem. Soc.*, **89**, 3212 (1967)) on the nmr spectra of the benzo[6,7]bicyclo[3.2.1]octa-2,6-dien-4-yl system (symbols are from the reference but note the numbering change). The assignments are as follows: aromatic hydrogens δ 7.0–7.4 (m), δ_6 3.31 (m, $J_{64eq} = 1.9$, $J_{64ax} = 5.0$, $J_{55n} = 4.5$, $J_{55x} = 0.9$, $J_{53} = 1.2$ Hz), δ_{4ax} 2.59 (a doublet of a pair of overlapping triplets, $J_{4ax4eq} = 18.0$, $J_{4ax3} = 3.0$, $J_{4ax2} = 3.0$ Hz), δ_{4eq} (also a doublet of a pair of overlapping triplets, but with each peak split by W-plan coupling to H_{5n}; $J_{4eq3} = 3.4$, $J_{4eq2} = 1.9$, $J_{4eq5n} = 0.8$ Hz), δ_3 5.24 (m, $J_{32} = 9.5$ Hz), δ_2 6.15 (m, $J_{12} = 6.4$, $J_{58n} < 1$ Hz), δ_1 3.27 (multiplet superimposed on H₅, $J_{15n} = 4.5$ Hz), δ_{2n} 2.34 (overlapping doublet of triplets, $J_{5x5n} = 10.0$ Hz), δ_{5x} 2.05 (doublet). The dideuterated analog of II showed the absence of H₂ and the absence of one bridgehead proton at $\delta \sim 3.3$. The missing proton was assigned as H₁ because the 5-Hz coupling between H₅ and H_{4ax} is retained. The 3.0-Hz coupling of H_{4ax} to H₂ has been lost, as would be expected.

(17) J. Ipaktschi, *Chem. Ber.*, **105**, 1989 (1972). The trapping experiment was done with a 7-spiro derivative of dibenznorbornadiene.

dienes, where a photoproduct analogous to I has been isolated and a postulated carbene analogous to VI has been trapped.

With regard to the excited state responsible for the photochemistry of 2-MBN, we can only say at this time that both the excited *singlet* (67% reduction in fluorescence intensity ($\phi_f = 0.08$) and lifetime ($\tau = 4.5$ nsec) relative to a dihydro derivative) and *triplet* (no observable phosphorescence) give evidence for bichromophoric interaction.¹⁸ However, it is worth noting that the excited singlet interaction, though marked, is considerably less than the 96% reduction in emission and lifetime observed with 6-phenyl-2-hexene (where the requisite "sandwich" arrangement of chromophores is feasible) and the complete lack of fluorescence in benznorbornadiene¹⁹ (where both p lobes of the olefin are in a position to interact with the benzene ring).²⁰

Acknowledgments. We are grateful to the National Science Foundation for support of this research and to Professor Fred Lytle for assistance in the lifetime measurements.

(18) For a discussion of a coupling of the chromophores, and the ORD spectrum of 2-MBN, see D. J. Sandman and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 645 (1969). See also W. H. Inskeep, D. W. Miles, and H. Eyring, *ibid.*, **92**, 3866 (1970).

(19) J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 7103 (1969).

(20) Attempts to sensitize the reaction with acetone have so far been without success.

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Received April 2, 1973

Book Reviews

Progress in Solid State Chemistry. Volume 7. Edited by H. REISS and J. O. CALDIN. Pergamon Press, Inc., New York, N. Y. 1972. xi + 273 pp. \$30.00.

This volume is a continuation of the series presenting advances in fundamental and technological areas of solid-state chemistry. The volume covers a broad spectrum of topics, written by various experts at different degrees of depth and breadth. Despite these inevitable variations, a common thread of critical presentation, present interest, and significance runs throughout the six articles of the volume. The theory of the thermoelectric power of solid-state cells with electrolytes displaying mixed ionic and electronic conduction is presented in the first article by C. Wagner. As far as this reviewer is concerned, this is the first time that the calculation of the Soret effect for these dual conduction systems is carried out. The derivations are developed to the point of permitting the comparison with experimental results for cases of prevailing cationic or anionic transport. In the second article, M. B. Panish and M. Ilegems examine the phase equilibria of III-V ternary systems. They present calculations of the phase boundaries and the detailed description of several temperature-composition diagrams. The computational approach followed is that of treating a ternary system as a mixture of two binaries. This is a somewhat pragmatic approach that gives generally quite satisfactory results.

In the third article, A. V. Novoselova, V. P. Zlomanov, S. G. Karbanov, O. V. Matveyev, and A. M. Gas'kov review binary phase and composition diagrams of Ge, Sn, and Pb chalcogenides. They include X-ray reflection data, unit cell parameters, partial pressures, enthalpies and entropies of formation, and equilibrium constants for various defect reactions. The topic of liquid phase epitaxy is treated in the fourth article by L. R. Dawson. Interest in this area stems primarily from deter-

mining the conditions for optimum growth of semiconductor materials. The article discusses factors influencing epitaxial deposition from solution, reviews the advantages of the method, and considers the application to specific growth systems with emphasis on III-V semiconductors.

In the fifth article, J. T. Kummer reviews several physicochemical properties of β -Al₂O₃ with emphasis on electrochemical characteristics, chiefly ion-exchange behavior in molten salts, aqueous and nonaqueous solutions, ionic diffusion, ionic conductivity, and dielectric loss. Throughout the discussion, the role of the crystal structure and of the atomic arrangements in β -Al₂O₃ on the electrochemical properties is emphasized. The article is noteworthy for its clarity, critical outlook, and emphasis on practical applications. The last article by L. A. Bursill and B. G. Hyde is an account of the structure, texture, mechanism, and thermodynamics of crystallographic shear in titanium oxides. Experimental and theoretical structural studies on oxides with various stoichiometries ($1.66 \leq O/Ti \leq 2$) together with pictorial models and various reactions for the production of crystallographic shear are shown and analyzed. The article is critically written and it extends to cover the presence of hysteresis loops, the effect of texture on phase thermodynamics. Researchers currently active in the above areas, as well as those interested in the broader fields of solid state chemistry, would find the book very useful indeed.

G. Parravano, University of Michigan

Molecules and Life. By JOSEPH S. FRUTON. John Wiley and Sons, Inc., New York, N. Y. 1972. x + 579 pp. \$19.95.

Fruton traces the development of the chemical basis for biological processes in this historical treatise. The period covered by the

book, roughly between 1800 and 1950, is treated in an introduction and five essays. The 22-page introduction traces the development from medicine of the now separate disciplines of chemistry, botany, physiology, and biochemistry. The first essay, dealing with fermentation, describes the development of thought about fermentation from ancient times to 1800, and then goes on to trace the development of the concept that microorganisms are the agents of fermentation and that substances isolable from living cells catalyze the chemical reactions associated with fermentation and other processes. The second essay, "The Nature of Protein," traces the development of our knowledge of protein structure from the early observations of albuminoids, through the peptide theory of protein structure and the determination of the primary structure of insulin by Sanger. The series of observations which led to the characterization of the structure of DNA in terms of the Watson-Crick double helix are treated in the first half of the third essay. The second half of this essay traces the development of kinetics and the characterization of DNA as the genetic material. The fourth essay, "Intracellular Respiration," begins with Lavoisier's analogies between combustion and respiration, and then goes on to trace the establishment of the role of hemoglobin in the transport of oxygen, and the role of enzymes and vitamins in biological oxidations. A detailed description of the discovery and characterization of pathways involved in respiration such as glycolysis, the citric acid cycle, and the electron transport chain is given in this essay. The last essay, "Pathways of Biochemical Change," traces the establishment of several metabolic pathways, such as the biosynthesis of glycogen, urea, amino acids, and fatty acids. The important roles tracers and mutants played in this phase of biochemistry are discussed in this essay.

Although the book contains an extensive bibliography and a name index, it contains no subject index. The author explains this omission in the preface in terms of the confusing terminology which characterizes the period of 1800-1950. About 10 to 20% of the book consists of quotations from the scientific literature. These quotations are woven smoothly into the text and give the reader a feeling for the views of the scientists at the time of his contribution. This book should be considered as a scholarly account of the development of biochemistry. It does not read like a historical novel, nor is it embellished with personal anecdotes about any of the scientists. None of the scientists, with the exception of perhaps Hopkins, is presented as a hero. Time and time again, Fruton shows how great scientists go astray by formulating theories and generalizations for which they have no experimental basis. On completing this book, one is convinced that Fruton proved his thesis that the development of biochemistry was a continuous process and not just a series of breakthroughs.

Jules A. Shafer, *University of Michigan*

The Electrochemistry of Organic Compounds. By A. P. TOMILOV, S. G. MAIRANOVSKII, M. YA. FIOSHIN, and V. A. SIRNOV (Leningrad University). Halsted Press (a division of John Wiley & Sons), New York, N. Y. 1972. xii + 628 pp. \$38.00.

In the years that have passed since Kolbe's conclusive demonstration of the electrochemical oxidative coupling of carboxylic acids (1849) and Haber's masterful elucidation of the complex mechanism for the electrochemical reduction of nitrobenzene with its host of primary and secondary reactions (1898), the electrolytic preparation of organic compounds has been extensively investigated. For the past three or four decades, polarographically derived technics, including controlled electrode potential electrolysis, have been used to study the mechanistic and kinetic aspects of a host of organic electrode reactions. However, the actual use of electrochemical organic synthesis has been limited on both a laboratory and an industrial scale, although in recent years there seems to have been greater utilization of electrochemical approaches in organic and organometallic compound manufacture. The present book, which is a translation of the original Russian edition published in 1968, is a useful addition to the organic electrochemical literature.

While the literature on the polarography of organic compounds—largely at mercury electrodes—is adequately covered, the stress is on the preparative use of electrolysis with extensive coverage of the effects of variation of experimental conditions on the natures and yields of products obtained at all types of electrodes. After introductory chapters on the theoretical aspects and experimental methods for investigation of the electrochemistry of organic compounds (75 pp) and electrolytic apparatus (58 pages), there follows a group of five chapters (168 pp) on cathodic processes (reduction of carbon-carbon multiple bonds, carbonyl compounds, nitrogen-containing functional groups, and sulfur- and arsenic-containing

compounds; cathodic dehalogenation), a group of three chapters (157 pp) on anodic processes (oxidation in general; condensation and substitution processes), and a group of three chapters (80 pp) dealing with secondary electrolytic processes involving organic compounds (formation of organometallic compounds by electrolysis and their electrolysis; reactions of free radicals, ions, and ion-radicals formed during electrolysis; alkali amalgam reduction and carrier catalyst processes). The references to each chapter (total claimed to exceed 2,000) are gathered at the end of the volume and have a cut-off date of 1965; the coverage of the patent literature seems to be adequate.

The authors are realistic in their approach, recognizing, for example, that electrochemical synthesis of organic compounds on an industrial scale cannot currently compete with many catalytic, thermal, and photochemical processes. However, the value of the electrochemical approach in terms of selective reduction or oxidation (with particular reference to processes occurring electrochemically in successive redox steps) is thoroughly explored; *e.g.*, the potentialities for dimerization (especially hydrodimerization) reactions and preparation of organometallic compounds are amply illustrated. It is interesting that, compared to electrolytic reduction reactions, electrolytic oxidations of organic compounds, except for the anodic electrolysis of carboxylic acids, are generally of a considerably lower degree of selectivity. The extensive recent literature on the polarographic investigation of the intermediate free radical, carbanion, and carbonium ion species formed on electrolysis, which was already apparent by 1965, may provide significant leads for synthesis on both laboratory and commercial scale.

Among the virtues of the book are the numerous references to the Russian literature, which seems to have been thoroughly covered, the large number of tables summarizing data for families of related compounds, and the appreciable number of diagrammatic flowsheets for industrial electrochemical manufacture of organic compounds. A major limitation is the cut-off date of 1965; *e.g.*, much of the development during the past decade of the understanding of organic electrode processes—especially in reference to chemical reactions preceding, accompanying, and following electron transfer—is not covered. At times, the 1965 termination date results in a biased view of an area. Thus, discussion of the electrochemical oxidation of purines is based on three papers published in 1897, 1926, and 1936; the dozen papers published since the middle 1960's are not noted. The translation is awkward at times, including the use of uncommon terms; however, the sense of the text is usually evident. A minor source of irritation is the occasional omission of references to the sources of figures and textual statements. The apparatus chapter, while interesting in a general way, is rather dated.

More serious are the occasional errors in equations, whose inclusion in large number is a welcome aspect of the book. While most of the errors are more or less readily recognizable, some are rather serious. For example, the series of equations for the reduction of acetylenedicarboxylic acid at the foot of page 139 omits one step and ends up with a compound containing two trivalent carbon atoms (the final product is also not identified as being the racemic form). A few erroneous statements, which likely resulted from a hasty reading of the original reference, were noted, *e.g.*, the statement (page 291) that butadienetetracarboxylic acid produced on reduction of bromomaleic acid is unstable and decarboxylates to form butadiene.

Although the presence of errors such as those indicated should warn the reader to proceed with care, this difficulty is more than compensated for by the convenience of having a rather thorough, well-organized, and generally readily readable and well-illustrated survey of the literature on the electrochemistry of organic compounds up to 1965, which covers both polarographic and preparative studies.

Philip J. Elving, *University of Michigan*

Organic Peroxides. Volume 3. Edited by DANIEL SWERN (Fels Research Institute and Department of Chemistry, Temple University). Wiley-Interscience, New York, N. Y. 1972. ix + 384 pp. \$24.95.

This volume is the third and last in the series and like the first two presents a collection of reviews by various reporters covering the field of peroxides. Included are sections on alkyl peroxides, cyclic peroxides, reactions of organometallic compounds with peroxides, epr studies, and hazards in the handling of peroxides. The literature is generally covered through 1970.

The series by now represents one of the most complete ready

references to the literature pertaining to peroxides, but this third volume represents only a modest addition to the coverage. Although an occasional lapse of editorial scrutiny is evident (the complexity of an epr spectrum discussed on page 322 is more probably due to the adjacent diastereotopic protons than to a rotational barrier as suggested), the reviews are relatively free of errors. Two chapters (cyclic peroxides and reactions of organometallic compounds with peroxides) have been translated into English with no apparent damage.

John T. Groves, *University of Michigan*

The Isoquinoline Alkaloids—Chemistry and Pharmacology. By MAURICE SHAMMA (Pennsylvania State University). Academic Press, New York and London. 1972. 594 pp. \$35.00.

The logically unifying quality of biogenetic relationships is a fundamental theme implicit in this treatment of isoquinoline alkaloids. A chart of established and presumed pathways connecting the structural types, printed on an inside cover, can be seen as a stage on which the compounds are set and considered relative to each other. The alkaloids are discussed by structural types in 31 chapters of very unequal lengths, which reflects the long chemical history of some of the compounds and the newness or rarity of others. Structure elucidation, synthesis, chemistry, biosynthesis, and pharmacology are considered in representative detail for each group. The chapters are arranged in conveniently short subsections with informative and particular headings. Conciseness and simplicity mark the writing, and the author's great knowledge of the field is skilfully used for emphasis and comparison between different groups of compounds. All these qualities make the book attractive for study and teaching. As a reference book, it contains much useful information, even spectral data being given generously but selectively, without being voluminous. Altogether this book is an excellent up-to-date summary of isoquinoline alkaloids which deserves wide usage.

P. W. Le Quesne, *University of Michigan*

Techniques of Nucleic Acid Fractionation. By S. R. AYAD and J. BLAMIRE (University of Manchester). Wiley-Interscience, London. 1972. xiii + 234 pp. \$14.95.

This book is a good guide to the very extensive literature on the techniques which have been utilized for the fractionation of nucleic acids and to the methods which may be used for following separations achieved by the various procedures. The authors also have discussed the role of fractionation techniques in obtaining information concerning the participation of various nucleic acids in biological phenomena.

It would have been most helpful if the book had been written not only as a guide to the literature, but also as more of a laboratory manual. For those just entering the field, it also would have been desirable to include an appendix which summarized the abbreviations used throughout the book.

The book is well written, in general, but occasionally unnecessarily ponderous, and confusing phraseology is used by the authors. For example, on page 33, there occurs the sentence, "To shadow, a filament of a heavy metal atom (*e.g.*, platinum, palladium or uranium) is heated in a vacuum until the individual atoms have sufficient energy to break away from the filament and disperse into the container (see Figure 2.1)".

In summary, the book will prove useful to those investigators interested in both the chemistry and biology of nucleic acids.

David Lipkin, *Washington University (St. Louis)*

Organic Electrochemistry: An Introduction and Guide. Edited by M. N. BAIZER (Monsanto). Marcel Dekker, Inc., New York, N. Y. 1973. xvii + 1072 pp. \$49.50.

Synthetic Organic Electrochemistry. By A. J. FRY (Wesleyan). Harper and Row, New York, N. Y. 1972. x + 336 pp. \$19.95.

These books were written to bridge the gap between organic and electrochemistry. Both cover approximately the same ground, but with rather different emphases. They devote about the same space to the results of electrochemical theory and survey to the types of experiments, 154 pp (by G. Cauquis and V. D. Parker) in the Baizer book, and 168 pp in Fry. The discussion by Fry is particularly readable and well illustrated; we feel it is the main strength of the book. Much more space is devoted to how experiments are actually conducted in Baizer, with a 92-page section including many illustrations of cells and a list of commercial potentiostats by H. Lund and P. Iverson, and a four-page discussion of the relation between polarographic observations and the results of bulk electrolyses by P. Zuman, whereas only 22 pp of very gen-

eralized discussion are included by Fry. Fry devotes 144 pp to review of electrochemical transformations, arranged by functional group. The treatment in Baizer is much more comprehensive, 653 pp in 23 chapters by 13 authors. In addition to functional group transformations, sections are included on electrochemistry of heterocycles (H. Lund), organometallics (H. Lehmkuhl), electrogenerated reagents (Lund), and stereochemistry (L. Ebersson and L. Horner), among other topics. The reviews of industrial electrochemistry (D. Danly) and polymerizations (G. Parravano) are not to be found elsewhere. The ten-page bibliography (Cauquis and D. Serve) of books, reviews, journals, and less easily classified secondary references will be appreciated by workers new to the field. The lack of an author index in Fry will not be appreciated by anyone. We believe both books serve their purpose of acquainting organic chemists with the potential applications, as well as the results of electrochemistry, and deserve to be widely consulted.

Stephen F. Nelsen, *University of Wisconsin*

Glycoprotein. Parts A and B. Second Edition. Edited by ALFRED GOTTSCHALK. Elsevier, New York, N. Y. 1972. xxiv + 1378 pp. \$138.00.

Recognition of the broad occurrence and important biochemical effects of glycoproteins, coupled with the influx of new methods for their characterization, has led to a dynamic growth in the work on these substances. Almost all the growth has occurred during the last dozen years and most of this in the last six or seven years. The present review attests to this growth. The first edition appearing in 1966 contained 628 pages. Only six years later a revision was required containing 1378 pages. Rapid growth in the glycoprotein field is attested also by the appearance of numerous other reviews including a chapter in the *Annual Review of Biochemistry* during each of the last three years.

The field of glycoproteins, encompassing compounds with one or more carbohydrate-protein covalent linkages, includes a great and growing number of structures which at one time were considered protein only. Furthermore, almost all animal polysaccharides and many plant polysaccharides must now be recognized as covalently bound to protein and hence are glycoproteins. These "proteoglycans" are often found in the intercellular matrix. Thus, chitin, dermatan sulfate, chondroitin 4- and 6-sulfates, keratan sulfate, and heparin are now known to be covalently linked to protein and in their original locations must not be looked upon as discrete polysaccharides. This group of carbohydrate-protein compounds is not extensively discussed in the revised edition. Instead a chapter by V. Lindahl and L. Roden examines the carbohydrate-protein linkages in such compounds found in animals, plants, and bacteria.

The carbohydrate portion of glycoproteins can vary from one covalently linked sugar unit to many units and most often consists of two to seven sugar types in the form of branched oligosaccharide appendages, with the carbohydrate content varying from 1% to more than 80% of the weight of the molecule. Hence the review, after devoting two chapters to history and definitions, sets aside about 500 pages to describe physical, chemical, and enzymatic methods for determination of homogeneity, molecular weight, molecular shape, chemical behavior, analytical procedures, and methods for linkage determination. Because of the wide use of neuraminidase, a chapter is devoted to the characteristics of this enzyme.

After a chapter on the general occurrence of glycoproteins in animals and plants, specific glycoproteins are discussed in separate chapters. Biosynthesis and breakdown are then discussed in some 200 pages.

The format for chapters is generally uniform with only the expected variation in a multiauthored compilation. Likewise some difficulty must have arisen in getting chapters typeset on time since most chapters end with the 1969 literature and are extended by Addenda through 1971. However, this does not detract from the very extensive review. Each chapter is well written and gives excellent coverage of the subject. Astute choice of authors brings expertise to review this difficult area.

The printing is good with but few errors and is on excellent paper. The greatest criticism I have concerns the price which clearly removes the book from ownership of students and even from the personal collections of many mature investigators.

The book is excellent for bringing one abreast of glycoprotein science and should be examined by biochemists and more thoroughly read by all persons interested in this research field.

Roy L. Whistler, *Purdue University*