Book Reviews*

Analytical Uses of Immobilized Enzymes. Modern Monographs in Analytical Chemistry Series. Volume 2. By George G. Guilbault (University of New Orleans). Marcel Dekker, Inc.: New York. 1984. ix + 453 pp. $75.00 ISBN 0-8247-7125-7.

This monograph contains a wealth of tables and illustrations and is intended to provide a fundamental introduction to the basic principles and practices of the use of immobilized enzymes in chemical analysis. It was written for potential users of this technology, and emphasis has been placed on the practical and applied aspects. In Chapters 1 and 2, the author provides a summary and general description of the fundamental concepts of the use of enzymatic reagents and of immobilized enzymes in analytical chemistry. Topics covered include enzyme nomenclature, structure, and properties, as well as information about factors affecting reactivity in enzyme-catalyzed reaction systems, immobilization methodology, and experimental protocols on the use of such enzymes in practical applications.

The remaining three chapters are devoted to immobilized enzymes as analytical tools. Specifically, Chapter 3 describes the theory, methods, and applications of enzyme electrodes. Chapter 4 focuses on enzyme reactors and membranes and describes their construction and use for enhancing a variety of electrochemical, ultraviolet–visible, thermal, as well as luminescence detection schemes. Chapter 5 concerns methodologies and applications of enzyme layers. Assays based on semisolid surface fluorescence, dip-sticks, enzyme stirrers, mass spectrometry, and piezoelectric devices are detailed. Additionally, Chapter 5 contains a brief description and listing of available commercial instrumentation which has been designed for use with immobilized enzyme systems. The monograph also contains four extremely useful appendices which describe the numbering and classification scheme of enzymes and which list over 40 immobilized and over 400 soluble enzymes along with their different suppliers. Following these appendices are author and subject indexes.

The monograph is well written, produced, and presented. Overall, it is relatively free from errors and well referenced (over 780 literature articles are cited), and the coverage is up to date (current to 1983). As with any monograph on such a diverse and rapidly developing area, it is inevitable that some potential topics of interest may be overlooked. For instance, no mention was made in Chapter 1 (page 69) of the new technique using reversed micelles, by which enzymes can be solubilized in organic solvents with retention of their reactivity. However, this is a minor point and the author is to be highly commended for consolidating the diverse literature in this area into a clear and concise presentation.

In summary, this is an excellent and useful monograph about an important area of analytical chemistry. Anyone who is, or expects to become, involved in this rapidly growing area of research should seriously consider purchasing this monograph.

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Oxidation of Organic Compounds. Medium Effects in Radical Reactions. By N. M. Emanuel, G. E. Zaikov, and Z. K. Maizus (Academy of Sciences of the USSR, Moscow). Translators A. K. Henn and I. G. Evans; Translation Editor M. M. Hirschler. Pergamon Press: Oxford and New York. 1984. xv + 611 pp. $95.00. ISBN 0-08-022067-3.

The oxidation of organic compounds is a topic of great theoretical interest and enormous industrial application. It is therefore surprising that there are very few books that review this area. (Exceptions are the 1969 book by L. Reich and S. S. Stivala and Volume 16 in the kinetic series edited by C. H. Bamford and C. F. H. Tipper.) In general, the worker in this field must look to the excellent but independent review articles written by K. U. Ingold, J. A. Howard, the late L. R. Mahoney, the group at SRI, and others for guidance. For this reason, this book could have filled an important need. Unfortunately, it is so poorly organized and so marred with flaws that it cannot be recommended.

The first part of this book, consisting of the first two chapters, reviews liquid-phase oxidations of organic compounds by free-radical mechanisms and the methodology for studying these reactions. These chapters could have been a useful compendium. However, they contain errors (perhaps introduced during the translation) that would seriously mislead users. (For example, the correction factors necessary in the "gasometric" method, pp 75 and 76, contain errors. Furthermore, transducers are now used, rather than mercury manometers.) The typesetting and proofreading also leave a good bit to be desired. (For example, structures are incorrectly set on pp 13 and 77, and equation numbers are incorrectly set on p 15.)

The bulk of this book deals with the subject given in its subtitle, medium effects. The reactions of neutral free radicals involve solvent effects more often than might have been expected, and this subject has never been reviewed in book form. Therefore, a text that organized and integrated the many diverse facts on solvent and polar effects on radical reactions would be most welcome. However, this book again falls short of the mark. Solvent effects are organized and discussed in what seems to be a random and haphazard way. For example, in Chapter 4 on The Role of the Medium in Chain Initiation Reactions, an extensive discussion is given of the well-known studies of the solvent effect on the ratio between β-scission and hydrogen atom abstraction for alkoxyl radicals, a reaction that is not a "chain initiation reaction". Similarly, the discussion of solvent effects on the decompositon of hydroperoxides (pp 204 ff) is confused. General solvent effects, induced decomposition by radicals derived from the solvent, and general solvent effects on the induced decomposition step are not distinguished. The reaction of olefins with hydroperoxides is concluded to be an SH2 attack on an oxygen atom, but Walling's definitive kinetic isotope effect data are not quoted. The reaction of hydroperoxides with styrene is treated without regard to the enormous literature on molecule-assisted homolysis reactions of hydroperoxides in styrene.

Some of the difficulties with this book derive from the fact that the literature reviewed is quite dated; the most recent reference is to literature published in 1975, although the Appendix does give a list of publications up to 1983 that is not integrated into the text.

So, in conclusion, an important opportunity has been missed. This book was written by eminent Russian chemists whose contributions have been enormous. One, therefore, suspects that the fortunate few who can read Russian might have found the Russian version of this text more useful, particularly some years ago when it was first published.

William A. Pryor, *Louisiana State University*

MMI Press Polymer Monograph Series. Volume 2. Practical Macromolecular Organic Chemistry. Third Edition. By D. Braun (Institut für Makromolekulare Chemie der Technischen Hochschule Darmstadt und Deutsches Kunstsoff-Institut, Darmstadt), H. Cherdron (Hoechst AG Kunstsoff-Forschung Frankfurt, Mainz), and W. Kern (Organisch-Chemisches Institut der Universität Mainz). Translated from the German by K. J. Ivin (The Queen's University of Belfast). Edited by H.-G. Elias. Harwood Academic Publishers: Chur (Switzerland) and New York. 1984. xiii + 332 pp. $96.00. (Text price for 10 or more copies: $34.95). ISBN 3-7186-0059-5.

This is the third edition of a book originally published as "Praktikum der Makromolekularen Organischen Chemie" in 1966 with revision in 1971 and 1979; the current text is a 1984 translation. The aim of this work as stated by the authors is "...to provide students with laboratory work which will bring alive the theoretical concepts taught in lectures".

After an introductory chapter (31 pages) which defines the usual terms in polymer science (CRU, thermal transitions, etc.), a chapter on general methodology is presented (88 pages) which deals with preparative techniques (reaction vessels, choice of reaction conditions, etc.) along with product isolation, characterization (solubility, viscosity, etc.), and processing into films or foams. Chapter 3 (110 pages) details 56 experiments on chain-growth polymerization after a short discussion of general concepts. Experiments which study reactions proceeding by free radical, ionic, and coordination mechanisms are written in the style usually found in organic chemistry lab manuals. Chapter 4 (64 pages) presents 26 experiments on the synthesis of step-growth polymers by familiar techniques (melt condensation, interfacial reaction, etc.). The book ends with a chapter (28 pages) on polymer modification reactions (20 experiments) such as cellulose degradation and the synthesis of ion exchange resins from polystyrene.

The translation is excellent, and there are very few typographical errors. The experiments are clearly written and allow for the effective study of the many concepts in polymer synthesis, characterization, and kinetics. The experiments are all suitable for teaching purposes given that they can be accomplished in a reasonable length of time with readily available apparatus. Appropriate cautions to possible hazards are noted throughout the text though syntheses involving chloromethyl methyl ether and phosgene may be too dangerous for routine laboratory experiments.

It must be emphasized that this text is appropriate only for a laboratory course given in conjunction with a separate lecture course with its own, more thorough, textbook. Chemical equations are not used to

*Unsigned book reviews are by the Book Review Editor.

illustrate any of the separate experiments, and many concepts require more extensive treatment than the book allows for. The original publication date probably explains the large number of references dating from 1950 to the mid 60's; for example, of the 130 references in Chapter 2, 70% are to works published before 1965. This can be a disadvantage at times: there is no mention of the now-routine molecular weight determinations by vapor-phase osmometry or membrane osmometry and the leading references for this topic are to 1953/1955 texts; additionally, the reference dealing with the NMR of polymers dates to 1963. It may be, though, that the clarity of the experiments might counterbalance the dated references which can be compensated for by appropriate lectures. Indeed, many of the concepts appropriate to a laboratory course are noted, some topical experiments are given (e.g., microencapsulation), and useful tips abound on such matters as dissolving polymers, purifying monomers, and setting up glassware.

In summary, then, this can be a useful text for an advanced laboratory course which follows an introductory organic chemistry course. The experiments are well-designed and can be a valuable learning experience for the chemistry and engineering major when supplemented with a complementary lecture course. As the importance of polymer chemistry continues to be better appreciated by academia, texts of the sort reviewed here will fill an essential need.

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Chemistry of the Elements. By N. N. Greenwood and A. Earnshaw (University of Leeds, U.K.). Pergamon Press: Oxford and New York. 1984. XXI + 1542 pp. $34.95 paperback. ISBN 0-08-022057-6.

This book gives a systematic and detailed account of the chemistry of the elements. It encompasses predominantly the areas of inorganic and organometallic chemistry. Since the borders among the branches of chemistry are not sharp, other areas such as bioinorganic and industrial chemistry are included to give a more balanced view. The stated aim of the authors was to emphasize experimental, factual material rather than theoretical concepts, the latter being more prone to change.

There are 31 chapters. The first two, (1) Origin of the Elements and (2) the Periodic Table, are general in scope. The remaining chapters present the chemistry of individual elements or of a family of elements until there is complete coverage of the periodic table. (It is not clear why the authors included six questions at the end of chapter two on the Periodic Table, and in no other chapter.)

In this arrangement of topics by elements, a concept is presented more than once as the occasion arises. For example, NH_3 and N_2O_4 as solvent systems are discussed in two different sections of the chapter on nitrogen, the solvent systems $AsCl_3$ and $SbCl_3$ are in the chapter on As, Sb, Bi, and the solvent system BrF_3 in the chapter on halogens, etc.

Two other features are worth noting. The authors include information on industrial uses and production of many important elements and compounds. This gives the reader a greater appreciation of the role of chemistry in the industrial world. Also, there are "Time Charts" which list in chronological order important dates in the development of selected chemical areas.

The book contains a vast store of information on chemical reactions, structures, and industrial uses. It is an excellent book, suitable for use at the advanced undergraduate–beginning graduate level as a reference text. The authors are to be commended for a job well done.

Milton Tamres, *The University of Michigan*

Calcium in Biology. Edited by Thomas G. Spiro (Princeton University). John Wiley and Sons, Inc.: New York. 1983. ix + 278 pp. $75.00. ISBN 0471-88543-6.

This brief book is Volume 6 of the series "Metal Ions in Biology". The overall emphasis is to convey the ideas that Ca^{2+} is a second messenger in biological systems and as such exerts its regulatory effect by either interacting directly with a target system or with a Ca^{2+}-binding protein which then modulates the targeted process. These ideas are illustrated in six chapters.

The book begins with a discussion by K. B. Seamon and R. H. Kretsinger on the structure and properties of several Ca^{2+}-binding proteins, with special attention paid to parvalbumin, troponin C, and calmodulin. A section is devoted to the homology of the proteins in terms of homology domains (EF-hand) originally proposed by Kretsinger. This is followed by a discussion of the static and dynamic features of the Ca^{2+}-binding sites as revealed by a variety of physical techniques, e.g., NMR, lanthanide luminescence, and x-ray absorption. Chapter 2 by M. J. Corimer deals with the regulatory functions of calmodulin: Ca^{2+} and drug binding, mode of calmodulin-dependent activation of enzymes, and other calmodulin-dependent regulatory processes in both animal and plant cells. The specific processes reviewed include cyclic nucleotide metabolism, glycogen metabolism, myosin light chain kinase and other protein kinases, Ca^{2+}-transport ATPases, and NAD kinase in light-induced chloroplasts. C. C. Ashley reviews in Chapter 3 the studies leading to the current ideas of Ca^{2+} regulation in muscle cells. Although the experiments described are mostly from invertebrate muscle fibers, the conclusions are certainly applicable to vertebrate muscle. Included in these experiments are studies performed with ^{45}Ca and various optical probes (absorption indicators, fluorescent indicators, and photoproteins) to monitor extracellular and intracellular free Ca^{2+} levels.

Ca^{2+} is involved in stimulus-secretion coupling. These processes include release of neurotransmitters, hormones, enzymes, etc. A brief chapter by R. P. Rubin on exocytosis provides a summary on the requirement of increased cellular ionic Ca^{2+} for secretory processes. The author gives examples on reconstituted model systems of secretory granules and several cytoplasmic components of the cell that are involved in the secretory process such as the cytoskeletal system, non-muscle actin and myosin, calmodulin, and phospholipase-mediated phospholipid turnover. These topics are tied together to provide an overall view of the role of intracellular Ca^{2+} in secretion. The chapter on calcium in mineralized tissues by E. D. Evans and J. D. Termine begins with a discussion on the physical and chemical aspects of mineral salts, followed by discussions on the mechanisms of normal mineralization in skeletal tissues and the role of mineralization in calcium homeostasis. The final chapter addresses the structural chemistry of Ca^{2+} and the use of lanthanide ions as luminescence probes for Ca^{2+}. R. B. Martin in this chapter gives a very good account of the application of these probes to a variety of proteins. As in another chapter, the specific proteins discussed are parvalbumin, troponin C, and calmodulin.

This book contains several very important and timely topics, and each chapter generally provides an adequate bibliography. The brevity of each chapter prevents an in-depth exposition of certain topics. In spite of this shortcoming, the book will be a useful reference to those already engaged in the fields covered by the authors.

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Advances in Chemical Physics. Volumes 56 and 57. Edited by I. Prigogine and S. A. Rice. John Wiley & Sons: New York. 1984. Volume 56: ix + 586 pp. $90.00 ISBN 0-471-87829-4. Volume 57: ix + 467 pp. $85.00. ISBN 0-471-87830-8.

Volume 56 contains five reviews focussing on the statistical mechanics of electrostatic phenomena: quadratic transport and soluble Boltzmann equations (Hoare); the statistical mechanics of the electrical double layer (Carnie and Torrie); Keer-effect relaxation in high electric fields (Watanabe and Morita); the internal field problem in depolarized light scattering (Keyes and Ladanyi); a consistent molecular treatment of dielectric phenomena (Madden and Kivelson). Volume 57 contains four reviews in the area of molecular dynamics: overtone frequencies and intensities in the local mode picture (Child and Halonen); multimode molecular dynamics beyond the Born–Oppenheimer approximation (Köppel, Domcke, and Cederbaum); Jahn–Teller trajectories (Judd); structure, dynamics and dissipation in hard-core molecular liquids (Lippert et al.).

Pyridine and Its Derivatives. Part Five. Edited by George R. Newkome (Louisiana State University). John Wiley and Sons: New York. 1984. xii + 714 pp. $175.00. ISBN 0-471-05072-5.

This volume is the fourteenth in the series "The Chemistry of Heterocyclic Compounds", edited by A. Weissberger and E. C. Taylor. The volume editor has chosen to abandon the format of earlier works and has provided a topical update in key areas of pyridine chemistry. Thus, the monograph covers three broadly encompassing chapters on pyridine compounds as well as a final chapter compiled by G. R. Newkome which cites reviews of pyridine chemistry published from 1968 to 1982. These papers are grouped under seventeen categories and include, along with their titles, authors, journal, language, and number of references, useful comments regarding their content.

The first chapter, entitled Synthetic and Natural Sources of the Pyridine Ring, is a particularly comprehensive work (1786 references) by T. D. Bailey, G. L. Goe, and E. F. V. Scriven (Reilly Tar and Chemical Corp.). I found the description of the large variety of pyridines present in nature to be especially illuminating. The large, clearly depicted structures prevalent throughout the text make scanning this and the other chapters for structure-types quite facile, a feature of the more recent monographs of this series. The generous use of tables throughout the text of this chapter to summarize sources, series, yields, etc., is also appreciated and contrasts the usual format of the extensive use of tables at the end of chapters. The preponderant portion of this chapter deals with the synthesis of pyridines in two main categories: those utilizing other ring systems (more than two dozen methods), and those utilizing acyclic compounds. I found the careful fragmentation of these major approaches into dozens of different subgroups helpful in locating a desired synthetic method. The size of this chapter (194 pages) is perhaps the main crit-

icism, since it could have been readily treated as two, more manageable chapters.

In Chapter II, Carbocyclic Annelated Pyridines, R. P. Thummel (University of Houston) has assembled the first extensive review of this topic, covering the literature through 1981. Specifically included are ortho mono- or bis-annelated neutral pyridines in which the fused ring is composed only of carbon atoms. Quinolines, isoquinolines, compounds annelated on nitrogen, annelated pyridones, or dihydro-, tetrahydro-, and hexahydro-annelated pyridines are not encompassed in the chapter. It is organized into the following sections: synthesis of (8 reaction types), reactions of (4 subgroups), naturally occurring, and biologically active annelated pyridines (both two page discussions). There is also a comprehensive listing of the physical properties of these compounds in 23 tables (ca. 100 pages) at the end of the chapter. The organization of the synthetic approaches is well planned and adequately delineated into descriptive subgroups. Discussion of mechanisms of less obvious transformations is included where appropriate. The limited biological activity which has been reported to be associated with a variety of these structures is a valuable overview.

The third chapter, Macrocyclic Pyridines, by G. R. Newkome, V. K. Gupta (Louisiana State University) and J. D. Sauer (Ethyl Corp.), describes the syntheses of 2,6-, 2,5-, 2,4-, 2,3-, 3,5-, 3,4-, and 2,3;5,6-pyridine macrocycles with and without heteratoms and aromatic rings in the bridging appendages. The propensity of these macrocycles to complex with various cations is presented both in the text and the tables (18) at the chapter's end. X-ray analysis results of these systems, when available, are also discussed and provide interesting aspects of crystal conformations. This chapter is also a timely, well-organized, comprehensive account of a more contemporary aspect of pyridine chemistry.

Overall, this volume, which also includes an author and subject index, is a carefully conceived, well-executed, and refreshing work. It should be useful to both the student of and the active investigator working in pyridine chemistry.

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Vibrational Spectra and Structure: A Series of Advances. Volume 13. Edited by J. R. Durig (University of South Carolina). Elsevier Science Publishers: Amsterdam and New York. 1984. xvii + 460 pp. $119.25.

This new volume of a respected series contains six chapters, each prepared by a different author, or authors, and is distinguished by the significant contributions that the various authors have made to the research topics under their review. Five of the chapters are devoted to important areas of vibrational spectroscopy, ranging from solid-state spectra through Raman spectra of matrix-isolated species to the vibrational spectra of electronically excited molecules and also including a survey of recent advances in the modeling of vibrational optical activity.

The other chapter focuses on the methods that have been developed to either manage or make use of vibrational effects in the determination of molecular geometries, particularly using the gas-phase methods of microwave spectroscopy and electron diffraction.

The international composition of the set of authors is as varied as the topics under discussion. This adds authenticity and authority to the presentation of the topics; e.g., it seems appropriate that the review of applications of Davydov splitting to studies of crystal properties be provided by the Russian authors Zhizhin and Goncharov. However, an unevenness of treatment and a good deal of fractured English also results. For example, a chapter by Jodl (Germany) on Raman matrix-isolation spectroscopy describes a wealth of very interesting science and includes an informative section on experimental techniques, but it suffers from questionable organization and the quality of the descriptive presentation.

On the other hand, the chapters on molecular parameters in crystals (Frech), vibrational optical activity (Polavarapu), and vibrational effects in the determination of molecular geometries (Nemes) are nicely organized and presented with crispness and clarity. Each of these chapters can be recommended as an excellent source for the establishment of an insight into the particular research area. The chapter by Frech (U.S.) provides a complementary perspective to solid-state spectroscopy to that offered by Zhizhin and Goncharov in their review of Davydov splitting. In particular, a much broader theoretical base is presented that points to Davydov (correlation field) splitting as one implication. Taken together, these solid-state authors give comparable recognition to researchers in the different hemispheres, but both reviews are marked by a sparseness of post-1980 results (e.g., Zhizhin and Goncharov cite only two post-1975 non-Russian publications).

The chapter by Mitchell and Guillory describing advances in the measurement of vibrational spectra of electronically excited molecules is timely, but nevertheless it conveys the impression that such data have yet to contribute definitive answers to important questions of physics or chemistry. Because of the time-resolution limitations of the techniques, most of the high-quality Raman data, and all of the infrared, have been limited to the triplet excited states of relatively large molecules. As the authors stress, with the techniques now developed and demonstrated, and with psec time resolution accessible to Raman spectroscopists, a systematic study of smaller molecules should be forthcoming. This chapter presents reasonable background for anticipation of these developments.

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An Introduction to Specialty Polymers. Edited by Norio Ise and Iwao Tabushi (Kyoto University, Japan). Cambridge University Press: New York. 1983. ix + 226 pp. $42.50.

This book consists of a brief introductory chapter followed by six chapters dealing with as many selected topics in Specialty Polymer science. The first of these, Synthesis of Reactive Polymers, gives a general review of the standard organic functional group transformations that can be applied to polymers to produce materials which are either reactive intermediates in the synthesis of other polymers or end products themselves. A few applications of these systems are described.

Chapter 3 deals with Macromolecules and Catalysts. It first treats systems which employ only one or two types of interaction at the same time. The first of these are the polyelectrolytes, and activation parameters for several reaction types with various polyelectrolytes are discussed. Catalysis by macroions and micelles is treated in terms of hydration/dehydration effects on the reactants and activated complexes. Other polymeric catalysts such as polypeptides for asymmetric synthesis, polymer-bound nucleic acid bases for template polymerization, polymer–metal complexes, and heterogeneous catalysts are superficially treated. The second portion of this chapter deals with synthetic polymer catalysts with enzyme-like activities. It begins with the criteria for such a catalyst and then offers three general methods for producing systems which meet these criteria to various extents. These include (a) chemical modification of commonly used polymers, (b) polymerization of monomers with appropriate functional groups, and (c) use of the polymer as a support for immobilized enzymes. It concludes with a few examples of polymer catalysts that do display some "enzymatic" activity.

The chapter entitled Polymers Having Energy-converting Capability briefly describes the photosynthetic and muscular systems and how synthetic polymers may or may not be useful in approximating them. A few examples of thermal-to-mechanical, photo-to-mechanical, and photo-to-chemical energy transformations are given. It concludes by stating that "there is no practical energy-converting system at the moment in which synthetic polymers play a major role". Their current contribution stems from their mechanical properties.

Chapter 5, Transport Phenomena and Functional Polymers, gives a brief overview of the transport of gases and liquids through neutral synthetic polymer membranes and ions through charged ones. It presents phenomenological equations for transport and provides examples of the various transport mechanisms (simple, facilitated, and active). It concludes with a descriptive section on high molecular weight substances which have transport functions such as ionophores (peptides, macrotetrolides, same antibiotics), biological membrane-active substances, and haemoglobin.

The next chapter introduces a Synthetic Bilayer Membranes, dealing with both single- and double-chain amphiphiles. Through electron micrographs, it illustrates the morphological effects that accompany changes in five key structural elements. It goes on to discuss membrane–polymer composites and outlines some of the physico-chemical characteristics of the bilayer assemblage of these synthetic membranes (phase transitions, spectral changes). The chapter concludes with a section on reaction control with synthetic membranes, including specific activation, catalysis, and substrate entrapment.

The final chapter deals with information transmission in native biological systems. The synthesis and properties of DNA and RNA constitute much of the chapter, but there is a final short section on completely artificial information- (albeit low-grade) transmitting polymers.

As indicated in the preface, this book was originally published in Japanese in 1980 and intended for undergraduate and graduate students. This updated English edition was published in 1983, and several references to the literature through 1982 are included. It will be useful as a brief overview of some selected topics in the field of specialty polymers.

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