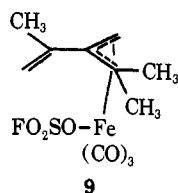


cross-conjugated pentadienyliron tricarbonyl cations is strong. Increasing the amount of FSO_3H beyond the two equivalents necessary to produce the organometallic cation and hydronium ion caused no change in the -65° nmr spectrum. This rules out multiple protonation.¹⁵ Isomerization cannot be caused by rapid C_2-C_3 rotation in a small amount of the neutral allyl complex 9 because exactly the same chemistry and



intermediates (A, B, and C) were observed in 1:1 SbF_5-FSO_3H in $SO_2(l)$. The very low nucleophilicity of this solvent-acid system¹⁶ makes the formation of 9 highly unlikely.

The nmr spectrum of the acidic solution at -65° reveals the presence of two species A and B. They

(15) D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **91**, 6968 (1969).

(16) Cf. G. A. Olah and A. Commeyras, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

appear to be in equilibrium since the A:B ratio is independent of the precursor (3 or 5) and they disappear at equal rates (see below). Their nmr spectra permit assignment of structures 7 and 8 to A and B only if some chemical shift assignments untypical of simple allyliron tricarbonyl cations are made. Warming the sample to -49° in an attempt to speed their interconversion caused conversion to a new species, C, which produced olefin 6 on quenching.

Since the allyl structure, 1c, is the only one which is consistent with rotation about the C_2-C_3 bond,^{17,18} our observations require that the energy of the allyl structure (1c) and that of the equilibrium structure be similar if in fact they are not the same. Thus, our model provides an insight into the chemistry of these cations which would be completely overlooked by straightforward application of the EAN rule. Broader applications will be presented in a full paper.

Acknowledgments. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

(17) The contribution destabilizing steric interactions involving methyl substituents in the planar conformers (7 and 8) make to lowering the energy barrier to rotation cannot in itself explain the isomerization. Anti (cis) methylated conjugated pentadienyliron tricarbonyl cations, which should be significantly more crowded than 7 or 8, are configurationally stable under these conditions; Cf. T. S. Sorensen and C. R. Jablonski, *J. Organometal. Chem.* **25**, C62 (1970); C. P. Lillya and R. A. Sahatjian, *ibid.*, **25**, C67 (1970).

(18) A referee has suggested a monohapto intermediate with a σ bond between iron and C_1 or C_3 . However, simple π -allyliron carbonyl cations show no tendency to form σ -allyl isomers. Thus, syn and anti substituted cations are configurationally stable, while Faller has shown that formation of σ -allyl isomers leads to syn-anti isomerization in complexes of palladium and other metals. Cf. J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, **93**, 2642 (1971).

(19) Alfred P. Sloan Foundation Fellow, 1969-1971.

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Book Reviews

Organic Reagents in Metal Analysis. By K. BURGER (L. Eötvös University, Budapest, Hungary). Pergamon Press, Oxford. 1973. 268 pp. \$17.50.

This book is an enlarged translated version of Burger's Hungarian text which was originally published in 1969. Its appearance in English is timely. Organized in three parts, the book (i) treats the coordination chemistry of analytical reactions, (ii) reviews the application of selective reagents (organic chelates such as the oximes flavones, dithizone, β -diketones, and dithiocarbamates), and (iii) provides tabulary summaries of over 100 specific reagents, their metal specificities, general properties, and selected stability constants. A table of organic solvents has 73 entries and should be of value to both synthetic and physical chemists. The coverage of fundamentals embodies current principles of coordination chemistry. The accent is on metal-ion selectivity and sensitivity. The discussion is restricted to reagents for classical analytical methods including gravimetric, volumetric, and spectrophotometric analyses, polarography, chromatography, and ion exchange. In view of increasing interest in trace metal detection for environmental pollution control and in the identification of trace metals in biology, this book should command a respectable market.

Stephen J. Lippard, *Columbia University*

Enzyme Engineering. Edited by L. B. WINGARD. Wiley-Interscience, New York, N. Y. 1972. iv + 412 pp. \$12.50.

This book is the result of papers presented at the Engineering Foundation Conference on "Enzyme Engineering," August 9-13, 1971, Henniker, N. H., and the 64th Annual Meeting of the American Institute of Chemical Engineers, December 1, 1971, San Francisco, Calif. There were thirty-three contributors to this book, comprised of chemical engineers, biochemists, organic chemists, and microbiologists, and one might expect that the book would be disorganized and uneven, but suprisingly enough, it is very well organized and the presentations are written evenly. This is undoubtedly due to the efforts of the editor, L. B. Wingard, who must have exerted an enormous influence.

The book is concerned primarily with the development of techniques for immobilization of enzymes with retention of catalytic activity to minimize the economic problem of recovery and reuse of costly enzymes, with the result that a variety of opportunities exist for industrial, medical, and analytical applications using enzyme catalysts. In such applications, enzymes would be attached to columns and thus not be used up—a so-called "enzyme reactor."

Platforming is a well-established procedure for refining gasoline.

It uses platinum, a very precious commodity (\$5.72/g at present), but since it can be used many times there is no hesitation to use it. Now that enzymes, the cost of which is of the same order of magnitude, can be used many times, there is no reason why they cannot be used as catalysts in the same way.

There are six sections in this book, encompassing (1) Introduction; (2) Microbial Sources of Enzymes; (3) Isolation and Purification of Enzymes; (4) Immobilization of Enzymes; (5) Kinetics and Performance of Enzyme Reactors; and (6) Applications and Future Directions of Enzyme Engineering. Each of these sections has many contributions in it. From the various sections one can get an idea of the diversity and scope of the topics covered. The book is pointed to the industrial applications of enzymes as catalysts when immobilized. This concept is a real possibility in the not too distant future and this book presages events which are just around the corner in a matter of a few years.

Myron L. Bender, *Northwestern University*

Quantitative Analysis by NMR Spectroscopy. By F. KASLER (University of Maryland). Academic Press, London and New York, 1973. vii + 190 pp. £4.50 or \$10.80.

This volume is comparatively modest in both size and purpose. It aims to give a reader with practical analytical interests and requirements an introduction to the fundamentals of the theory and practice of nmr, and to provide him with the rationale and documentation necessary to use nmr in everyday analytical applications. Although there are now many nmr textbooks with varying emphases, this appears to be the first to deal with this aspect exclusively, although this is of course one that has been long and widely understood and utilized. The peculiar strength of nmr is that peak areas are directly proportional to the number of nuclei they represent, regardless of chemical binding; no extinction coefficients need to be established.

The first section of the book (three chapters, 46 pages) is a general introduction to nmr at a level which is elementary but adequate for the purpose. In fact, it could be even more elementary; it is probably not really necessary to expose the reader to the Bloch equations, for example. Such matters as time-dependent phenomena and shift reagents are included, as well as a slightly dated discussion of instrumentation. In this latter chapter, 10 pages are devoted to a detailed program for the operation of a particular variety of CAT; this could well be omitted. One also notes on page 64 the dubious statement that the nuclear Overhauser effect is "uninteresting for proton nmr"; this will be surprising to the authors of a recent and well-known treatise on just this subject.

The second part of the book (40 pp) deals with the proper means of obtaining quantitative spectral measurements and increasing observing sensitivity—useful to the beginner if familiar to the practiced nmr spectroscopist. Chapter 6 (Methods of Quantitation) is in a sense the heart of the book. The third part of the book (70 pp) describes specific procedures for specific problems (molecular weight determination, elemental analysis, isotopic composition, isomerism, active hydrogen content, water determination, etc.) and for the determination of functional groups. Examples are provided from industry, mainly pharmaceutical. Hydrocarbon analysis is not discussed, although literature references are given. A final brief section (15 pp) deals with polymers, wide-line methods, and nuclei other than hydrogen.

A weakness of the book is that it is, with the exception of the last four pages, exclusively devoted to hydrogen. This tends to limit its future utility, as carbon-13 will (as the author recognizes) at least rival and probably soon overtake proton nmr in significance and use. The author points out that there are difficulties in quantitative ^{13}C spectroscopy, which is true, but at this date readers will expect more discussion and more guidance on overcoming these difficulties than they will find here. Within its limits, nevertheless, the book does an acceptable job and will prove useful to many workers.

F. A. Bovey, *Bell Laboratories*

Structures, Mechanisms and Spectroscopy. By J. C. MAIRE and B. WAEGELL, Gordon and Breach, New York, N. Y. 1971. xii + 300 pp. Hardcover, \$17.50; paperback, \$9.50.

This problem book represents Volume 2 in the series "Documents on Chemistry." It is intended for undergraduate and graduate students in organic chemistry. However, the level of the problems is such that it will be most useful for graduate courses and independent study. Practicing organic chemists should enjoy the mental exercise of the problems as they provide an access to a wide variety of interesting chemistry. There are 120 problems taken

from the recent literature (1966) with solutions to 60 of the problems. Several fields of organic chemistry are represented by the problems. These include small ring compounds, photochemistry, natural products, heterocyclic compounds, boron and phosphorus compounds, organometallics, and conformational analysis. Literature references for each problem are provided. The problems are chosen to emphasize the application of physical methods to structure determination along with the chemical reasoning which accompanies this process. Although data from several spectroscopic techniques (ir, uv, nmr, and mass spectra) are included, the major emphasis is clearly on nmr. Questions concerning possible mechanisms of conversion of one compound into another are raised throughout the problems.

The problems are divided into five chapters and are in order of increasing difficulty. Chapter One contains 34 problems dealing with structures whose solution depends upon the use of chemical shifts and coupling constants. The 26 problems in Chapter Two deal primarily with applications of the Karplus equations concerning the relationship between coupling constants and stereochemistry. Chapter Three contains ten problems dealing with various applications of time-dependent phenomena. Eighteen problems concerned with the application of nmr data on nuclei other than ^1H are presented in Chapter Four. The 32 problems in the final chapter are concerned with the determination of complex structures using all possible sources of information from nmr. Perhaps the strongest point of this book is the discussion given in the solutions to the problems. The authors provide a step-by-step discussion of each piece of data and give the thought process involved in reaching a final decision for a structure. This book is relatively error free and is recommended to those chemists wishing to improve their knowledge of the applications of nmr to structural determinations.

Richard H. Cox, *University of Georgia*

Carbides: Properties, Production, and Applications. By T. YA. KOSOLAPOVA (Institute of Ferrous Metallurgy, Academy of Sciences of the Ukrainian SSR). Plenum Press, New York, N. Y. 1971. xiv + 298 pp. \$30.00.

"Carbides" by T. Ya Kosolapova, which was published originally in the Soviet Union in 1968 and recommended for translation into English in 1969, is a reference text on metal-carbon compounds. It contains general discussions of structures, physicochemical properties, and production methods in the early sections and discussions of chemical properties and applications at the end. In between, there are chapters on individual carbide systems arranged in order of the group in which the metal is found in the periodic table. Group I and II metals receive less attention than do the more important elements of the transition metals. The chapter on transition-metal carbides accounts for nearly one-third of the text, with the commercially important carbides such as WC, TiC, NbC, etc., dominating the chapter. This arrangement of the chapters is not satisfactory for the individual who has to hunt through four chapters to glean all of the data that Kosolapova has included in the book. The chapters on producing carbides and on their chemical properties are too general; the information they contain could have been incorporated into the chapters on the specific carbides.

Perhaps the best discussion in the book is found in those pages that present details on methods for synthesizing the metal-carbon compounds. The presentation, while not very specific in some instances, might be helpful as a starting point for the research chemist or metallurgist who wishes to study carbides. There are many complicating factors, such as the effect of oxygen, which will influence the purity of the product, that are not discussed. Control of oxygen is an important consideration because all of the methods of synthesis involve high-temperature reactions. For those initiating programs on carbides, this book should serve as only one item in an extensive review of the technical literature.

The book also contains numerous tables of data on properties of metal carbides. A few phase diagrams of some metal-carbon systems are included. Although the book by Kosolapova is more recent than a reference work by Samsonov (G. V. Samsonov, "Handbook of High Temperature Materials," No. 2, Properties Index, Plenum Press, New York, N. Y., 1964), most of the data that are used appear in the Samsonov book. In fact, the data in Samsonov's are more complete than that found in Kosolapova's tables. For example, Samsonov includes the temperature dependence of the heats and free energies of formation of the carbides, whereas Kosolapova lists only the values at 298K. Similarly, Samsonov lists test temperature and loads used for determining hardness values of the carbides; Kosolapova lists only the hardness

values themselves. For the researcher or engineer interested in these properties, the omissions are significant. (The criticism of the data should not be construed to mean that Samsonov is the only reliable source of property data; it appears that Kosolapova did rely on Samsonov's book, however.)

Western readers of "Carbides" will have access to much more up-to-date and reliable phase diagrams than those presented by Kosolapova. In fact, many of the phase diagrams in this book are either poorly drawn or have serious errors in them. Numerous diagrams show four phases in equilibrium under isothermal conditions, which is a highly improbable occurrence; other diagrams indicate that, at a particular temperature, one phase can be in equilibrium with multiple compositions of a second phase. While such errors may be of interest only to a few physical chemists and metallurgists, they do indicate a degree of inaccuracy that could be carried over into the tables of properties which are not so easily checked and corroborated.

In conclusion, "Carbides" can be recommended only for those who have no other source of data on this important class of compounds, or for those who may require a single text on this subject. There are several other books on the subject of carbides, hard materials, and interstitial alloys that ought to be considered first before purchasing the book by Kosolapova.

James M. Dahl, *Climax Molybdenum Company of Michigan*

Electroanalytical Chemistry: A Series of Advances. Volume 6. Edited by A. J. BARD (University of Texas). Marcel Dekker, Inc., New York, N. Y. 1973. x + 373 pp. \$23.50.

This book contains three separate reviews: the electrochemistry of selected biological compounds, electrode processes in solid-electrolyte systems, and the application of mathematics to the principles of current distribution and mass transport in electrochemical cells.

The first review concentrates on the electrochemistry of biological compounds involved in the transfer of food energy into energy available for human activity. Clear, brief examples of metabolic processes are provided to illustrate the roles of various enzymes prior to discussion of their electroanalytical studies. A minor problem for the nonbiochemist is the tardy definition of some key abbreviations. The electroanalytical works cited deal mainly with the coenzyme nicotinamide-adenine dinucleotide (NDA) and related pyridine compounds. Also included are some studies of purine and pyrimidine derivatives, flavines, quinones, and iron porphyrins. The techniques applied were mainly of the polarographic and coulometric type. The review appears effective up to 1972 and provides a good instructional and reference base for bioelectrochemical investigators.

The second review on electrode processes in solid-electrolyte systems begins with a helpful introduction to the nature of conductivity in ionic solids. Examples are given for high ionic conductivity due to crystal lattice defects, unusual crystal structures, $RbAg_{1.5}$, and doped electrolyte compositions. A major portion of the review is devoted to studies of the metal-solid electrolyte interface. There is a section of electrode interface preparation and classification of three basic electrode types. Studies of each electrode type are reviewed with many interpretive comments by the author. Multiphase electrodes are discussed in the last section.

Much of the work cited was undertaken to examine ionic solids for electrode double layer effects, electrode polarization, and electrode kinetics. Most studies centered on systems with silver or platinum electrodes and silver salt electrolytes. Very little reference is made to lithium electrodes and electrolytes, which have been studied for battery applications. However, the examples presented well illustrate the problems and uses of solid-state electrochemical cells.

The third review extensively covers the mathematical methods applied to the principles of current distribution and mass transport in electrochemical cells. It seems to be very complete, utilizing one-half of the book, providing over 150 references, and requiring ambitious readers to have a solid education in advanced mathematics.

Keith Fester, *Medtronic, Inc.*

Advances in Biochemical Engineering. Volume 1. By T. K. GHOSH (Indian Institute of Technology, New Delhi, India) and A. FIECHTER

(Swiss Federal Institute of Technology, Zurich, Switzerland). Springer-Verlag, New York, N. Y. 1971. 194 pp. \$13.90.

Biochemical engineering is defined in the opening sentence of the Foreword as being "concerned with the effective practical application of the knowledge amassed by the biological sciences." Really, the book deals primarily with the more restricted field of fermentation processes. The book comprises a collection of edited articles by research workers. The first two articles, written by Japanese authors, are stimulating. The Japanese are in the forefront of fermentation research and engineering. Unfortunately, their literature is denied to many of us in the United States because of language differences. These Japanese authors supply fresh insights derived from use of the Japanese literature, their own efforts, and a critical evaluation of work outside Japan. For example (p 31), the concept of cellular material as another state of matter in addition to solid, liquid, and gas is interesting. An editorial balance is achieved between science and technology. This is apparent in two instances. For example, the article on enzyme synthesis by cells (Demain) complements industrial production of enzymes (Faith, *et al.*); in a similar vein, a discussion of possible future fermentation products (Schlegel) is set against a background of articles dealing with improvement of current industrial, antibiotic fermentations (Taguchi).

This book should be required reading for students entering the fermentation industries; it will be useful as well to scientists and engineers currently working in this field.

L. L. Kempe, *University of Michigan*

Advances in Linear Free Energy Relationships. By N. B. CHAPMAN and J. SHORTER (The University of London). Plenum Press, London and New York. 1972. xiv + 487 pp. \$28.00.

This book consists of a compendium of ten chapters covering a number of different aspects of linear free energy relationships. The first chapter, by O. Exner, reviews the Hammett equation. In the second chapter, Dr. Shorter discusses the separation of polar, steric, and resonance effects by the use of linear free energy relationships. The third chapter, by Katritsky and Topsom, covers the relationship between free energy relations and optical spectroscopy, and the fourth, by Tribble and Traynham, deals with nmr spectra of proton, fluorine and ^{13}C . In the next two chapters, Kopple and Palm, on the one hand, and Pearson, on the other, discuss the influence of the solvent and of the reagent on organic reactivity, respectively. Chapter 7, by Chipperfield, covers the use of linear free energy relationships in inorganic chemistry; Chapter 8, by Kirsch, that in enzymology. Chapter 9 deals with the interpretation of drug action through LFE's (Camarata and Rogers). In the last chapter Bursey deals with the interpretation of mass spectrometry data through LFE's. As pointed out by the editors in the beginning, the book suffers from the weaknesses of all such compendia in that the chapters are not homogeneous. The worst problem of such publications, that of serious overlap in different chapters, appears to have been quite successfully avoided. Some of the chapters are truly exhaustive treatments of the subject, sometimes with very extensive literature references; *e.g.*, Exner's chapter contains over 800 references. Others, like the chapter by Katritsky and Topsom, for instance, are more summarizing and evaluating than encyclopedic. The last three chapters are much more sketchy, as would be expected by the nature of the subjects they treat in which the use of linear free energy relations is relatively new and undeveloped. Each author has found a different pattern for his treatment. Although most seem to be organized along more or less conventional lines, treating different subjects in separate sections, Shorter has chosen to review separately the contributions of the principal investigators involved in the development of his area.

Most of the chapters appear to be very well up to date. The only criticism I have of the book is that one might have hoped for a more critical evaluation of the status of the art and of the true progress made in recent years. However, the book has such a wealth of information that I do not believe that anyone working in the realm of the extrathermodynamic relations or even with a serious interest therein can afford not to do a great deal of reading in this volume. In view of the extremely wide coverage of the literature, it will also serve as a reference volume for many years to come.

H. H. Jaffé, *University of Cincinnati*