

Table I. Solvolysis Rates for Allylic Systems in 80% Aqueous Acetone

Compd	10^7k at 100°, sec ⁻¹	k_{rel} at 100°
<i>exo</i> -VII	3.5×10^8 ^a	1.2×10^8
<i>endo</i> -VII	6.6	2.3
<i>exo</i> -VIII ^c	176	63
<i>endo</i> -VIII ^c	47	17
<i>exo</i> -IX ^c	2.8	1 ^b
<i>endo</i> -IX ^c	2.7	1 ^b
X ^d	37	13

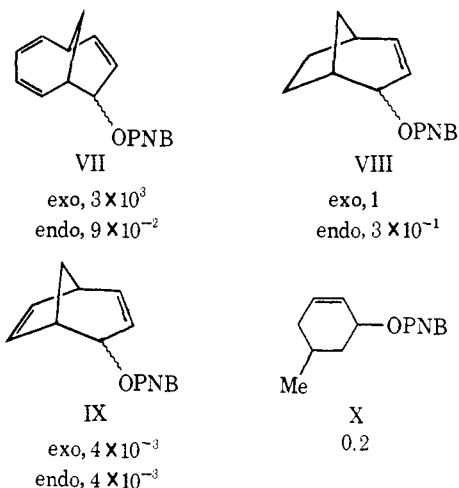
^a Extrapolated. ^b These values are not corrected for acyl-oxygen cleavage. ^c Reference 14. ^d E. C. Friedrich, Ph.D. Thesis, University of California, Los Angeles, Calif., 1961.

Taking the *exo*-2-bicyclo[3.2.1]oct-3-enyl *p*-nitrobenzoate (*exo*-VIII)¹⁴ as a standard for rates of solvolysis of allylic *p*-nitrobenzoates in fused six-membered ring systems, we find that the butadiene moiety in VII, while inductively destabilizing, actually enhances the rate by at least 10^3 . Further insight is gained by comparing the effects of one and two double bonds on the stability of the allylic cation. Whereas in going from *exo*-VIII to *exo*-IX the solvolysis rate is lowered by a factor of 240, the opposite effect is observed by comparison with *exo*-VII. The rate ratio of *exo*- and *endo*-VII bears out our choice of models and the fact that we are indeed dealing with anchimeric assistance to solvolysis since we would not expect backside participation in the *endo* case.

These results are consistent with the intervention of the bishomotropylidium ion II, in which charge is delocalized significantly into the butadiene moiety,¹⁵ in the rate-determining step. We ascribe the greater stability

(14) A. F. Diaz, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 7477 (1970).

(15) An unsymmetrical homoconjugative-type charge delocalization can be ruled out by the opposite effects of two and one double bonds in systems VII and IX, respectively, as compared to VIII, and the magnitude of these (*vide infra*).^{1b} A theoretical explanation for the lower energy of the symmetrical species has been provided by perturbation theory calculations: D. Blagdon, S. Yoneda, and S. Winstein, submitted for publication.



of II over I to the more favorable overlap of p orbitals on C₅ and C₇ (and C₂ and C₆) as evidenced by models of both ions.^{1b}

Acknowledgments. We thank the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for continued support of the late Professor Winstein's research programs. Dr. Pommer of the Badische Anilin und Soda-Fabrik in Ludwigshafen, Germany provided us with a generous supply of cyclooctatetraene. A critical review of the manuscript by Professors F. A. L. Anet and A. F. Diaz was most helpful.

(16) Author to whom correspondence should be addressed at the Instituto Militar de Engenharia, Pós-Graduação-Química Orgânica, ZC 82, Rio de Janeiro, Brazil.

(17) Organization of American States Predoctoral Fellow, 1968-1970.

(18) Deceased Nov 23, 1969.

P. Seidl,^{*16,17} Mark Roberts, S. Winstein¹⁸

Contribution No. 2830
 Department of Chemistry, University of California
 Los Angeles, California 90024

Received May 1, 1971

Book Reviews

Organometallic Reactions, Volumes 1 & 2. Edited by E. I. BECKER (University of Massachusetts) and M. TSUTSUI (Texas A&M University). Wiley-Interscience, New York, N. Y. 1971. Volume I: x + 389 pp. \$17.95. Volume 2: x + 450 pp. \$17.95.

This new series proposes, in the editors' words, "to provide complete chapters on selected categories of organometallic compounds, describing the methods by which they have been synthesized, and the reactions they undergo. The emphasis is on the preparative aspects, although structures of compounds and mechanisms of reactions are briefly discussed and referenced. Tables of all of the compounds prepared in the category under consideration and detailed directions for specific types make these chapters particularly helpful to the preparative chemist." Furthermore, the book jacket promises, "for the first time, a single source to which the preparative chemist may refer for information on reaction mechanisms, references to analogous reactions, and particularly the experimental details of the typical reactions."

The foregoing purposes of the new series echo the goals of the highly successful and classic series, "Organic Reactions," and

invite comparison with similar existing reviews in the field of organometallic chemistry. In this series the word "reaction" is interpreted far more broadly than in individual chapters of "Organic Reactions," where the focus is narrowed to a well-defined reaction of broad applicability. "Organometallic Reactions," on the other hand, includes treatments of specific classes of carbon-metal bonds and often tries to cover broad aspects of their behavior in monographic style. Volume I contains chapters on the redistribution reactions of organoaluminum compounds (T. Mole) and on the chemical fixation of molecular nitrogen (M. E. Vol'pin and V. B. Shur). An eleven-chapter treatment of the reactions of organomercury compounds (L. G. Makarova), comprising two-thirds of the book, is an extensive survey of carbon-mercury bond cleavage reactions. Volume II contains an additional six chapters on this same theme covering 90 pages. The balance of Volume II consists of a general survey of the redistribution reaction (K. Moedritzer) and an account of the reactions of organotellurium compounds (K. J. Irgolic and R. A. Zingaro). Although the real utility of an author index in compilations of this kind can be questioned, it is curious that Volume I has such an index while Volume II does not.

These surveys of certain broad aspects of organometallic reactions by chemists actively engaged in the research areas reviewed are certainly valuable, but unfortunately similar treatments are to be found in a large number of monographic and review series. The Subject Reviews section of "Organometallic Chemistry Reviews," chapters in "Progress in Inorganic Chemistry" and in "Advances in Inorganic Chemistry and Radiochemistry," and various established monographs all try to meet the need for periodic appraisals of selected aspects of organometallic chemistry. In light of the excellent references already available, it is difficult to be completely convinced of the editorial claims for this series, as quoted earlier in this review. What is appealing is that the series promises, for the guidance of the preparative chemist, experimental details of the typical reactions. However, the realization of such guidance could be improved; the amount of experimental discussion and description varies widely and often cannot be considered adequate. Thus in illustrating redistribution reactions of organoaluminum compounds, the author gives one page of general comments on experimental technique and seven abbreviated descriptions of specific reactions, which do not cover the important variations in experimental procedure. A good number of pages could profitably have been employed in instructing the reader explicitly in the techniques of safe and reliable experimentation with such air- and moisture-sensitive compounds. In the chapter on the fixation of nitrogen, Vol'pin and Shur devote only three pages to experimental detail, without including any of the techniques developed by van Tamelen and coworkers. Makarova gives a large number of specific experimental procedures for organomercury reactions, but the reader cannot decide whether the methods chosen are the best to be found in the literature or what advantages in convenience or reliability recommend them.

As is the fate of most hard-bound reviews, the chapters are now being published up to three years after their preparation. Generally, the authors seem to have covered the literature only through 1968, although an addendum to the nitrogen-fixation chapter brings the coverage into 1969.

In summary, "Organometallic Reactions" has proved to be another interesting source of review articles on important facets of carbon-metal bond reactions. Interest in this series will be maintained, if the editors can, in their choice of topics reviewed, avoid overlap with existing books and review series and if they can shorten the publication time of future review chapters.

John J. Eisch, *The Catholic University of America*

Acidity Functions. By C. H. ROCHESTER (University of Nottingham). Academic Press, London and New York. 1970. vi + 291 pp. £4.50.

Proton transfer is the most general of organic reactions, and acid-base catalysis is the most general method for activating organic molecules. Very few classes of compounds are strong enough Brønsted acids or bases to allow study of their equilibria within the range of the pH scale. To do this has required the development of other acidity functions for the quantitative comparison of the majority of organic acids and bases in strong bases and strong acids, respectively.

Professor Rochester's book is the first comprehensive review of the enormous literature about strongly acidic and basic solutions which has grown up during the thirty-eight years since Hammett and Deyrup first proposed a method for developing acidity functions outside the aqueous pH range. Only the two classic reviews of Long and Paul [*Chem. Rev.*, **57**, 1, 935 (1957)] are comparable.

Professor Rochester is an authoritative critic who has mastered this intricate field. Accordingly his book is very well organized and has been written with the reader continually in mind. Thermo-

dynamic and kinetic results are covered with completeness for strongly acidic and basic aqueous systems as well as in mixed solvents. Basic formal principles are used when needed, and serve to clarify rather than to obfuscate arguments. The author's style is simple and clear so as not to intrude on the reader's consciousness. This is an excellent contribution to an important area of physical organic chemistry and will be useful for many years.

Edward M. Arnett, *University of Pittsburgh and Mellon Institute*

Organometallic Compounds of Arsenic, Antimony, and Bismuth. By GEORGE O. DOAK and LEON D. FREEDMAN (North Carolina State University). John Wiley and Sons, Inc., New York, N. Y. 1970. xiv + 509 pp. \$25.00.

There are several areas of organometalloid chemistry that have been hideous nightmares in which to perform a literature research—notably derivatives of group V—the compounds containing phosphorus, arsenic, antimony, and bismuth. The present volume adequately serves as a definitive source book for the three latter elements.

There is little doubt that the meticulous nature of its organization, its painstaking bibliography, and its comprehensive coverage will endear it to those chemists adventuring in the area.

The undertaking of such a survey—involving a terrain best described as a morass—deserves commendation. Such in-depth reviews may not involve many direct purchases because of the small scope of the subject matter, but future workers in the area will find it the equivalent of Kharasch and Reinmuth's treatise on Grignard reagents.

Raymond E. Dessy

Virginia Polytechnic Institute and State University

Metal and Ceramic Matrix Composites. By L. W. DAVIS and S. W. BRADSTREET. Cahners Publishing Co., Inc., Boston, Mass. 1970. xi + 227 pp. \$13.95.

This book collects the notes for a week-long extension course on inorganic composites given yearly at UCLA, which is aimed at serving "... the technical and managerial interests of graduate students and government representatives. . . ." It is a survey of the title subject as viewed by the authors at a point in time, and makes no pretense of being a lasting pedagogical text or even a serious reference work. It is handicapped by an all-too-sketchy Table of Contents, no index, and an unevenness in the treatment of the topics. For example, some 22 pages are devoted to a chapter on a spatial and valence bond development of the theory of metals, but the chapter on metals used as matrices is only 5 pages long. The book is at its best in its discussions of the methods for making metal matrix composites, for nondestructive methods for testing the soundness of composites, and in presenting experimental information on mechanical properties. It is asserted in the preface that "Unfortunately, reinforced polymer composites do not so efficiently exploit the very high elastic moduli and strengths of the newer inorganic whiskers and filaments as inorganic matrices do." Support for this view is not offered in the text, nor is it obvious that this should be or actually is the case. Other biases include a very heavy emphasis on boron-fiber-reinforced composites, while giving minimal discussion of the very promising area of *in situ* grown whiskers by solidification methods (oriented eutectics). Graphite fiber composites are not discussed, nor are the significant advances by Nixdorf and others in casting strong metal filaments by the Taylor process. Nevertheless, this pragmatic book can serve as a useful starting point for learning about this rapidly moving area of materials research and development.

William B. Hillig, *General Electric Company*