

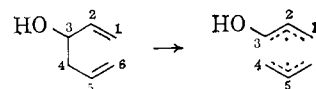
of *n*-caproaldehyde. Oxidation of the suspected hexenal with permanganate in acetone according to the method of Nunn¹¹ afforded glutaric acid, thereby unequivocally establishing the structure of the rearrangement product as 5-hexenal.

As we were mainly interested in the utilization of the rearrangement for the syntheses of Δ^5 -unsaturated carbonyl compounds on a preparative scale, we did not fully investigate the nature of the low-boiling fraction. The relative amount of this fraction increased with increasing temperatures and also appeared to be a function of the column packing. Thus, alumina gave the largest amount of low-boiling components, possibly due to acid-catalyzed cracking reactions. Acrolein was always present in small amounts, as could be readily ascertained by its characteristic odor, its v.p.c. retention time, and its 2,4-dinitrophenylhydrazone.

Berson and Jones² have suggested the occurrence of several competing reactions which the diradical intermediate may undergo, among which are single inversion, double inversion, and hydrogen transfer.¹² In our system both single inversion (by C-1-C-4 bond formation) and double inversion (by C-1-C-6 bond formation) would give rise to the same end product. Single

(11) J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

(12) Hydrogen transfer in our system leads to the formation of the observed acrolein. We did not attempt to isolate or identify any other three-carbon species such as allene or methylacetylene.



inversion by C-6-C-3 bond formation re-forms the starting material.

A cyclic four-membered transition state, as required by either single-inversion pathway, seems unlikely to us on steric grounds. However, in the internal Diels-Alder cyclization of hexatriene to cyclohexadiene, a reaction which appears extremely similar to the one discussed here, the formation of a secondary product has been reported.¹³ Since the nature of the minor product was not established a vinylcyclobutene structure remains a possibility.

In the rearrangement of simple 1,5-hexadiene-3-ols, the utilization of a nonsymmetrical radical intermediate, produced by substitution at C-4 or C-6, should permit a differentiation among these different mechanistic possibilities. We are currently engaged in a study to establish the scope of the reaction, intended as a general method for the preparation of 5,6-unsaturated carbonyl compounds.

(13) G. F. Woods and A. Viola, *J. Am. Chem. Soc.*, 78, 4380 (1956).

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Received January 4, 1965

Book Reviews

Preparative Inorganic Reactions. Volume 1. By WILLIAM L. JOLLY, Department of Chemistry, University of California, Berkeley, Calif. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. ix + 271 pp. 16 × 24 cm. Price, \$9.00.

The progress in the ten areas of preparative inorganic chemical research in concise, well-written form has been collected into the first volume of this new series. General preparative procedures for each topic are discussed in some detail and are followed by specific synthetic details illustrating these methods. The aim "to develop in inorganic chemists the same 'chemical intuition' which has been the foundation of the great synthetic achievements in organic chemistry," falls short. Occasionally references to mechanistic ideas have been made and most of the authors have correlated the reaction conditions for the synthetic procedures they are discussing; yet, the over-emphasis on what to do or what has been done, instead of on how or why something happens, may cause readers to feel that much of the synthetic inorganic chemistry presented herein is more art than science.

The reviews begin with very general topics; namely, coordination polymers by John C. Bailar, Jr., and optically active coordination compounds by Stanley Kirschner. Although both are well written, the reviewer was disturbed to find no mention in the first chapter of the interesting silicon phthalocyanine polymers, which have Si-O-Si-O-type linkages, and to read about racemic compounds and racemic mixtures in Chapter 2 for two pages before they are defined. The latter chapter gets bogged down at times in a concern over dissymmetry as separate from asymmetry so why not call all optically active compounds S_n -less compounds, since the definitive tests for potential optical activity is the lack of any S_n symmetry elements.

Also, the formulas on pages 46 and 48 should be multiplied by 100% rather than by 100.

Reaction principles for metal derivatives of unsaturated β -ketoamines and the corresponding aldamines have been well organized by Dean F. Martin in Chapter 3. (Even though n.m.r. evidence to the contrary has been known for several years, the ketimine nomenclature has been used in this volume.) The tabulations of the note-worthy chapters which follow on metal carbonyls by Jack C. Hileman and on halide and oxyhalide complexes of the titanium, vanadium, and chromium subgroups by G. W. A. Fowles should serve as guides for contributors to future volumes of this series. For completeness Professor Fowles could have included the $W_2Br_9^{3-}$, the $Mo_8X_8^{4+}$, and $W_8X_8^{4+}$ complexes, since all have been known for many years. Fewer illustrations of commercial equipment in the carbonyl chapter might have lowered the price of this book and would not have been missed. Numerous typographical errors also were noted in this otherwise superb chapter.

The volume is rounded out by chapters on anhydrous metal nitrates, halogen and halogenoid derivatives of silanes, saline hydrides, sulfur-nitrogen-fluorine compounds, and hypohalites and compounds containing the -OX group. These chapters have been written by C. C. Addison, N. Logan, Alan G. DacDiarmid, Charles E. Messer, Oskar Glemser, and Stanley M. Williamson, respectively. Tabulation of most of the boring one- and two-sentence paragraphs in Chapter 7 and donation of Chapter 9 to *Inorganic Syntheses* (since the chapter is a preface and six detailed syntheses in the style of that series) would have improved the latter part of the volume considerably. Alternatively, the latter chapter could have included other sulfur-nitrogen-halogen compounds. The editor's use of random-sized areas of inorganic chemistry is probably the most disappointing aspect of this new series.

The systematic principles used in preparing compounds of the various types discussed are not sufficiently well defined for the reviewer to recommend that every scientist should buy a copy of this book. On the other hand, every chemist who wants to improve preparative inorganic chemistry will find this book useful; and some noninorganic chemists may even be surprised at the organization which can be found in these areas.

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Inorganic Reaction Mechanisms. By JOHN O. EDWARDS, Department of Chemistry, Brown University, Providence, R. I. W. A. Benjamin, Inc., 2465 Broadway, New York, N. Y. 1964. xii + 190 pp. 15 × 22.5 cm. Price, \$7.00.

This book is part of the W. A. Benjamin, Inc., series on Physical-Inorganic Chemistry. According to the author's preface, it has been designed to fit the needs of undergraduate seniors and beginning graduate students who seek an introduction to the topic of inorganic reaction mechanisms. After three fine chapters devoted to definitions of terms and descriptions of concepts such as reaction order, molecularity, reaction coordinate, symmetry number, Brønsted theory of acids, general and specific acid catalysis, etc., the author presents separate chapters covering nucleophilic displacements, nonradical mechanisms for peroxide reactions, replacements in octahedral complexes, electron-transfer reactions of complexes, reactions of oxyanions, and free radical reactions.

The author is clearly aware of almost all of the pertinent literature in the fields covered, and has indicated in very brief form the existence of much of the pertinent work on the topics considered. Concepts are covered very briefly. For the worker beginning a research problem in inorganic reaction mechanisms, this book will provide a valuable entry into the literature. On the other hand, this reviewer found the book so terse that logical development suffers; many highly significant points were made as assertions with little attempt at real development. Even a few definitions such as that of symmetry number on page 20 were passed over so lightly that many students will not comprehend the significance of the points raised. On pages 57 and 58 the author has arranged nucleophiles on the basis of their rate of attack on boron compounds, sulfur compounds, carbon compounds, etc. Little reference to the literature or basis for the order is given. Such information seems pertinent.

In short this is a valuable book for all inorganic chemists, but this reviewer hopes that in any revision Dr. Edwards will take time and space to give his readers a little more help in the development of a detailed view of the transition from experimental observation to mechanistic conclusion. This reviewer is only sorry that the book isn't longer.

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Mechanism of Oxidation of Organic Compounds. By W. A. WATERS, Fellow of Balliol College, Oxford Reader in Physical Organic Chemistry, Oxford University. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1964. 152 pp. 14.5 × 22.5 cm. Price, \$5.00.

As usual in this series, this monograph treats its subject in a very concise manner. Correspondingly, many of the references are made to review articles, rather than to original papers. Nevertheless, the subject itself is defined rather broadly to include, e.g., electrophilic substitutions such as halogenation, sulfonation, nitration, etc. On the other hand, only liquid phase oxidations are included. The book is organized according to the type of compounds to be oxidized: peroxides (Chapter 3), alcohols (Chapter 4), 1,2-glycols (Chapter 5), aldehydes (Chapter 7), ketones and carboxylic acids (Chapter 7), unsaturated compounds and aromatic hydrocarbons (Chapter 8), and phenols and aromatic amines (Chapter 9). Besides molecular oxygen, ions of various transition metals are discussed as oxidants in considerable detail. References are often made to biological oxidations, which may correspond to the particular *in vitro* oxidations discussed. The book is a useful short introduction to the mechanisms of oxidation, in general.

There are minor inconsistencies, mistakes, and repetitions in the chapter on peroxides with regard to the chemistry of hydroperoxides (pp. 34 and 45). The organization of the book is not consistent. The order of discussing homolytic and heterolytic oxidations changes from chapter to chapter. This reviewer feels that a separate chapter should have been included on the oxidation of saturated hydrocarbons. It is also felt that the mechanism of oxidations by molecular oxygen, in general—which is of great industrial significance—has not been given enough attention in this otherwise excellent book.

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Amino Acids and Serum Proteins. Advances in Chemistry Series, No.

44. Based on the Richard J. Block Memorial Symposium Sponsored by the Division of Biological Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 11, 1962. JACOB A. STEKOL, Symposium Chairman. Edited by ROBERT F. GOULD. Special Issues Sales, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 1964. xxiii + 154 pp. 16 × 23.5 cm. Price, \$5.50.

The papers in this volume were for the most part presented at a Symposium at the Atlantic City meeting of the American Chemical Society in September 1962, arranged by the Division of Biological Chemistry to honor the memory of Richard J. Block who met death tragically in February of that year.

The slim volume contains ten contributions in addition to a very brief biography and a complete bibliography (151 contributions) of his scientific work. The papers presented at the symposium do have a tenuous relationship to Dr. Block's consuming passion for the amino acids. No doubt owing to the wide scope of his interest in amino acids and proteins, he would have been fascinated by every one of these contributions. Unquestionably, those in attendance at the symposium found many if not all of the papers interesting. However, the published work presents neither a systematic survey nor the summation of the current stage of our knowledge in a special area of interest but rather a collection of papers bearing but an extremely remote, if any, relationship one to another. The general biochemist would consider them diverse indeed despite the recurring protein and amino acid theme. Such being the case, it is essentially impossible to review the volume and avoid "refereeing" the individual contributions.

Apart from the significance of the individual papers, and for the most part they are well worth studying, this volume must be considered primarily as a tribute by his colleagues to a dedicated biochemist who contributed significantly to the field of amino acid and protein biochemistry.

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Molecular Orbitals in Chemistry, Physics, and Biology. A Tribute to R. S. Mulliken. Edited by PER-OLOV LÖWDIN, Department of Quantum Chemistry, Uppsala University, Uppsala, Sweden, and Quantum Theory Project, University of Florida, Gainesville, Fla., and BERNARD PULLMAN, Institut de Biologie Physico-Chimique, Université de Paris, Paris, France. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1964. xiii + 578 pp. 16 × 24 cm. Price, \$22.00.

As the title indicates, this collection of papers forms a tribute to R. S. Mulliken. The individual papers range from delightful personal reminiscences to highly technical discussions of almost every phase of quantum chemistry, molecular structure, theoretical chemistry, or whatever one prefers to call this subject. To say that these papers reflect Mulliken's interests is to say simply that he is interested in everything related to molecules.

The first paper by C. A. Coulson gives an excellent general summary of Mulliken's work and discusses in particular its significance in the development of molecular orbital theories and in methods of interpretation of molecular spectra. The results of Mulliken's work have become so much a part of our way of thinking that we may tend to believe that the ideas were *always* there. It is well to