

first drift region<sup>5</sup> were found to be in the ratio  $m^*_3 : m^*_4 = 1.06$ .<sup>6</sup> This ratio is not significantly different from unity and indicates that the fragmentation reaction responsible for the metastable peaks proceeds from an intermediate in which the carbons have become equivalent. In agreement with Shannon and McLafferty, we consider that the most logical structure for this intermediate is I. To explain the over-all <sup>13</sup>C retention one must postulate that CHO<sup>+</sup> is formed by a second fragmentation reaction which does not exhibit a metastable transition and proceeds with much higher <sup>13</sup>C retention. We propose that this route is the direct fragmentation from structure II leading to 100% <sup>13</sup>C retention. Simple calculations show that the data can be explained if at 70 eV 52% of the C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> ions fragment from structure I and 48% from structure II, while at low energy 64% fragment from structure I and 36% from structure II.

(5) K. R. Jennings, *J. Chem. Phys.*, **43**, 4176 (1965).

(6) The metastable peaks observed for fragmentations in the second drift region also were in an approximate 1:1 ratio; however, this ratio could not be determined accurately owing to overlap of the "flat-topped" metastables for  $m/e\ 45^+ \rightarrow 29^+$  and  $m/e\ 46^+ \rightarrow 29^-$ .

It should be noted that the above conclusions refer only to those ions with sufficient internal energy to fragment by reaction 2. The appearance potentials of C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> ions from 2-alkanols lead to  $\Delta H_f(\text{C}_2\text{H}_5\text{O}^+) = 145$  kcal/mol.<sup>7</sup> If this is assumed to refer to structure I, the proton affinity of ethylene oxide is calculated to be  $\sim 208$  kcal/mol, a value which appears much too high when compared to PA (CH<sub>3</sub>OH)  $\approx 170$  kcal/mol.<sup>8</sup> Assumption of structure II leads to the reasonable value PA (CH<sub>3</sub>CHO)  $\approx 180$  kcal/mol. We therefore suggest that the C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> ions from 2-alkanols have structure II at the threshold and that rearrangement to the symmetrical structure occurs only for ions with internal excitation.

**Acknowledgment.** The authors gratefully acknowledge the financial support of the National Research Council of Canada.

(7) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).

(8) M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964).

(9) Holder of a Province of Ontario Graduate Fellowship, 1967-1968.

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## Book Reviews

**Aromatic Amine Oxides.** By EIJI OCHIAI, Emeritus Professor of Pharmaceutical Chemistry, University of Tokyo (Japan). Translated by DOROTHY U. MIZOGUCHI, Chemotherapy Information Center, Cancer Institute, Tokyo, Japan. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1967. ix + 456 pp. 16.5 × 23 cm. \$30.00.

The year 1940 represents the turning point in the interest and research dealing with aromatic amine oxides. In that year Linton reported an unexpectedly low dipole moment for pyridine N-oxide which suggested structural contributions from canonical forms that required electron release by the N-O oxygen. This paper immediately attracted Ochiai's attention. He recognized the potential for electrophilic substitution and other reactions and over the next two and one-half decades contributed a massive amount of research on aromatic amine oxides. Other workers entered the field in the late 1940's and subsequent years and are continuing to expand and develop the chemistry of aromatic amine oxides.

Thus it is quite fitting that Professor Ochiai should write the most extensive review in the "Aromatic Amine Oxides," a further mark of his contributions to this growing field of chemistry. The book is well organized and reflects Ochiai's mastery of the subject. After an interesting introductory chapter and a quick survey of the field, Ochiai discusses in depth the methods for the preparation of aromatic amine oxides and the various physico-chemical properties characterizing this class of compounds. The latter chapter gives extensive tables listing dipole moments, reduction potentials, dissociation constants, nmr chemical shifts, infrared frequencies, and uv absorption spectral data for numerous aromatic amine oxides and their derivatives. The discussion of chemical properties follows next and covers in considerable detail the deoxygenation of the N-oxides (Chapter V), electrophilic substitution, particularly nitration (Chapter VI), and the nucleophilic substitution reactions with organometallics, reactive halides, and acid anhydrides (Chapter VII). Chapter VIII clarifies the influence of the amine oxide function on other substituents on the heterocyclic

ring located *ortho* or *para* to the N-oxide grouping. In addition this chapter contains other topics such as rearrangements which are not suitable for treatment under the other chapter headings. The concluding chapter describes the biological properties of aromatic amine oxides. Although there is some overlap of material in a few of the chapters, this does not detract in any way from the book.

The book is well documented and covers the literature thoroughly up to the beginning of 1964. Much of the early work on aromatic N-oxides was published in the Japanese language; these reports are thoroughly reviewed in this book. One interesting feature of the book is the insertion of experimental procedures at the conclusion of most sections, describing representative examples of reactions just discussed. All but two of these experimental procedures were taken from the Japanese literature or private communications, thus making available in the English language information previously difficult to obtain.

One of the problems of writing in a field of active, current interest is the rapidity with which new knowledge is reported in the literature. Thus the extensive work on the mechanistic aspects of the reaction of aromatic amine oxides with acylating agents, discovery of new oxidative reactions, information on rearrangement reactions, new reports in the growing field of photochemical processes, and other developments reported since 1964 were not available for inclusion in this book. Although this information gap exists, the book provides a solid foundation in the preparation, properties, and reactions of aromatic amine oxides. Mechanistic interpretations are presented for numerous reactions but play a secondary role in the book.

This reviewer recommends the "Aromatic Amine Oxides" to all organic chemists who have an interest in this class of compounds. The extensive factual information presented in this work will provide the base for frequent use as a reference source.

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**Aromatic Rearrangements.** Monograph 6 in the Series "Reaction Mechanisms in Organic Chemistry." Edited by C. EABORN and N. B. CHAPMAN. By H. J. SHINE, Professor of Organic Chemistry, Texas Technological College, Lubbock, Texas. American Elsevier Publishing Co., Inc., 62 Vanderbilt Ave., New York, N. Y. 1967. ix + 405 pp. 14.5 × 21.5 cm. \$23.50.

In his Preface Professor Shine clearly and succinctly defines his intentions and objectives in the composition of this book. His reasons are given for including considerations of some reactions and for excluding treatment of others. He directs attention to the uncertain state of the evidence bearing on many of the proposed mechanisms and to his own efforts to give critical appraisals of prevailing views.

The book is divided into six chapters, each of which deals with a class of aromatic rearrangements. Chapter 1, "The Acid-Catalyzed Rearrangement of Alkyl- and Halogeno-Aromatic Compounds," includes, in addition to the obvious subjects in this category, a treatment of the dienone-phenol family of rearrangements. Chapter 2 is concerned with "The Rearrangement of Esters and Ethers," e.g., the Fries and Claisen rearrangements. Chapter 3, by far the largest, occupying a third of the book proper, treats "The Rearrangement of N-Substituted Amino-Aromatic Compounds," e.g., the benzidine, quinamine, phenylhydroxylamine, Orton, Fischer-Hepp, Hofmann-Martius, and Reilly-Hickinbottom rearrangements, and the Fischer indole synthesis. Chapter 4, "The Rearrangement of N-Oxides," deals with the Wallach and amine oxide rearrangements. Chapter 5, "Based-Catalyzed Rearrangements, and Rearrangements Accompanying Nucleophilic Substitution," reviews the Smiles and Sommelet rearrangements, the von Richter reaction, and the rearrangements of trihalogenobenzenes and of carboxylates. The final, brief chapter is concerned with photochemical aromatic rearrangements and analogs of transformations induced by heat, acids, or bases, which were considered in the earlier chapters.

The treatment focuses on reaction mechanisms, the subject of the series of volumes of which this book is a member. The pertinent experimental evidence bearing on each reaction is summarized and the inferences and conclusions drawn from the evidence are examined critically. The narrative style frequently consists in tracing the development of evidence and of postulated mechanisms, in alternating order, in such a manner as to portray clearly the application of the scientific method and to convey something of the excitement and suspense inherent in investigations of this kind. The reviewer finds the section on the von Richter reaction a particularly captivating example of this technique.

Of course, any author brave enough to inject some of his own ideas and interpretations into a book on organic reaction mechanisms must be aware of the woods filled with sharp-eyed huntsmen eager to gun him down. Particularly when the light of evidence is meager and the trail through the thickets indiscernible, the man who attempts to pick a pathway will be the target of those who are less venturesome but, by their own standards, more perceptive. This book will be valuable to graduate students and to active researchers in the field because it summarizes the state of development in each of the many problem areas treated and points up the questions remaining to be resolved; whether the mechanisms proposed ultimately survive in the light of the evidence is relatively unimportant.

The book appears to have had the benefit of superior editorial work, for the number of errors in this category is relatively small. As a matter of detail, one might wish that the numbers denoting references were more obviously differentiated in type style from those representing structural formulations.

Professor Shine's style is crisp and incisive, and there are very few passages indeed where the reader is likely to halt and ask, "How's that again?" The only consistent defect in the writing that some may find serious is a vagueness in the identification of the sources of some of the observations and particularly of the ideas. Frequently the text does not make it clear whether an expressed concept is the author's own or whether it comes from the literature. Also it is sometimes difficult to assign experimental observations to a specific reference. This deficiency could make it difficult for the reader who wishes to go to the original literature for more detail.

The book is compulsory reading for anyone involved in research in the areas of coverage. Unlike much compulsory reading, its style and organization make the reading a pleasure.

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**The Chemistry of Boron and Its Compounds.** Edited by E. L. MUETTERTIES, Central Research Department, E. I. duPont de Nemours and Co., Inc., Wilmington, Del. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. xiv + 699 pp. 16 × 23.5 cm. \$27.50.

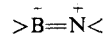
In a book review it is frequently safe to disregard the publisher's description of the volume. This case is different. Much of what the publisher says about the book is an accurate description of its content. I quote from the summary on the jacket: "It covers the major areas of current research (in boron chemistry) in a critical fashion encompassing structure, dynamics, reactivity, and theoretical considerations. Accounts of specific areas are personal evaluations and systematics presented by acknowledged experts in their respective fields." The reviewer agrees.

This book is one of several books on boron and its compounds to appear in recent years. The current volume is somewhat broader in scope than the earlier works, and its frequent reference to unsolved research problems makes it a must for those doing research in boron chemistry. In general, literature appears to be covered up to about 1965.

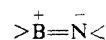
The first chapter by E. L. Muetterties gives a short, realistic, critical, and subjective review of boron chemistry by one of the acknowledged experts in the field. The second chapter by J. L. Hoard and R. E. Hughes is entitled, "Elemental Boron and Compounds of High Boron Content." Forms of elemental boron, boron nitride, boron carbide, and metallic borides are considered. About 50 substances, mostly crystalline, with melting points in the range of 1000 to over 3000° fall within the province of this chapter. Structural correlations are carefully drawn as a basis for the systematization of the mass of experimental data on these compounds.

"The Structural Chemistry of the Borates" is the title of a chapter by V. F. Ross and J. O. Edwards. The chapter includes a brief review of methods used to establish structure in borate systems, a review of available structural data, and a discussion of pertinent principles of bonding. A closely related, brief chapter by R. P. Bell, J. O. Edwards, and R. B. Jones considers boric acid and borates in solution. The chapter on "Boron Hydrides" by M. F. Hawthorne is well done. The discussion summarizes structural and bonding information and then gives a systematic summary of the chemistry of each of the boron hydrides. This reviewer particularly enjoyed the discussion of "aromatic" boron hydride chemistry and carborane chemistry. The latter topic includes a brief treatment of the new carborane-metal chemistry, an area pioneered by Professor Hawthorne.

The chapter by Grant Urry on "Boron Halides" is a realistic and critical review of the extensive experimental information on these compounds. The interpretation, using currently fashionable theory, is interlaced with just enough skepticism to demonstrate clearly the author's scientific realism. Catalysis by boron halides and a review of the boron subhalides are both well handled. An excellent review by Niedenzu and Dawson on "Boron Nitrogen Compounds" is presented. Some icons are broken. For example, the authors note that the long-used formulation of aminoboranes as

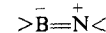


shows an unrealistic charge distribution. Current theoretical approaches indicate that a better representation may be



or even perhaps  $>\text{B}-\text{N}<$ . On the whole the chapter is well done.

The longest chapter in the book is a review of "Boron-Carbon Compounds" by M. F. Lappert. The length of the chapter is not unexpected when the author's goal is noted: "to provide an account of all significant aspects of organo boron chemistry." This chapter tends to be more exhaustive in coverage than the others and somewhat less selective and critical. A total of 1213 references are cited. It is interesting that the older notation



decried in the previous chapter, is used here freely.

The last two chapters are relatively brief. G. W. Parshall has reviewed boron-phosphorus compounds and E. L. Muetterties has reviewed boron-sulfur compounds. A first class review of the available literature is presented in each case.

No one interested in nonmetal inorganic chemistry should be without this critical personal evaluation of the field as done by experts.

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