stereochemistry of the rearrangement requires that the energies of the breaking bonds are different at any point of the reaction coordinate. The extreme case of unsymmetrical bond breaking leads to a diradical intermediate in which one bond is completely broken. Comparison of Tables I and II, however, shows that the results are consistent with a diradical mechanism only if one assumes that the intermediates resulting from the dimethylbicyclobutanes collapse to dienes before rotamer equilibration is achieved while the diradicals derived from the monomethyl derivatives are required to have a longer lifetime to account for the observed equilibration.

In contrast a concerted mechanism accommodates the results in a less strained manner. While it is obvious that III and IV should give different product mixtures in a concerted reaction, it is worthwhile pointing out that similar reaction mixtures from VII and VIII are not unexpected. Since the over-all stereochemistry requires that one ring opens conrotatory and the other disrotatory, it is possible to obtain two products from any bicyclobutane lacking a C_2 symmetry axis. However, the rearrangement of IV shows that, presumably for steric reasons, the *exo*-substituted ring prefers a conrotatory motion while the *endo*-methylated ring opens disrotatory. The opposite stereochemistry would lead to *cis,cis*-2,4-hexadiene, which is not observed. The same reasoning explains the results obtained from VII and VIII.[12]

It should be pointed out that, although a rigorous symmetry–orbital correlation cannot be carried out for path C, it is possible to show by qualitative overlap considerations that the two-center σ orbitals of bicyclobutane correlate with Ψ_1 and Ψ_2 of butadiene if the rearrangement occurs by path C.[13] It is interesting to note that path C corresponds to the reversal of a *cis,trans* cycloaddition of ethylene to give cyclobutane.[14]

[12] The results listed in Table I effectively rule out still another mechanism in which bicyclobutane rearranges first to cyclobutene followed by conrotatory ring opening to butadiene. The over-all stereochemistry of this symmetry-allowed process corresponds to either A or B.

[13] Very recent quantitative calculations of the CNDO type support the qualitative argument: K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

[14] We are grateful to Professor R. B. Woodward for drawing our attention to this analogy.

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Received February 9, 1968

Book Reviews

Structure and Bonding. Volume 1. By C. K. JØRGENSEN, J. B. NEILANDS, R. S. NYHOLM, D. REINEN, and R. J. P. WILLIAMS. Springer-Verlag, 175 Fifth Ave., New York, N. Y. 1966. 281 pp. 15.5 × 23 cm. $12.00.

In the preface the editors make the statement that this new series is intended for the publication of "authoritative reviews from the different fields of modern inorganic chemistry, chemical physics, and biochemistry, where the general subject of chemical bonding involves (usually) a metal and a small number of associated atoms." They note that they are "specially interested in the role of the 'complex metal–ligand' moiety, . . ., are purposely avoiding the more classical organic chemistry and even organometallic chemistry, . . ., and wish to direct attention towards borderline subjects." This appears to be a worthwhile goal since too frequently boundaries are distinctly drawn and borderline subjects given less attention than they may deserve.

Of the five editors, three of them have offered four of the nine articles in the first volume. "Recent Progress in Ligand Field Theory" is described in very colorful terms by C. K. Jørgensen in a 27-page paper which was updated from notes distributed at earlier lectures. A second article by Jørgensen entitled "Electric Polarizability, Innocent Ligands and Spectroscopic Oxidation States" deals with the topic of hard and soft acids and bases as do contributions by S. Ahrland ("Factors Contributing to (b)-Behavior in Acceptors"), R. F. Hudson ("Displacement Reactions and the Concept of Soft and Hard Acids and Bases"), and R. J. P. Williams with J. D. Hale ("The Classification of Acceptors and Donors in Inorganic Reactions"). Williams and Hale present convincing arguments which underline admitted deficiencies of SHAB. "The Ambident Nature of Cyanide" is reviewed by D. F. Shriver while the biochemistry review articles include "Naturally Occurring Non-porphyrin Iron Compounds" by J. B. Neilands, "The Chemistry and Function of Ferredoxin" by B. B. Buchanan, and "The Transferrins" by R. E. Feeney and S. K. Komatsu. The reference lists with these latter reviews are extensive and especially valuable since the names of articles have been included in the reference citations. However, since the series is presumably aimed at an audience with a broad spectrum of backgrounds and interests, the depth of details on experimental facts, reaction conditions, or physical properties presented here is questionable.

There is also the question concerning the kind of articles that may be expected in "Structure and Bonding." From the contents of the first volume we may conclude that, in addition to reviews, papers based on a single aspect of a topic will appear. It is clear that the editors must define more explicitly the intended role of the series. Perhaps then it will be possible to rationalize four "reviews" on one topic in one volume.

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Reactivity of the Photoexcited Organic Molecule. By the SOLVAY INSTITUTE. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. ix + 350 pp. 15.5 × 23.5 cm. $15.00.

This volume consists of the reports and discussions of aspects of organic photochemistry by the members of the Thirteenth Conference on Chemistry at Brussels in October 1965. One may have immediate doubts concerning the value of a belated publication in a field of fomenting activity. To the reviewer's delight, clarity of presentation and continued emphasis on fundamentals of excited-state reactivity by the various authors adequately counteract this deficiency and imbue the book with a more lasting worth.

C. A. Coulson initiates matters by discussing the theory of the change in shape and size of small molecules which accompanies their electronic excitations. The Hellman–Feynman theory, Walsh–Mulliken correlation diagrams, Jahn–Teller distortions, and Renner effects are discussed in pictorial terms palatable even to those with an elementary background in quantum mechanics. Although the reader finishes this chapter with the feeling that electronically excited molecules are *generally* very different chemical species from their ground-state counterparts, a woeful dearth of experimental data renders useless many of the qualitative arguments concerning the structures of electronically excited states.

R. Daudel then discusses (in French) the correlation of excited-state reactivities with quantum mechanical calculations on dienes, aromatic hydrocarbons, and spiropyrans. Attempts to relate calculated charge densities and free valences with excited-state reactivity must reckon with all the hazards inherent in ground-state calculations. Nevertheless, one is able to rationalize a surprisingly broad range of excited-state phenomena by this method.

G. Porter then begins the bridging of theory and organic photochemistry with his discussion of reactivity, radiationless conversions, and electronic distribution in excited states. He carefully and clearly defines the rate constant of an elementary step as the true measure of excited-state reactivity and then discusses the problems encountered in measuring this important parameter, especially with respect to the competition between chemical reaction and radiationless conversions. Finally, there is a discussion of chemical reactivity and various methods employed to deduce the electronic distribution of electronically excited states.

G. S. Hammond discusses energy transfer in organic photochemistry (a subject dear to the heart of this reviewer). Photosensitized *cis–trans* isomerizations and dimerizations are considered from the standpoint of kinetic- and photostationary-state measurements. He also presents phenomenological reasons for invoking nonvertical energy transfer and some brief speculation and theory of this interesting concept.

A further transition toward organic photochemistry occurs in the reports of N. C. Yang, W. G. Dauben, and E. Havinga. Yang discusses his extensive and important contributions to the photochemistry of ketones in solution, with an emphasis on hydrogen abstraction by ketones. Dauben summarizes the work of his group on the photochemistry of conjugated dienes. Problems are pointed out concerning the state in which isomerization of dienes occurs. E. Havinga reviews heterolytic photochemical substitution reactions of substituted benzenes. Quantitative and kinetic analyses of these reactions are presented. The differences in quantum efficiencies of aromatic substitutions are discussed in terms of different positional reactivity and lifetime differences.

The final paper by G. M. J. Schmidt is a résumé of the fascinating and relatively unexplored area of solid-state photochemistry. The combination of X-ray crystallography and photochemistry of molecular crystals reveals that lattice control explains both the stereochemistry of product formation and the "go-no-go" features of these reactions.

Each paper is followed by a discussion. Some of these sections are excellent in that incisive comments on many areas of photochemistry are made not only by the lecturers but an impressive list of invited members to the conference.

Because of the substantial time lag between the date of the conference and publication of the reports, most of the material in this volume has been published. Thus, for the research worker in photochemistry there is not much new to be gained by reading this book, except perhaps an occasional insight, reminder, or unpublished datum. Graduate students in the field will probably find this work exciting reading. The price seems reasonable these days for a book of its size and quality of printing.

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Spectroscopy. By D. H. WHIFFEN. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. *1966.* vii + 205 *pp.* 14 × 21.5 cm. $4.25.

Dr. Whiffen describes this book as an "attempt to encompass in less than 200 pages all the essentials to understanding spectroscopy and its subdivisions at an undergraduate level." When he says encompass he really means it. The book covers nmr, pure quadrupole resonance, esr, Mössbauer effect, and the rotational, vibrational, and electronic spectra of diatomic and polyatomic molecules.

The ordering of subjects is novel and makes a good deal of sense. The inclusion of Mössbauer spectroscopy, in view of its relationship to magnetic resonance, is a nice idea. A good balance of emphasis is maintained, the examples and illustrations are well chosen, and the writing reflects Dr. Whiffen's clarity of thought.

The emphasis throughout is on experimental fact and its interpretation rather than on basic theory. A very good, though brief, set of problems shares the same emphasis. Thus this book would be an admirable supplementary text for a first course in quantum theory. It skims through such a welter of material in such short space that I cannot imagine its being used by itself as an introduction to spectroscopy.

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