

In view of the numerous examples of dimerizations of cyclobutadiene derivatives to tricyclooctadienes⁶ there can be little doubt that VIII–XI are formed by dimerization of trimethylchlorocyclobutadiene (VII). The precursor of VII must be the carbenoid V because the cyclobutene VI, which is formed by a thermally induced rearrangement from IV, fails to react with butyllithium under comparable conditions. It is tempting to speculate on the mode of formation of VII from V. Al-

though the rearrangement may proceed in a single step by ring expansion, one cannot exclude the possible intermediacy of trimethylchlorotricyclobutane.

(7) A. P. Sloan Foundation Fellow, 1962–1966.

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Book Reviews

Diels–Alder Reactions. Organic Background and Physico-Chemical Aspects. By A. WASSERMANN, Reader in Chemistry, University College, London. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. viii + 114 pp. 15 × 22 cm. \$5.50.

One of the pioneers of the study of the mechanisms of thermal associations has produced this slender volume on the Diels–Alder reaction. Researchers in this area will appreciate having his current thoughts and opinions.

The book does not contain a comprehensive survey of the synthetic aspects, which is probably not a major fault since several excellent reviews are available elsewhere. Its discussion of mechanism provides the main focus and is concerned with a critical appraisal of most of the theoretical, kinetic, and stereochemical evidence which has been accumulated in attempts to define the structure of the transition state. The documentation is quite complete, although unfortunately the publication lag has prevented discussion of several important papers which appeared after 1964. One would be interested, for example, in whether Wassermann's view (p 64) that the use of isotope effects is not a promising means of deciding between one-step and two-step mechanisms remains unchanged after recent work reporting the application of primary heavy atom isotope effects to this question.

One unattractive feature of the presentation is the excessively condensed style. Cross-references, both forward and backward, result in annoying inconvenience in reading. The appendix of standard formulas for entropy calculations is too brief to be of much use to the neophyte attempting to learn how to do such calculations and would be of only mnemonic value to the initiate.

There are a few inaccuracies. Thus, indene does not give a "normal" adduct (p 8). The ring-strain calculations (pp 43 and 46) should be updated, since they do not take into account the effects of hybridization change on the nonreacting bonds. The discussion on page 54 of the "compensation affect" is not up-to-date, and an important paper of rebuttal bearing on the controversial issues discussed on page 96 is not cited.

Wassermann's book will interest and inform all those concerned with research on organic reaction mechanisms and is required reading for anyone working on the elusive mechanism of the Diels–Alder reaction.

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Nonclassical Ions. Reprints and Commentary. By PAUL D. BARTLETT, Harvard University. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. xiv + 559 pp. 19 × 23 cm. \$12.00.

Professor Bartlett has assembled, in chronological order, 75 reprints which span the years 1937–1965 and which bear on the subject of nonclassical ions. This collection is intended for the second-year student of organic chemistry and "for others whose attention has been attracted by the vigorous current activity in this field." One of its stated purposes is to demonstrate to the student "how we know what we know, and why we hold our present opinions"

on this particular subject. Each paper is accompanied by Professor Bartlett's comments, which are incisive, terse, and often dryly humorous. In the preface, for example, he states that the commentary for each paper is written "on the assumption that the reader of it will also read the paper." Again, on page 65, Bartlett presumes the term "nonclassical" has been widely used whereas "synartetic" has not because: "A generation emancipated enough to synthesize 'barrelene' and 'twistane' may feel that even earthy English is preferable to graceful Greek." In the main, Bartlett's remarks are gentle, except when he deals with the contributions of H. C. Brown (papers 30, 31, and 63). With Brown's celebrated paper at the Transition-State Symposium (paper no. 63, termed "A Dissenting View" by Bartlett) there is included a 10-question quiz which, if solved, is supposed to allow the reader to write his own criticism of that paper. My answers would allow me to write a favorable review of paper 63, but it is by no means clear that these answers are the same as Professor Bartlett's.

As one who has often wavered uncertainly in the debate over the existence of nonclassical ions, I was struck by the logic and reasonableness of the development of nonclassical theory—from I. Roberts and G. Kimball's paper on the bromonium ion (paper no. 1) through the contributions of Winstein and Shoppee and J. D. Roberts; then to the work of LeNy and Lawton on the " π -route" (Bartlett generously omits his own contribution here), and finally to the nmr studies of Saunders, Schleyer, and Olah (paper no. 75). Such an impression is hard to achieve unless one has the pertinent papers before him, and Professor Bartlett has performed a service in providing us with this collection. He makes no defense of his selections except to say that each paper "contributes to our understanding of the present position of the field." In my opinion, all of the important papers have been either included or acknowledged in the commentary and in the appendix. Although only one of Ingold's papers (no. 11, "Ingold on Synartetic Ions") is to be found in the collection, one finds the clear statement on page 1 that what follows "rests on a foundation laid in the thirties" by Sir Christopher and his colleagues.

I had the impression that I was reading a historical narrative as I proceeded through the book, and this impression was assisted by such headings as "Before Nonclassical Ions" and "Hughes and Winstein at Montpellier." In addition, I was surprised at how greatly this field has been dominated by American scientists, for only seven of the seventy-five reprints are from laboratories outside the United States.

There are some things about the book I do not like, and one of them is Professor Bartlett's occasional lack of objectivity, for he shows us nonclassical ions all polished and scrubbed and in their Sunday clothes, and does not tell us how they sometimes behave during the rest of the week. For example, in papers 70 and 71, P. von R. Schleyer presents a method, based on 52 examples, for correlating acetolysis rates of arenosulfonates with carbonyl stretching frequencies of the related ketones. Schleyer claims this method indicates in which systems nonclassical ions are possible. Yet the 3-phenyl-2-butyl tosylates—the celebrated examples for which phenonium ion intermediates were first proposed—are not even mentioned (see also paper 69 by C. Foote). Professor Bartlett does not comment upon this strange omission, although he continually chides H. C. Brown on the embarrassing position of certain reaction rates of cyclobutyl derivatives with respect to other cyclic

compounds. Again, in his commentary on pages 525 and 526 under the heading "The Long-Lived Nonbornyl Cation," Bartlett characterizes the classical nonbornyl ion here as "a picture of decaying molecular structure" requiring that "... C-6 flops about randomly in an untidy box." This particular conclusion rests on Winstein's "calculation" (reproduced on page 526) which says that during acetolysis of the tosylate classical norbornyl ions would have to interconvert at about the same rate as a molecular vibration. Bartlett thus concludes, with Winstein, that nonclassical ions must be intermediates. The result, however, is at best a crude estimate and can be only fortuitously correct. In my opinion, the conclusion, which is one of the most important in the book, deserves to rest on firmer ground.

I doubt that one can study the book, however, without being convinced that we are better off because someone has already invented nonclassical ions. This is Professor Bartlett's message, and, with the exceptions noted, he presents it elegantly, even going to the trouble of giving us cut-out models of the twelve bicyclobutonium ions (on pages 274 and 275 and again at the end of the book) which illustrate the ease with which these presumed isomers can interconvert. It is unfortunate that the papers by Olah and Pittman and by Winstein, *et al.*, giving nmr evidence for the phenonium ion and a 9-anthryl analog could not be included, but these appeared after the book went to press. The references to these papers are given in the appendix, however, as are references to several other important papers which also appeared too late for inclusion.

Some may question my use of the word "book" in connection with such a "collection," for there are less than 50 full pages of Bartlett's own commentary in the entire volume. The success of this collection rests in great measure, however, on what has been said in these 50 pages. In this sense "Nonclassical Ions" is no less a book and Bartlett no less its author than if he had chosen to write it in the conventional form.

There is a comprehensive author index, a subject index being unnecessary. The volume is well bound but some of the papers suffer in readability, and appear to have been reduced below their original print size. "Nonclassical Ions" is also available in paper binding for \$6.95. I recommend either form for all students of organic chemistry (including university staff members, postdoctorates, and industrial chemists) who are interested in reaction mechanisms. I think it is a good book. I hope other fields of chemistry will be treated in this way.

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BOOKS RECEIVED, July 1966

- JAMES BONNER and J. E. VARNER, Editors. "Plant Biochemistry." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. 1054 pp. \$19.00.
- THE CHEMICAL SOCIETY. "Molecular Relaxation Processes. Lectures Delivered and Synopses of Papers read at a Chemical Society Symposium held at Aberystwyth 7-9 July 1965." Chemical Society Special Publication No. 20. Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London W1, England. 1966. 304 pp. 65s.
- WILHELM EITEL. "Silicate Science." Volume III. "Dry Silicate Systems. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. 553 pp. \$22.00.
- PER EKWALL, KJELL GROTH, and VERA RUNNSTRÖM-REIO. "Surface Chemistry. Proceedings of the Second Scandinavian Symposium on Surface Activity, Stockholm, November 18-19, 1964." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. 315 pp. \$15.50.
- GLADYS L. HOBBY, Editor. "Antimicrobial Agents and Chemotherapy-1965. Proceedings of the Fifth Interscience Conference on Antimicrobial Agents and Chemotherapy and IVth International Congress of Chemotherapy, Washington, D. C., 17-21 October 1965." American Society for Microbiology, 115 Huron View Blvd., Ann Arbor, Mich. 1966. 1138 pp. \$15.00.
- ERNEST D. KAUFMAN. "Advanced Concepts in Physical Chemistry. McGraw-Hill Book Co., Inc., 330 West 42nd St., New York, N. Y. 1966. 271 pp. \$9.95.
- ERNEST R. M. KAY. "Biochemistry. An Introduction to Dynamic Biology." The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1966. 374 pp. \$7.95.
- JAMES MUILE LEITCH (deceased), Editor. "Food Science and Technology. Proceedings of the First International Congress of Food Science and Technology, London, September 18-21, 1962." Volume II. "Biological and Microbiological Aspects of Foods." Gordon and Breach Science Publishers, 150 Fifth Ave., New York, N. Y. 1965. 646 pp. \$45.00.
- EMIL J. MARGOLIS. "Chemical Principles in Calculations of Ionic Equilibria. Solution Theory for General Chemistry, Qualitative Analysis, and Quantitative Analysis." The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1966. 482 pp. \$7.95.
- C. MENTZER, Editor. "Actualités de Phytochimie Fondamentale." Deuxieme Serie. Masson et Cie, Editeurs, 120 Boulevard Saint-Germain, Paris, France. 1966. 320 pp. 119 F.
- SAUL PATAI, Editor. "The Chemistry of the Carbonyl Group." Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. 1027 pp. \$32.50.
- E. S. PROSKAUER, E. H. IMMERGUT, and C. G. OVERBERGER, Editors. "Perspectives in Polymer Science. A Volume Dedicated to Herman F. Mark on the Occasion of his 70th Birthday." Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. 376 pp. \$15.00.
- OKTAY SINANOĞLU, Editor. "Modern Quantum Chemistry. Istanbul Lectures." Part III. "Action of Light and Organic Crystals." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1966. 323 pp. \$12.00.
- T. SWAIN, Editor. "Comparative Phytochemistry." Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London, W1, England. 1966. 360 pp. 93s.
- P. SYKES. "Initiation aux Mécanismes Réactionnels en Chimie Organique." Dunod, Editeur, 92 rue Bonaparte, Paris, France. 1966. 260 pp. Broché, 28 F.
- L. ZECHMEISTER, Editor. "Progress in the Chemistry of Organic Natural Products." Volume 23. Springer-Verlag, Molkenbastei 5, Wien 1, Germany. 1965. 397 pp. \$23.40.