electron. This effect must be felt to some extent at the beginning of rearrangement with a lowering of the potential energy surface. Second, there is more relief of strain by migration of one of the geminal phenyl groups of the 4,4-diphenyl enone. Third, in the 4,4-diphenyl enone at least one phenyl group is axial and in a conformation to migrate; the 4,5 isomer appears to be *trans* and has no axial group. The fourth factor is the extra delocalization of the odd electron by the phenyl at C-5 of species **5** (or **9**). It is probably this extra stabilization which gives species **5** (or **9**) the possibility of migration beyond C-3 to C-2, leading to the cyclobutanone product.

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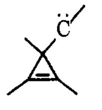
A Cyclopropenylcarbene–Cyclobutadiene Rearrangement[1]

Sir:

Recently there has been much interest in derivatives of cyclopropenylcarbene (I) because of the apparent use of such molecules as possible precursors to the as yet unknown tricyclo[1.1.0.0^{2,4}]butane system.[2] We wish to report the formation of the chlorotrimethylcyclopropenylcarbenoid V and its rearrangement to a transient cyclobutadiene derivative.

Trimethylcyclopropenium chloride (III), prepared by photolysis of the readily available 3H-pyrazole (II)[3] followed by treatment with anhydrous hydrogen chloride, was allowed to react with a suspension of dichloromethyllithium[4] in tetrahydrofuran at −100°. Treatment of the resulting 3-dichloromethyl-1,2,3-trimethylcyclopropene (IV) with *n*-butyllithium in ether at −20° gave a mixture of four isomeric compounds in 85% yield. Separation by chromatography and examination of the ultraviolet (only end absorption at 210 mμ), infrared, mass, and nmr spectra led to an unambiguous assignment of the tricyclooctadiene ring structure to all four compounds. The number of nonequivalent sets of methyl groups in each isomer was determined by nmr in two different solvents. This information together with the observed long-range coupling between methyl groups attached to the same double bond narrows down the structure assignments to the alternatives listed in Table I. The infrared spectra, which showed weak absorptions for dimethyl-substituted double bonds at 1680 cm^{-1} and stronger bands at 1660 cm^{-1} originating from double bonds with chlorine substitution, confirmed the assignment. With the available data it is impossible to distinguish between the two alternatives in each substitution group as well as to assign either *syn* or *anti* structures to the dimers.[5]



I

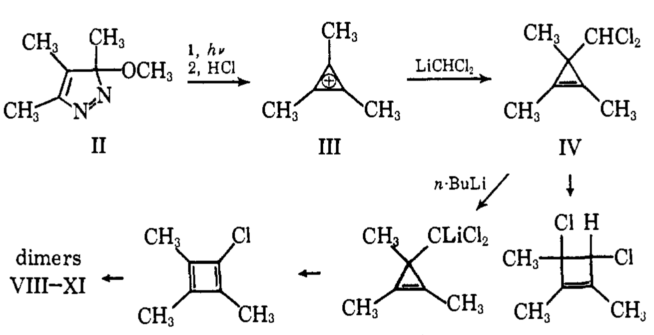
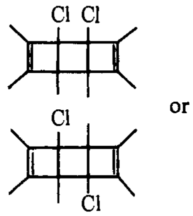
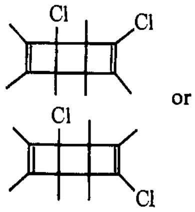
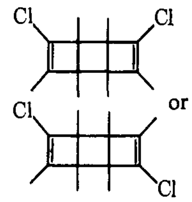


Table I. Chemical Shifts of Methyl Protons of Isomers VIII–XI[a]

	Solvent		Suggested structures[b]
	CS$_2$	C_6H_6	
VIII	1.20 (6), s 1.55 (12), s	1.28 (6), q (1.2 cps) 1.42 (6), q (1.2 cps) 1.48 (6), s	
IX	1.06 (3), s 1.08 (3), s 1.14 (3), s 1.53 (6), m 1.56 (3), s	0.88 (3), s 1.11 (3), s 1.29 (3), q (1.2 cps) 1.33 (3), s 1.36 (3), s	
X	1.07 (3), s 1.10 (3), s 1.50 (3), s 1.55 (6), m 1.59 (3), s	1.70 (3), q (1.2 cps) 1.04 (3), s 1.16 (3), s 1.18 (3), s 1.42 (3), s 1.50 (3), q (1.2 cps) 1.54 (3), q (1.2 cps)	
XI	1.05 (6), s 1.06 (6), s 1.61 (6), s	0.85 (6), s 0.96 (6), s 1.66 (6), s	

[a] Chemical shifts are in parts per million downfield from internal tetramethylsilane. Numbers in parenthesis following the chemical shift values designate the number of protons causing the signal. The multiplicity of the signal is given by s for singlet, q for quartet, and m for unresolved multiplet. [b] Methyl groups are omitted from structures.

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(1) Supported by National Science Foundation Grant GP-4214.

(2) *Cf.* S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965); **88**, 610 (1966); E. H. White, G. E. Maier, R. Graeve, U. Zirngibl, and E. W. Friend, *ibid.*, **88**, 611 (1966).

(3) G. L. Closs and H. Heyn, *Tetrahedron*, **22**, 463 (1966).

(4) G. Köbrich and W. Drischel, *Angew. Chem. Intern. Ed. Engl.*, **3**, 513 (1964).

(5) It is very likely, however, that all isomers have the same stereochemistry because the crystals appear to be isomorphous and have approximately the same melting points which are not depressed in mixtures. Partly because of the solvent dependence of the chemical shifts and partly because of precedent[6] we presently prefer the *anti* configuration.

(6) *Cf.* R. Criegee, *Bull. Soc. Chim. France*, **5**, 1 (1965), and references cited therein; L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).

In view of the numerous examples of dimerizations of cyclobutadiene derivatives to tricyclooctadienes[6] 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. Although 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 arenesulfonates 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