tion of some type. A preliminary X-ray crystallographic study indicates that IV exists in a chair form.[8]

[8] D. S. Breslow and H. Skolnik, "Multi-Sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles," Part Two, Interscience Publishers, Inc., New York, N. Y., 1966, p 629.

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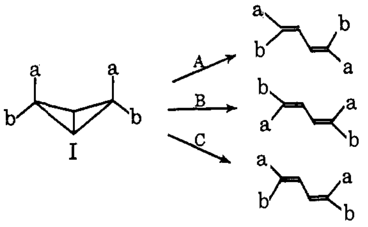
The Steric Course of the Thermal Rearrangements of Methylbicyclobutanes[1]

Sir:

Two problems arise from the observed thermal rearrangement of bicyclobutane to butadiene.[2] First, the detailed stereochemistry of the ring opening is as yet unknown, and second, no evidence exists either proving or disproving the existence of an intermediate in this reaction.[3] Answers to both questions are of considerable importance to an understanding of thermal rearrangements in general.

Considering a symmetrically labeled bicyclobutane, I, three sterically different modes of ring opening can be envisioned. In modes A and B reactants and products have a common symmetry element (C_2), but the rotations required to bring the substituents at carbon atoms 2 and 4 of the bicyclobutane into the molecular plane of butadiene are of opposite sense in the two modes. Mode C gives a product which shares no symmetry element with the reactant. A more detailed analysis shows that in a concerted reaction to *s-trans*-butadiene mode A corresponds to a quasi-disrotatory opening of both rings while B requires quasi-conrotatory motions. In mode C one ring is opened disrotatory and the other conrotatory.[4] If one assumes a concerted mechanism, it follows that correlation diagrams can be constructed with symmetry orbitals only for A and B but not for C.[5] Furthermore, the results of such correlations predict high activation energies for A and B because the ground state of I correlates with $\Psi_1{}^2\Psi_4{}^2$ and $\Psi_2{}^2\Psi_3{}^2$ of butadiene, respectively.[6,7] The results of a previous attempt to determine the stereochemistry of ring opening of bicyclobutane-2-d_1 were ambiguous because the product analysis was compatible with either path C, or product formation by both A and B, or the occurrence of all three reaction modes.[8]



To gain information on these questions we have synthesized *exo,exo*- and *exo,endo*-2,4-dimethylbicyclobutanes (III and IV) *via* the cuprous cyanide catalyzed decomposition of *trans*-1-diazo-2-methylpent-3-ene (II), and *exo*- and *endo*-2-methylbicyclobutanes (VII and VIII) from *trans*- and *cis*-1-diazopent-3-enes (V and VI), respectively.[9] The product analyses of the vapor-phase pyrolysis (200°) are shown in Tables I and II.[10] The results obtained for the dimethyl derivatives can be summarized by stating that: (i) diene formation is stereoselective but not completely specific; (ii) the predominantly formed dienes are those expected from the unsymmetrical mode C; (iii) minor side products are *trans*-1-methyl-2-vinylcyclopropane and *cis*-1,4-hexadiene, a known rearrangement product of *cis*-1-methyl-2-vinylcyclopropane.[11] In contrast, the product distribution of the pyrolysis of the monomethyl derivatives VII and VIII is very similar for both isomers and consists mostly of *trans*-1,3-pentadiene.

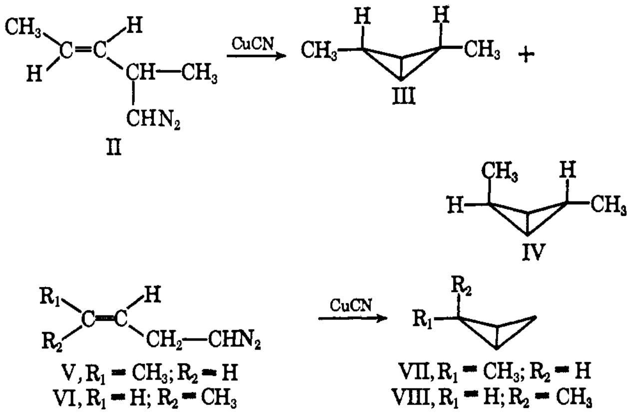


Table I. Pyrolysis Products of 2,4-Dimethylbicyclobutanes

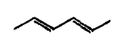
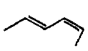
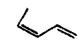
Reactant	Products, % 			
III	3.9	93.2	2.9	. . .
IV	95.0	1.2	2.2	1.6

Table II. Pyrolysis Products of 2-Methylbicyclobutane

Reactant	Products, % 		
VII	91.0	6.2	2.8
VIII	90.5	7.5	2.0

These observations eliminate the concerted symmetrical mechanisms A and B. Also, the unsymmetrical

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[1] Supported by National Science Foundation Grants GP-4212 and GP-7043.

[2] H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters*, 991 (1965).

[3] See, however, I. A. D'yakonov, V. V. Razin, and M. I. Komendantov, *ibid.*, 1127, 1135 (1966), on the rearrangements of 1,3-diphenyl-2,4-dicarbomethoxybicyclobutanes.

[4] Actually each of the three modes corresponds to two different pathways, one in which the initial product is *s-trans*-butadiene and another in which *s-cis*-butadiene is formed first. However none of the conclusions drawn in this communication is effected by this degeneracy.

[5] *Cf.* R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[6] This correlation neglects the "noncrossing" rule of levels of identical symmetry.

[7] A previous discussion of orbital correlation in the ring opening of bicyclobutane[8] should be disregarded because it was erroneously based on a *trans*-fused bicyclobutane.

[8] K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 5272 (1966).

[9] The bicyclobutanes were fully characterized by complete analyses of their nmr spectra and by mass spectra.

[10] The reactions were carried out in quartz flasks because pyrolyses in Pyrex vessels gave irreproducible results due to surface effects.

[11] W. R. Roth and J. König, *Ann.*, **688**, 28 (1965).

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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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 ex-