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Nicholas J. Turro,* Peter Lechtken, Gary Schuster
Jeffrey Orell, Hans-Christian Steinmetzer¹²
Chemistry Department, Columbia University
New York, New York 10027

Waldemar Adam
Chemistry Department, University of Puerto Rico
San Juan, Puerto Rico 00931

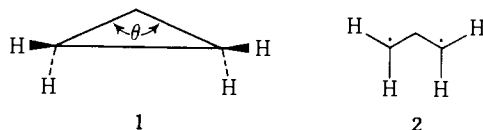
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Thermal $\sigma_2 + \sigma_2$ Isomerizations of the Conformationally Restricted Cyclopropanes 2,4-Dehydroadamantane and 2,4-Dehydrohomoadamantane

Sir:

The cyclopropane to propene rearrangement is the prototype $\sigma_2 + \sigma_2$ cycloreaction. According to current understandings, it proceeds in a nonconcerted fashion by way of a trimethylene diradical intermediate which may revert to cyclopropane or react with a C-H bond to give olefinic product.¹

Molecular orbital and valence bond calculations of several types and degrees of complexity on the trimethylene diradical are in general agreement:¹ the energy of the 90,90 form (1)² increases monotonically as the angle θ increases, reaching no energy well corresponding to an intermediate. Near $\theta = 110^\circ$, the 0,0-trimethylene species (2) becomes the lower energy



form, and it may exist as a discrete entity. Thus, the transformation of cyclopropane into the trimethylene diradical intermediate, according to these calculations, involves both increasing the angle θ and rotating C(1) and C(3) methylene hydrogens in a conrotatory or disrotatory manner into the plane defined by the carbon atoms.

How will a cyclopropane behave if it is conformationally restricted so that the geometry required for a 0,0-trimethylene diradical intermediate may not be attained? Is the 0,0-diradical intermediate a necessary stage in thermal structural isomerizations of cyclopropanes?

We have studied the thermal chemistry of two cyclopropane derivatives restricted to bond elongating distortions and prevented from reaching the geometry characteristic of 0,0-trimethylene diradicals. They give $\sigma_2 + \sigma_2$ cycloreactions quite smoothly: 2,4-dehydroadamantane³⁻⁶ (3) rearranges to protoadamantene

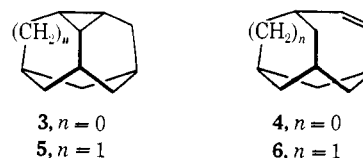
(1) R. G. Bergman in "Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, and references cited.

(2) Conformational designations follow the conventions introduced by R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(3) J. Boyd and K. H. Overton, *Chem. Commun.*, 211 (1971); *J. Chem. Soc., Perkin Trans. 1*, 2533 (1972).

(4) A. C. Udding, Doctoral Thesis, University of Groningen, The Netherlands, 1968. We are indebted to Mr. Gerrit DeWilde for translations of parts of this thesis. See also A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Commun.*, 657 (1966).

(4)^{3,7} in the gas phase with a first-order rate constant of about 10^{-5} sec^{-1} at 387° ; 2,4-dehydrohomoadamantane⁸ (5) is isomerized to homoadamantene (6)^{9,10} in the



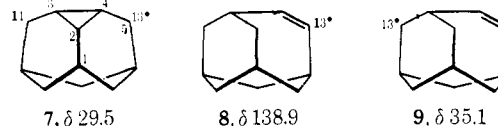
3, $n = 0$
5, $n = 1$

4, $n = 0$
6, $n = 1$

gas phase with a first-order rate constant of about 10^{-4} sec^{-1} at 400° . These rearrangements proceed 20 and 80 times faster than the formally analogous conversion of methylcyclopropane to 1-butene at the respective temperatures.^{11,12}

To identify the bonds involved in the isomerization of 5, 2,4-dehydrohomoadamantane-5-¹³C (7) and 4-homoadamantene-4-¹³C (8) were prepared from adamantanone and potassium cyanide-¹³C (61% enriched) by way of the cyanohydrin, the amino alcohol, homoadamantan-4-one-5-¹³C, and thermal decomposition of the lithium or sodium salts of the corresponding tosylhydrazones.^{8,10}

Pyrolysis of 7 gave recovered 7 of undiminished isotopic integrity and a 1:2 mixture of 8 and 9. The syn-



7, δ 29.5

8, δ 138.9

9, δ 35.1

thesized sample of 8 was subjected to the reaction conditions and found to suffer positional scrambling of the carbon-13 label to only a barely detectable extent. In a completely independent experiment, starting with adamantanone and labeled potassium cyanide, much larger samples of 7 and 8 were utilized; the same controls were run with the same findings, and the homoadamantene produced by pyrolysis of 7 at 400° for 3 hr was a 27:73 mixture of 8 and 9 according to the relative intensities of the cmr absorptions at δ 138.9 and 35.1.

These results are consistent with involvement of two $\sigma_2 + \sigma_2$ rearrangement modes: a [C(2)-C(4)/H-C(5)] bond reorganization and a [C(2)-C(4)/C(3)-C(11)] process. The more precise experimental results obtained with the larger sample of 7 correspond to these two modes obtaining in 54:46 proportions.¹³

We conclude that 0,0-trimethylene diradical intermediates are not required in $\sigma_2 + \sigma_2$ isomerizations of

(5) S. D. Isaev, A. G. Yurchenko, F. N. Stepanov, G. G. Kolyada, and S. S. Novikov, *Zh. Org. Khim.*, **9**, 430 (1973).

(6) R. K. Murray, Jr., and K. A. Babiak, *J. Org. Chem.*, **38**, 2556 (1973).

(7) R. M. Black and G. B. Gill, *Chem. Commun.*, 972 (1970); our chemical shift assignments differ from some given in this reference. See also M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969); C. A. Cupas, W. Schumann, and W. E. Heyd, *J. Amer. Chem. Soc.*, **92**, 3237 (1970); B. D. Cuddy, D. Grant, and M. A. Kervey, *J. Chem. Soc. C*, 3173 (1971).

(8) Z. Majerski, S. H. Liggero, and P. v. R. Schleyer, *J. Chem. Soc. C*, 949 (1970).

(9) J. E. Nordlander, F. Y.-H. Wu, S. P. Jindal, and J. B. Hamilton, *J. Amer. Chem. Soc.*, **91**, 3962 (1969).

(10) P. v. R. Schleyer, E. Funke, and S. H. Liggero, *J. Amer. Chem. Soc.*, **91**, 3965 (1969).

(11) D. W. Setzer and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **86**, 564 (1964).

(12) D. W. Placzek and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 2141 (1965).

(13) There are other [C-C/C-C] cycloreaction modes which, followed by rapid 1,3-carbon migrations, would account for the 7 \rightarrow 9 reaction.

cyclopropane systems and that [C-C/C-C] cycloreaction modes, though absent in some cases,¹⁴ are very much in evidence in the thermal isomerization of 2,4-dehydrohomoadamantane.

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(14) J. E. Baldwin and G. D. Andrews, *J. Org. Chem.*, **38**, 1063 (1973).

John E. Baldwin,* Michael W. Grayston
Department of Chemistry, University of Oregon
Eugene, Oregon 97403
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An Energetically Concerted Reaction Profile for the Thermal Conversion of Cyclopropane to Propene and for Related Cycloreactions

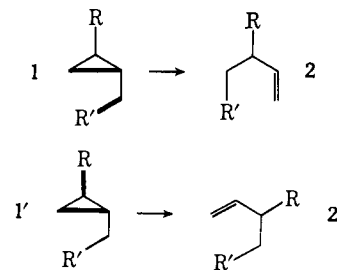
Sir:

Cyclopropane isomerizes thermally to propene.¹ Were this reaction to be discovered today it would be classed as a $\sigma_2 + \sigma_2$ cycloreaction; the stereochemistry of the process and its relevance to orbital symmetry theory would be high priority topics for investigation.

Chambers and Kistiakowsky² recognized two distinct mechanistic possibilities: homolysis of a carbon-carbon single bond to give a "radical," followed by a hydrogen migration; a direct isomerization according to the "1,2-unsaturation" proposals of Kassel.³ In time, the trimethylene diradical mediated two-step formulation gained a favored status relative to the concerted one-step mechanism, thanks largely to demonstrations that cyclopropanes could be thermally epimerized and to suppositions that epimerizations and structural rearrangements shared a common reaction profile.⁴ Orbital symmetry theory has prompted theoretical efforts to learn whether the 0,0-trimethylene diradical intermediate is formed preferentially in a conrotatory or disrotatory fashion, but it has not incited a challenge to the diradical schema for cyclopropane thermal chemistry.

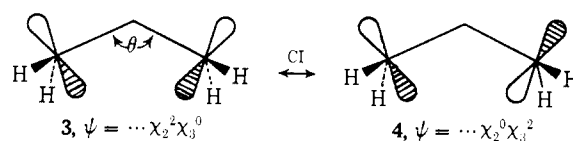
We have found that two conformationally restricted cyclopropanes, 2,4-dehydroadamantane and 2,4-dehydrohomoadamantane, rearrange smoothly in $\sigma_2 + \sigma_2$ processes to give protoadamantene and homoadamantene⁵ even though these polycyclic substrates would have severe difficulty attaining the 0,0-trimethylene diradical geometry. In the second example, both [C-C/H-C] and [C-C/C-C] rearrangement modes were demonstrated through a carbon-13 labeling experiment.⁵ In simplest form, these isomerization modes correspond to the reactions $1 \rightarrow 2$ and $1' \rightarrow 2'$. Geometrical considerations appropriate to the dehydrohomoadamantane system make a suprafacial, suprafacial reaction stereochemistry seem most plausible.

- (1) M. Trautz and K. Winkler, *J. Prakt. Chem.*, **104** [2], 53 (1922).
(2) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934).
(3) L. S. Kassel, *J. Chem. Phys.*, **1**, 749 (1933).
(4) R. G. Bergman in "Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, and references cited therein.
(5) J. E. Baldwin and M. W. Grayston, *J. Amer. Chem. Soc.*, **96**, 1629 (1974).



These experimental results prompt reconsideration of mechanistic form for such $\sigma_2 + \sigma_2$ cycloreactions ($1 \rightarrow 2$, $1' \rightarrow 2'$; R, R' = H or alkyl), and recognition of the possibility that they may be energetically concerted⁶ isomerizations.

Elongation of a cyclopropane bond causes a monotonic increase in the energy of the ground state configuration (3).⁷ Such bond lengthening is sufficient to make the ground (3) and lowest energy doubly excited (4) configurations comparable in energy; extended



Hückel⁹ and *ab initio* SCF-MO¹⁰ treatments both predict a crossing of these two configurations at an angle θ of 115 to 125°. This circumstance makes configuration interaction necessary for adequate descriptions of the distorted molecule and permits the elongated bond to react as an antisymmetric two-electron component.⁶

One antisymmetric and one symmetric two-electron bond may undergo thermal cycloreaction with suprafacial, suprafacial stereochemistry concertedly. Gaining antisymmetric character through molecular distortions is then the basic prerequisite a cyclopropane C-C bond must satisfy to participate in state-conservative $\sigma_2 + \sigma_2$ cycloreactions when orbital symmetry allowed paths are geometrically awkward and energetically prohibitive. Unconstrained cyclopropanes may gain antisymmetric character in a C-C bond through bond elongation or elongation plus rotations of the terminal methylene moieties.⁹

The same pattern—thermal chemistry with state conservation in energetically concerted processes—may be followed as well in cycloreactions involving cyclopropane C-C bonds and proximate double bonds, such as the vinylcyclopropane to cyclopentene conversion.

The hypothesis advanced here is a new instance of a known phenomenon; an orbital symmetry disallowed reaction may be energetically concerted and state con-

(6) J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forsch.*, **15**, 281 (1970); J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, **5**, 402 (1972).

(7) The single excitation determinant corresponding to a diradical, $\psi = \dots x_2^1 x_3^1$, where the x_i are Walsh orbitals from linear combination of peripheral p atomic orbitals of cyclopropane,^{8,9} is the most significant contributor to the 3B_2 and 1B_2 states.¹⁰ The triplet is comparable in energy to the most stable singlet at $\theta \approx 100^\circ$ and above, while the 1B_2 singlet is of much higher energy than the 1A_1 state at all θ .¹⁰

(8) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(9) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(10) R. T. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, **73**, 1299 (1969). See also A. K. Q. Siu, W. M. St. John, and E. F. Hayes, *J. Amer. Chem. Soc.*, **92**, 7249 (1970); J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. J. Wright, *ibid.*, **94**, 279 (1972); P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *ibid.*, **94**, 638 (1972).