

cyclopropane systems and that [C-C/C-C] cycloreaction modes, though absent in some cases,<sup>14</sup> 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).

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### An Energetically Concerted Reaction Profile for the Thermal Conversion of Cyclopropane to Propene and for Related Cycloreactions

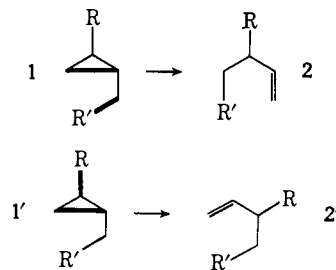
Sir:

Cyclopropane isomerizes thermally to propene.<sup>1</sup> 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 Kistiakowsky<sup>2</sup> 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.<sup>3</sup> 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.<sup>4</sup> 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.

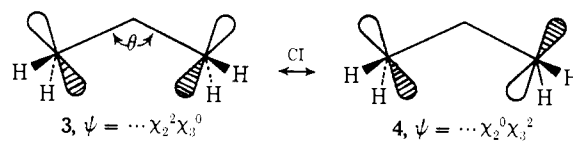
We have found that two conformationally restricted cyclopropanes, 2,4-dehydroadamantane and 2,4-dehydrohomoadamantane, rearrange smoothly in  $\sigma_2 + \sigma_2$  processes to give protoadamantene and homoadamantene<sup>5</sup> even though these polycyclic substrates would have severe difficulty attaining 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.<sup>5</sup> 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 concerted<sup>6</sup> isomerizations.

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



Hückel<sup>9</sup> and *ab initio* SCF-MO<sup>10</sup> treatments both predict a crossing of these two configurations at an angle  $\theta$  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.<sup>6</sup>

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.<sup>9</sup>

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,<sup>8,9</sup> is the most significant contributor to the  $^3B_2$  and  $^1B_2$  states.<sup>10</sup> 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  $\theta$ .<sup>10</sup>

(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).

servative through the consequences of configuration interaction.<sup>6,11-16</sup> It accounts for a variety of thermal structural isomerizations of cyclopropanes in a unified and theoretically plausible way. It does not provide a mechanism for the thermal epimerization of cyclopropanes, a reaction shown by many unconstrained cyclopropanes which is most simply treated as an independent competitive process.<sup>17,18</sup>

**Acknowledgment.** This work was supported by the National Science Foundation and by Hoffmann-LaRoche, Inc., and through partial predoctoral stipend support for M. W. G. by United States Public Health Service Training Grant No. GM-00715.

(11) J. E. Baldwin and A. H. Andrist, *J. Amer. Chem. Soc.*, **93**, 3289 (1971).

(12) W. Schmidt, *Helv. Chim. Acta*, **54**, 862 (1971).

(13) F. S. Collins, J. K. George, and C. Trindle, *J. Amer. Chem. Soc.*, **94**, 3732 (1972).

(14) J. E. Baldwin and J. Ollerenshaw, *Tetrahedron Lett.*, 3757 (1972).

(15) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **94**, 5845 (1972).

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(17) C. Ullenius, P. W. Ford, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **94**, 5910 (1972).

(18) J. E. Baldwin and C. Ullenius, *J. Amer. Chem. Soc.*, **96**, 1542 (1974).

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### Stereoelectronic Control in the Photorearrangement of $\alpha$ -Chloro Ketones. Mechanistic Studies in Organic Photochemistry<sup>1</sup>

Sir:

The current interest in photolysis of organic halides has prompted us to communicate our results on the photochemistry of a series of  $\alpha$ -chloro ketones. Generally, irradiation of  $\alpha$ -halo ketones leads to the photolysis of the carbon-halogen bond.<sup>2-6</sup> Attempted mechanistic rationales have concentrated on two possible modes of C-X bond breaking, (1) homolytic<sup>2,4,5</sup> and (2) heterolytic,<sup>3,5,6</sup> based on the nature of the products obtained (radical abstraction or coupling *vs.* nucleophilic substitution). Recently, examples of intramolecular photorearrangements of  $\alpha$ -halo ketones suggest that bridging occurs between the incipient electron-deficient carbon and a nonconjugated  $\pi$ -system.<sup>5,6</sup>

Four chloro ketones (1-4) were chosen to investigate the influence of aromatic *vs.* double bond participation<sup>7</sup> and the stereoelectronic requirements<sup>8</sup> for rearrange-

(1) For Part X, see R. G. Carlson, R. L. Coffin, W. W. Cox, and R. S. Givens, *J. Chem. Soc., Chem. Commun.*, 501 (1973).

(2) S. J. Cristol and G. C. Schloemer, *J. Amer. Chem. Soc.*, **94**, 5916 (1972).

(3) P. J. Kropp, T. H. Jones, and G. S. Poindexter, *J. Amer. Chem. Soc.*, **95**, 5420 (1973).

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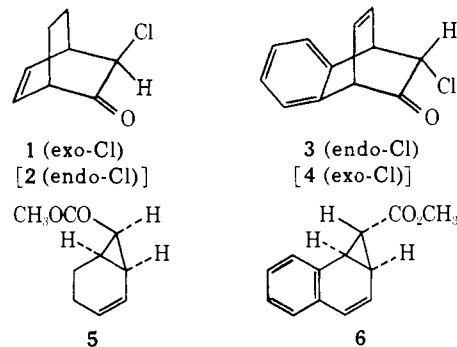
(5) J. C. Anderson and C. B. Reese, *Tetrahedron Lett.*, 1 (1962).

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(8) Kaplan and Hartwig (ref 6) suggested a possible stereoelectronic requirement in the rearrangement of **9** (*vide infra*), but no evidence was provided for it.

ment. Irradiation of *exo*-2-chlorobicyclo[2.2.2]octen-3-one (**1**)<sup>9</sup> in methanol at 300 nm gave *endo*-7-carbomethoxy- $\Delta^2$ -norcarene (**5**)<sup>10</sup> in 55% yield as the only major product.<sup>11</sup> Similarly, photolysis of *endo*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (**3**)<sup>9</sup> gave the  $\Delta^{2,4}$ -norcaradiene rearrangement product **6**<sup>12</sup> in 60% yield

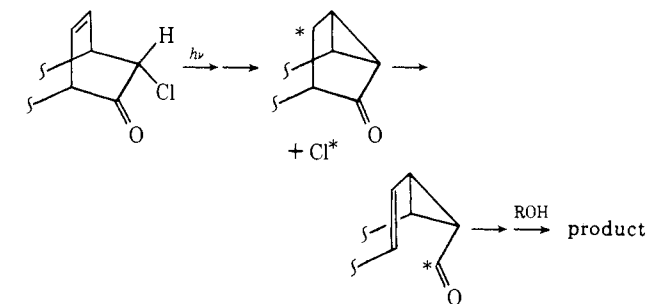


along with minor amounts of naphthalene (**7**, 13%) and methyl 1-naphthylacetate (**8**, 3%).

Contrasting results were found when *exo*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (**4**)<sup>9</sup> was irradiated. The relative yield of the  $\Delta^{2,4}$ -norcaradiene (**6**) dropped significantly to 34% and the naphthyl ester (**8**) yield increased to 26%. Although the  $\Delta^{2,4}$ -norcaradiene remains the major product, the competitive pathway to **8** is of equal importance in this rearrangement. Even more striking are the contrasting results for the *endo* isomer **2** which gave *no*  $\Delta^2$ -norcarene (**5**) under identical conditions.<sup>11</sup>

The major products from chloro ketones **1**, **3**, and **4** probably arise from a carbon skeleton reorganization described in Scheme I. The results from the product

Scheme I. A Possible Rearrangement Pathway for Chloro Ketones **1** and **3**



studies clearly indicate a stereoelectronic influence from the backside of the carbon-chlorine bond by the carbon-carbon double bond at some stage prior to product formation.<sup>13</sup>

Table I gives the results from quantum yield and multiplicity studies of chloro ketones including *exo*-2-chloronorbornenone (**9**).<sup>6</sup> Unfortunately, the *endo* isomer was not studied for comparison of stereoelec-

(9) Synthetic details will be given in our full paper. All new compounds gave satisfactory elemental analyses.

(10) J. A. Berson and E. S. Hand, *J. Amer. Chem. Soc.*, **86**, 1978 (1964).

(11) A number of minor products were detected by vpc. None of these were characterized and were present in less than 10% yield. A substantial amount of polymeric material (ca. 15%) was formed.

(12) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

(13) In the case of chloro ketone **4**, the phenyl ring is probably functioning like the double bonds in **1** and **3**. The lower efficiency of phenyl *vs.* olefin participation is seen in several photochemical studies (for example, see ref 7).