Russell, and D. J. H. Smith, *J. Chem. Soc., Chem. Commun.*, 133 (1975).
(15) Similar observations have been made on the 1,3-dithiane 1-oxide system: F. A. Carey, O. Hernandez, T. C. Taylor, Jr., and R. F. Bryan, *Am. Chem. Soc., Div. Pet. Chem., Prepr.*, **19**, 261 (1974).
(16) On the basis of electric moment measurements, it has been claimed that **7** is *nonplanar:* C. Pigenet, G. Jeminet, and H. Lumbroso, *C. R. Acad. Sci., Ser. C*, **272**, 2023 (1973).
(17) Mean values.
(18) The structural data for **7** may be compared to corresponding data for 2,2-dimethylthietane 1,1-dioxide: S–O 1.459 (4) and 1.452 (4) Å, ∠CSC, 80.20°, ∠OSO, 117.59°; M. L. Ziegler, J. Weiss, H. Schildknecht, N. Grund, and H.-E. Sasse, *Justus Liebigs Ann. Chem.*, 1702 (1973).
(19) J. K. George and C. Trindle, *Int. J. Sulfur Chem.*, **8**, 83 (1973).
(20) National Science Foundation Undergraduate Research Participant, 1975.

Eric Block,* Eugene R. Corey, Robert E. Penn
Terry L. Renken, Paul F. Sherwin[20]
Department of Chemistry, University of Missouri—St. Louis
St. Louis, Missouri 63121
Received March 15, 1976

Thermolysis of Bicyclo[2.2.0]hex-2-ene

Sir:

The cyclodissociation of bicyclo[2.2.0]hex-2-ene[1] (**2ab**, Figure 1) bridges two long studied series of similar reactions. Common to both is a problem still unresolved in any general way. How does molecular strain enhance reactivity when a "least-motion" mechanism is symmetry-forbidden?

Bicyclo[2.2.0]hexane (**1b**) employs its strain to select a symmetry-allowed but otherwise unanticipated ($_{\sigma}2_s + {}_{\sigma}2_a$) path to hexa-1,5-diene.[2] Dewar benzene (**3b**), at least in part, crosses over to the benzene triplet surface.[3] Bicyclo[4.2.0]oct-7-ene (**4a**) is believed to choose a sequence of two symmetry-allowed steps—conrotatory ring opening to the cis-trans diene and then 1,5-hydrogen shift—to provide the isomeric cis-cis diene.[4,5] The more thoroughly investigated cyclodissociation of **1a** to cyclopentadiene[6] remains mechanistically the most obscure.[7]

Our approach, as elsewhere,[2,8] has been to generate a complete list of mechanistic alternatives, both "plausible" and otherwise. Then, through experiment, as many as possible are rigorously excluded.

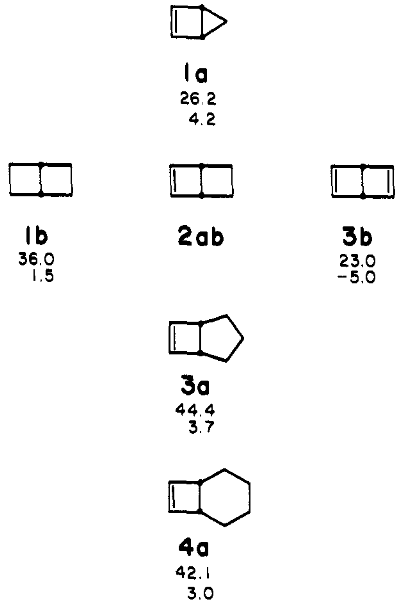


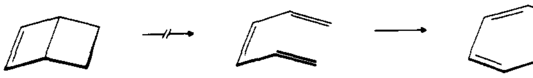
Figure 1. Hitherto available thermolysis $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data.

Table I. Gas Phase (240–420 Torr) Kinetic Data

Temp, °C	10^5k[a]	R factor[b]
102.5	.417 ± 0.006	0.011
110.9[c]	1.06 ± 0.06	0.032
123.4	3.89 ± 0.18	0.019
137.4	20.5 ± 1.0	0.038
151.6[c]	72.8 ± 2.5	0.018
$\Delta H^{\ddagger}$[d]	32.15 ± 0.09	0.071
$\Delta S^{\ddagger}$[d]	2.4 ± 0.2	
E_a[d]	32.95 ± 0.09	0.071
A[d]	(7.4 ± 0.8) × 10^{13}	

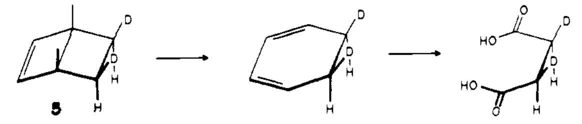
[a] Uncertainties are standard deviations. [b] W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964, p 157. [c] Insensitive to a sixfold increase in surface area. [d] Each set derives from concurrent nonlinear least-squares fitting of integrated GC area ratios obtained at all temperatures between 3 and 87% reaction.

In this case, product analysis (>97% cyclohexa-1,3-diene, uncontaminated by ^{1}H NMR- or GC-detectable impurities) and homogeneous first-order kinetic data (Table I)[9] rigorously excluded many C_6H_8 isomers as potential transient intermediates. Some are already known to provide other products (e.g., $\Delta^{1,4}$-bicyclo[2.2.0]hexene[10]) and/or to react too slowly at these temperatures (e.g., *trans*-hexa-1,3,5-triene,[11] cyclohexa-1,4-diene,[12] bicyclo[2.1.1]-[13] or bicyclo[3.1.0]hex-2-enes,[14] tricyclo[3.1.0.0^{2,6}]-[15] or *anti*-tricyclo[3.1.0.0^{2,4}]hexanes[16]). Still others (e.g., 2-vinylbicyclo[1.1.0]butane, tricyclo[2.2.0.0^{2,6}]hexane) may reasonably be presumed to fall into one or another of these two categories.[25] A particular effort was made to guarantee the absence (<1%) of *cis*-hexa-1,3,5-triene, both in residual reactant and in initial product. Otherwise, the reported rate of its transformation to cyclohexa-1,3-diene (10^5k = 0.22, 25.6 at 100°, 150°)[17] would strongly have implicated mechanism 1.

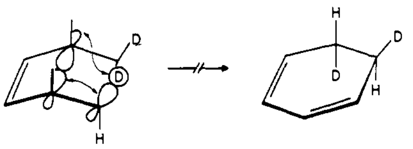


(1)

Next, cyclohexa-1,3-diene-d_2, obtained from the 5-exo,6-exo-d_2 substrate **5**, was oxidized to *meso*-dideuteriosuccinic acid of >95% isotopic and diastereomeric purity. In this way, the absence of the ($_{\sigma}2_a + {}_{\sigma}2_s$) − ($_{\pi}2_s + {}_{\pi}4_s$) variant of eq 1 is

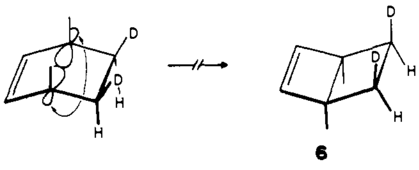


confirmed. More generally excluded is any mechanism that might violate the stereochemical integrity of the two adjacent methylene groups. Among these, eq 2 is analogous to the (more difficult) transformation of bicyclo[2.1.0]pentane to cyclo-

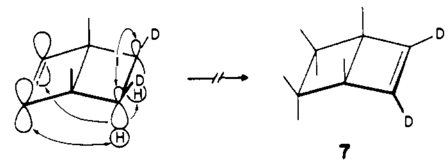


(2)

pentene.[18] Finally, the absence of >1.3% of **6** or of >0.2% of **7** in residual reactant requires that neither eq 3 nor 4 effectively compete with cyclodissociation.[19]

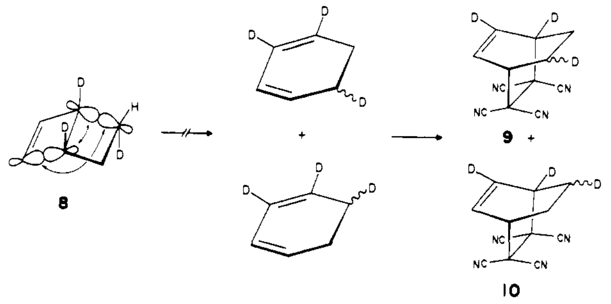


(3)

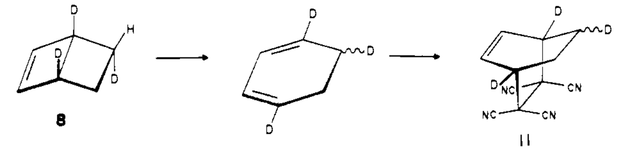


(4)

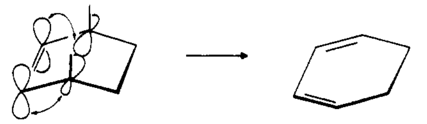
Next excluded were all mechanisms that would retain the central C-C bond and/or destroy one of its two adjacent sp^3-sp^3 C-C bonds (e.g., eq 5[6c,d]). In detail, the cyclohexa-1,3-diene-d_3 obtained from 1,4,5-endo-d_3 precursor **8** was transformed into its tetracyanoethylene adduct—**11**, contaminated with <5% of **9** + **10**.



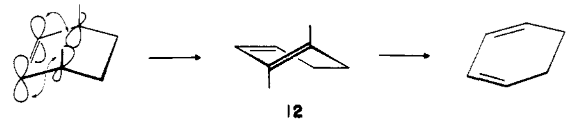
(5)



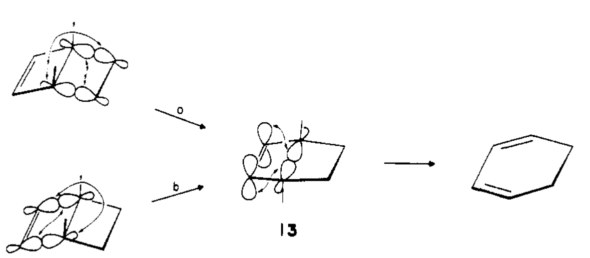
We thus can find no pericyclic alternative to the symmetry-forbidden least motion mechanism 6—but only if the reaction proceeds in a single step.[20] There still remain two as yet unknown C_6H_8 isomers, not excluded as reactive intermediates by any of the data now in hand. The first is the cis-trans isomer of the product **12**,[21,26] most transparently accessible by conrotatory ring opening (eq 7). The second, the trans isomer of the reactant **13**, would need arise in less customary ways. Two symmetry-allowed ones are illustrated in eq 8.



(6)



(7)



(8)

It is, of course, by no means obvious that **12** and **13** are bound states, much less that either one satisfies the necessary thermodynamic prerequisite. (A $\Delta H_f°$ no more than 33 kcal/mol above that of its precursor.) Nevertheless, both alternatives are worth considering if only because they can be tested experimentally—eq 7 by nonsteady state scavenging and eq 8 by isotopic labeling.[22] The data now gathered, we contend, exclude all other possibilities.

Supplementary Materials Available: Two reaction schemes (syntheses of **5** and **8**), five tables of ^{1}H NMR and kinetic data (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. N. McDonald and C. E. Reinecke, *J. Am. Chem. Soc.*, **87**, 3020 (1965); *J. Org. Chem.*, **32**, 1878 (1967).

(2) M. J. Goldstein and M. S. Benzon, *J. Am. Chem. Soc.*, **94**, 5119 (1972); M. J. Goldstein and M. R. DeCamp, *ibid.*, **96**, 7356 (1974), footnote 7.

(3) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3025 (1973).

(4) J. S. McConaghy, Jr., and J. J. Bloomfield, *Tetrahedron Lett.*, 3719 (1969); J. J. Bloomfield and J. S. McConaghy, Jr. *ibid.*, 3725 (1969).

(5) Note, however, that neither the necessity for such an intermediate nor the path for its decomposition was experimentally required in ref 4 nor in related gas phase studies of **3a** or **4a**: G. R. Branton, H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, **62**, 659 (1966); G. R. Branton, H. M. Frey and R. F. Skinner, *ibid.*, **62**, 1546 (1966).

(6) (a) J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968); D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969); (b) J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Am. Chem. Soc.*, **92**, 5249 (1970); (c) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970); J. E. Baldwin and G. D. Andrews, *J. Am. Chem. Soc.*, **94**, 1775 (1972); (d) S. McLean, D. M. Findlay, and G. I. Dmitrienko, *ibid.*, **94**, 1380 (1972); M. C. Flowers and H. M. Fry, *ibid.*, **95**, 5043 (1973); J. I. Brauman, W. E. Farneth, and M. B. D'Amore, *ibid.*, **95**, 5043 (1973); M. J. S. Dewar and S. Kirschner, *J. Chem. Soc., Chem. Commun.*, 461 (1975).

(7) Current theoretical and experimental consensus[6d] ignores a contrary experimental result ("rearrangement *without* hydrogen transfer . . . within . . . 3%")[6b] which has neither been retracted nor confirmed.

(8) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **87**, 1925 (1965); M. J. Goldstein and H. A. Judson, *ibid.*, **92**, 4119 (1970); M. J. Goldstein and M. S. Benzon, *ibid.*, **94**, 7147, 7149 (1972); M. J. Goldstein and W. A. Haiby *ibid.*, **96**, 7358 (1974).

(9) Cf. corresponding data for substituted[9a] and annelated[9b] bicyclo[2.2.0]-hex-2-enes: (a) D. Seebach, *Chem. Ber.*, **97**, 2953 (1964); R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H.-A. Brune, *ibid.*, **98**, 2339 (1965); R. Criegee, G. Bolz, and R. Askani, *ibid.*, **102**, 275 (1969); (b) A. M. Bloothoofd-Kruisbeck, and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas*, **91**, 1364 (1972); H.-D. Martin and M. Heckman, *Angew. Chem.*, **85**, 614 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 573 (1973); *Chimia*, **28**, 12 (1974); R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Slegeir, *J. Am. Chem. Soc.*, **96**, 7581 (1974); H. M. Frey, H.-D. Martin, and M. Hekman, *J. Chem. Soc., Chem. Commun.*, 204 (1975).

(10) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Am. Chem. Soc.*, **93**, 246 (1971); K. B. Wiberg and M. E. Jason, *ibid.*, **98**, 3393 (1976).

(11) S. W. Orchard and B. A. Thrush, *J. Chem. Soc., Chem. Commun.* 14 (1973); *Proc. R. Soc. London, Ser. A*, **337**, 243, 257 (1974); W. E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973).

(12) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 985 (1967).

(13) H. M. Frey, R. G. Hopkins, H. E. O'Neal, and F. T. Bond, *Chem. Commun.* 1069 (1969); H. M. Frey and R. G. Hopkins, *J. Chem. Soc. B*, 1410 (1970).

(14) R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 553 (1966); R. S. Cooke and U. H. Andrews, *J. Org. Chem.*, **38**, 2725 (1973); *J. Am. Chem. Soc.*, **96**, 2974 (1974).

(15) M. Christl, V. Heinemann, and W. Kristoff, *J. Am. Chem. Soc.*, **97**, 2300 (1975).

(16) M. C. Flowers, H. M. Frey, and H. Hopf, *J. Chem. Soc., Chem Commun.*, 1284 (1972); 28 (1973).

(17) K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).

(18) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962).

(19) For analogous processes, cf. ref 2, J. A. Berson, L. D. Pedersen and B. K. Carpenter, *J. Am. Chem. Soc.*, **98**, 122 (1976), and **39** → **40** and **41** → **42** in D. Ginsburg, *Tetrahedron*, **30**, 1487 (1974).

(20) Explicitly neglecting as "intermediates" any that would be experimentally indistinguishable from vibrationally or electronically excited states of reactant or product.

(21) Regarding *cis-trans*-cyclohepta-1,3-diene, cf. ref 15 and K. B. Wiberg and G. Szemies, *Tetrahedron Lett.*, 1235 (1968).

(22) Equation 8a can be excluded through use of a 1,5- or 1,6-labeled precursor; (8b) by 1,2- or 1,3-labeling.

(23) U. S. Public Health Service Trainee 1973–1976.

(24) Undergraduate Research Participant 1973–1974.

(25) The thermal stability of the recently prepared 1,2-diphenyltricyclo[2.2.0.0^{2,5}]hexan-2-ol supports this bias; E. C. Alexander and J. Uliana, *J. Am. Chem. Soc.*, **98**, 4324 (1976).

(26) Cf. *trans*1-Phenylcyclohexene; R. Bonneau, J. Joussot-Dubien, L. Salem, and A. J. Yarwood, *J. Am. Chem. Soc.*, **98**, 4329 (1976).

M. J. Goldstein,* R. S. Leight,[23] M. S. Lipton[24]
Department of Chemistry, Cornell University
Ithaca, New York 14853

Received April 13, 1976