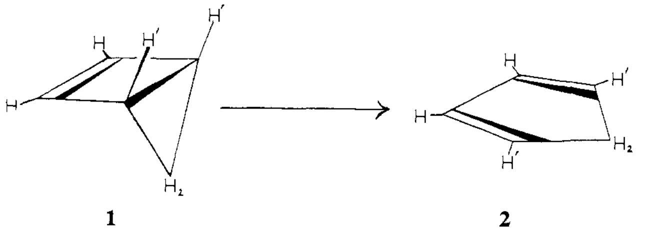
Bicyclo[2.1.0]pent-2-ene. Tests for the Retro-ene Mechanism of Thermal Isomerization[1]

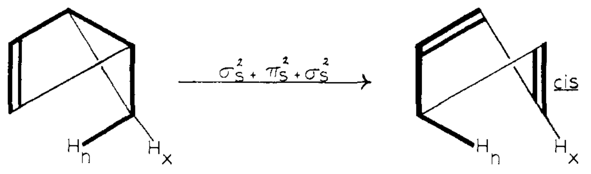
Sir:

The facile thermal conversion of bicyclo[2.1.0]pent-2-ene (**1**) to cyclopentadiene (**2**)[2,3] represents a striking counterexample both to the many unconstrained cyclobutenes which isomerize in the orbital symmetry allowed conrotatory mode[4,5] and to other *cis*-bicyclo-[*n*.2.0](*n* + 3)-enes (where *n* ranges from 2 to 5) which rearrange to 1,3-*cis,cis*-cyclic dienes only under far more stringent conditions.[6] A nonconcerted disrotatory electrocyclic process has been tacitly assumed for the reaction.[2,3,7]



1 **2**

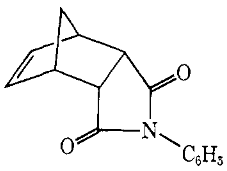
The simplest disallowed, disrotatory model and alternative mechanisms have not been evaluated experimentally. Among these alternative mechanisms, the symmetry-allowed[5] concerted one-step[8] ($\pi_s^2 + \sigma_s^2 + \sigma_s^2$) 1,5-sigmatropic hydrogen-shift process (**3** → **4**), conforming to the standard retro-ene prototype,[9] has been the first examined.



3 **4**

This retro-ene mechanism predicts 2-deuteriocyclopentadiene as product from bicyclopentene-*exo-5-d*, and a primary kinetic isotope effect $k_H/k_D \approx$ 7–12[10] for the endo-*5-d* isomer. The disallowed, disrotatory model, and a number of other mechanisms, would lead exclusively to 5-deuteriocyclopentadiene and would show only small secondary deuterium isotope effects on the reaction rate.

To avoid complications from thermal scrambling of hydrogens in the deuteriocyclopentadiene products,[11] they were trapped and analyzed as the *N*-phenylmaleimide (NPM) adducts (**5**).[12] The rate of isomerization of bicyclopentene did not depend on [NPM]; under the experimental conditions, cyclopentadiene produced through the thermal rearrangement combined bimolecularly with NPM some 10^3 times faster than it would have suffered intramolecular hydrogen migration.[11,13]



5

A mixture of cyclopentadiene-free *exo*- and *endo*-bicyclopentene-*5-d* in tetrahydrofuran was prepared by photolyzing[14,15] cyclopentadiene-*5-d*,[16] adding an excess of NPM to the initially secured mixture of product and unreacted diene, and, after 48 hr at −20°, transferring the volatile product to a second cold trap. The unreacted cyclopentadiene-*5-d* in the photochemical reactor and NPM gave an adduct for nmr analysis: the adduct corresponded to a mixture of 74% *5-d* and 26% *1-d* diene (Table I), indicating some thermal hydrogen scrambling prior to and possibly during the photoisomerization.

Table I. Relative Intensities of Proton Absorption in Adduct **5**

Diene	Type of proton		
	Vinyl (τ 3.70)	Methine (τ 6.55)	Methylene (τ 8.32)
Unlabeled	1.96	4.06	1.98
d_1, from thermal rearrangement	1.93	3.85	1.22
d_1, after photolysis	1.97	3.76	1.26
d_1, calculated for **3** → **4**[a]	1.63	3.76	1.63

[a] For retro-ene process, assuming equal proportions of exo- and endo-*5-d* isomers.

Thermal isomerization of the deuterium-labeled bicyclopentenes (26% *1-d*, 37% *exo-5-d*, 37% *endo-5-d*) at 40° in the presence of excess NPM in dry neutral THF gave adduct **5** which, after thorough purification, was analyzed by nmr spectroscopy. The observed absorption intensities (Table I) indicate rearrangement without hydrogen transfer. The agreement is quantitative, within an estimated 3% error limit.

To complement this result, first-order rate constants for the rearrangement of bicyclopentene and bicyclopentene-d_6[17] were determined in the gas phase at 80°

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[1] Supported in part by National Science Foundation Grant No. GP-9259, Cities Service Oil Co., and the Petroleum Research Fund of the American Chemical Society.

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[4] R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H.-A. Brune, *Chem. Ber.*, **98**, 2339 (1965); G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 5310, 6896 (1968); H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

[5] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[6] Reference 5, p 802 and footnote 16; the temperatures necessary for a half-life of about 2 hr are 50° for bicyclopentene, 195° for bicyclo[2.2.0]hex-2-ene, and 330–380° for the next three members of the series.

[7] E. C. Lupton, Jr., *Tetrahedron Lett.*, 4209 (1968).

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[9] H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

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[11] W. R. Roth, *Tetrahedron Lett.*, 1009 (1964); V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

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[13] J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

[14] J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, **88**, 846 (1966).

[15] A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., submitted for publication.

[16] From sodium cyclopentadienide and succinic acid-*O*-d_2 in D_2O–THF.

[17] The cyclopentadiene-d_6 precursor was obtained following the procedure suggested by C. A. Stewart, Jr.

in a 1 × 10 cm cylindrical quartz cell.[18] The rate constants at 1 and 740 mm are given in Table II. No large primary deuterium isotope effect is observed.

Table II. First-Order Gas-Phase Rate Constants for Bicyclopentene Isomerization

Substrate	$k \times 10^3$, sec$^{-1\,a}$	Pressure, mm^b	No. of runs
H_6C_5	3.7 ± 1.2^c	50–760	*d*
H_6C_5	2.8 ± 0.5	1	7
D_6C_5	1.2 ± 0.3	1	4
H_6C_5	2.8 ± 0.4	740	6
D_6C_5	2.5 ± 0.4	740	3

[a] At 80.0 ± 0.05°. [b] Bicyclic olefin diluted with propane. [c] Probable error. [d] Calculated from data in ref 2 and 3.

The labeling results and the small isotope effect on the rate constant for the isomerization rule out the orbital symmetry allowed retro-ene mechanism for the isomerization. They are consistent with the disrotatory, disallowed "biradical" process and with several other plausible formulations. A distinction among three of these is now being sought through the synthesis and rearrangement of bicyclopentene-*2,3-d*$_2$.

(18) The fair agreement between the present and earlier[2,3] kinetic results for unlabeled bicyclopentene, in spite of a threefold increase in the cell's surface-to-volume ratio, argues against a possible heterogeneous[2,3] process.

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The Microwave Spectrum, Structure, Molecular Dipole and Quadrupole Moments, and Magnetic Properties of Bicyclo[2.1.0]pent-2-ene

Sir:

We have assigned the microwave spectrum of homocyclobutadiene (**1**) and derived some structural information therefrom. We have also measured the electric dipole moment, the molecular *g* values, the magnetic susceptibility anisotropies, and the molecular quadrupole moments.

Bicyclo[2.1.0]pent-2-ene shown in Figure 1 was prepared by a modification of the known procedure[1] and was collected by preparative glpc in a carbon tetrachloride solution of *N*-phenylmaleimide. The sample was distilled directly from the solution at −80° into the microwave absorption cell[2,3] cooled also to Dry Ice temperature. The microwave spectrograph used has been described before[4] and 5-kHz Stark modulation was employed in the present investigation. The technique of searching for absorption lines was similar to that used earlier in our microwave study of cyclopropanone.[5] Bicyclo[2.1.0]pent-2-ene is stable in the waveguide at Dry Ice temperature although it was reported to have a short lifetime in solution at room temperature.[1] An initial assignment of the rotational spectrum of **1** was obtained on the strong $J = 1 \rightarrow 2$, *a* dipole-type transitions by their characteristic Stark effect. The observed and calculated transition frequencies are listed in Table I. A least-squares fit of all observed transition frequencies gives the rotational constants of $A = 10811.65 \pm 0.11$ MHz, $B = 6517.883 \pm 0.0025$ MHz, and $C = 5216.287 \pm 0.0024$ MHz. If we assume the four-membered ring in **1** to be planar as in cyclobutene,[6] the *a* and *c* principal inertial axes would lie in the plane of symmetry of **1**. The *a* axis is tilted about 22° from the plane of the four-membered ring. We were not able to observe the *c*-dipole transitions indicating that $\mu_c < \mu_a$.

Table I. Rotational Transitions in Bicyclo[2.1.0]pent-2-ene

Transition	Obsd ν,^{a} MHz	(obsd − calcd^b)ν, MHz
0_{00}–1_{01}	11734.19	0.02
1_{11}–2_{12}	22166.75	0.01
1_{01}–2_{02}	23214.68	0.06
1_{10}–2_{11}	24769.92	−0.02
2_{12}–3_{13}	33104.42	−0.01
2_{02}–3_{03}	34245.47	−0.01
2_{21}–3_{22}	35202.53	0.02
2_{20}–3_{21}	36159.53	0.00
2_{11}–3_{12}	36977.55	−0.04
4_{14}–4_{13}	12799.54	0.01

[a] Estimated uncertainty: ±0.1 MHz. [b] Calculated from $A = 10811.65$, $B = 6517.883$, and $C = 5216.287$ MHz.

To deduce information on the molecular structure of **1**, initial structural parameters were taken from bicyclo[1.1.0]butane[7] and cyclopentadiene[8] (see also the structures of cyclopentene[9] and cyclobutene[6]). The three-membered ring C–C bond lengths and the dihedral angle between the two ring planes, α, were varied to fit the experimental moments of inertia, giving $R(C_1–C_4)_{bridge} = 1.56$ Å, $R(C_1–C_5) = 1.53$ Å, and $\alpha = 114°$. The calculated moments of inertia in amu-Å^2 are $I_a = 46.70$, $I_b = 77.45$, and $I_c = 96.68$ and can be compared with the experimental values of $I_a = 46.7583$, $I_b = 77.5618$, and $I_c = 96.9153$, also in amu-Å^2 (conversion unit used: 505375 MHz amu-Å^2). The best fit structure is shown in Figure 1.

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(1) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, **88**, 846 (1966); A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., submitted for publication. For this study **1** was prepared by photolysis of cyclopentadiene in 1,4-dioxane followed by preparative glpc on a 5 m × 6 mm 21% β,β'-oxydipropionitrile on an aluminum Chromosorb P column at 25°.

(2) *N*-Phenylmaleimide effectively stabilizes solutions of **1** by removing cyclopentadiene; *cf.* J. E. Baldwin and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **92**, 5247 (1970).

(3) The vapor pressure of **1** at −80° is 45 μ. Reversion of **1** to cyclopentadiene proceeds at a significantly enhanced rate in the brass waveguide above −80° when compared with the rate of isomerization in a quartz vessel.

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