Thermal Unimolecular Decomposition of Bicyclopropyl and Deuterated Analogues: Infrared Photoactivation as a Diagnostic Tool in Mechanistic Organic Chemistry

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The infrared photochemistry of bicyclopropyl yields product mixtures that are not easily rationalized on the basis of the mechanistic scheme suggested by previous pyrolysis work. As a result of this inconsistency the thermal chemistry of bicyclopropyl and analogues deuterated specifically on one ring has been reexamined. A significant new reaction channel involving the chemically activated decomposition of cyclohexene to ethylene and butadiene has been demonstrated. Evidence for the involvement of chemically activated cyclohexene is as follows: (1) isotopic labeling studies implying a symmetric intermediate, (2) a pressure-dependent ratio of cyclohexene to butadiene and ethylene, (3) good agreement between experimental and calculated values for the unimolecular rate constant for retro-Diels–Alder decay of "hot" cyclohexene. A comprehensive mechanism for the unimolecular decay of bicyclopropyl is proposed. The important elements of this mechanism are a single first-formed 1,3 biradical common to all products and the intervention of chemical activation in the generation of several of the secondary products.

Bicyclopropyl (bcp) and related compounds have played an important role in the evolution of unimolecular rate theory through the work of Rabinovitch,[1] Doering,[2,5] and others. We have recently undertaken an examination of the unimolecular reaction of both bcp itself and specifically deuterated analogues using multiphoton IR laser pumping as the activation method. The infrared photochemistry of bcp yields product mixtures that are not easily rationalized on the basis of the mechanistic scheme suggested by previous pyrolysis work.[3] This inconsistency has caused us to reexamine the thermal chemistry of bcp and led to the elucidation of a reaction pathway not evident from previous data. In this paper we describe that pathway and discuss the thermal chemistry of bicyclopropyl and an analogue with deuterium specifically incorporated on one ring. The details of the infrared photochemistry of these compounds will be described elsewhere.[4]

The thermal unimolecular chemistry of bicyclopropyl was first reported by Flowers and Frey in 1962.[3] The bcp decomposition is complicated by secondary reaction of the primary products. This results in a complex product mixture which Flowers and Frey reported to contain at least 17 products. We have made a thorough effort to identify the major primary and secondary products of the unimolecular decay of bcp. Isotopic labeling and pressure dependences have been used to investigate the role of chemical activation in the overall mechanism of this reaction. In combination these data lead to a considerable simplification of the problem. A mechanism is proposed that can rationalize all of the products based on a single primary step, C(1)–C(2) [or C(1)–C(3)] bond cleavage, followed by competitive rearrangements.

This mechanism differs from that previously suggested[3] in two important respects: (1) no C(2)–C(3) bond cleavage pathways are required; (2) a new route to ethylene and butadiene via chemically activated cyclohexene is implicated.

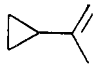
Results and Discussion

Irradiation of 0.20 torr of bicyclopropyl with the loosely focused beam of a Lumonics TEA-101-CO_2 laser leads to the formation of a complex product mixture. Reaction conditions were typical for experiments of this kind.[4] The observed products and the relative percentages of each as determined by GC integration are listed in Table I. All products have been identified by coinjection of known materials and by comparison of GCFTIR spectra with those of the knowns. By these techniques it was also established that **1**–**6** were not present in the mixture.

Table I. Product Distribution from IR Laser Photodecomposition of Bicyclopropyl

GC rel[a] retention time	product[b]	integ,[c] %
1.00	ethylene	19
1.08	acetylene	2
1.35	1-butene	6
1.54	1,3-butadiene	18
3.00	1,5-hexadiene	1
3.25	3-methylcyclopentene	7
3.85	*trans*-1,4-hexadiene	2
4.04	*cis*-1,4-hexadiene	2
4.21	allylcyclopropane	3
5.13	1,3-hexadienes	10
6.00	bicyclopropyl	
6.71	*trans,trans*-2,4-hexadiene	8
7.29	*cis,trans*-2,4-hexadiene	14
7.85	*cis,cis*-2,4-hexadiene	7

[a] From a 10-ft 10% DNP + 10-ft 22% β,β′-oxydipropionitrile on Chrom W-AWAS column, 55 °C, 27 mL/min; at least five other products were present in < 0.5% each. Cyclohexene has a relative retention time of 6.93 under these conditions. [b] Coinjection and GCFTIR spectral comparison with known. [c] GC integration, corrected for detector response for C_2 vs. C_4 vs. C_6, a common response factor assumed for all C_6 materials. Complete GC data are available as supplementary material.



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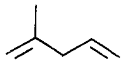

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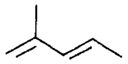

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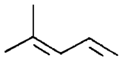

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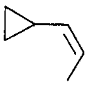

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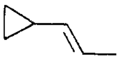

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Most of the observed products are consistent with previous pyrolysis work on bicyclopropyl. For example,

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[1] (a) Rynbrandt, J. D.; Rabinovitch, B. S. *J. Phys. Chem.* **1970**, *74* 4175. (b) Rynbrandt, J. D.; Rabinovitch, B. S. *J. Chem. Phys.* **1971**, *54*, 2275.

[2] Avery, N., Thesis, Harvard University, 1972.

[3] Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1962**, 1689.

[4] Farneth, W. E.; Thomsen, M. W. *J. Am. Chem. Soc.*, in press.

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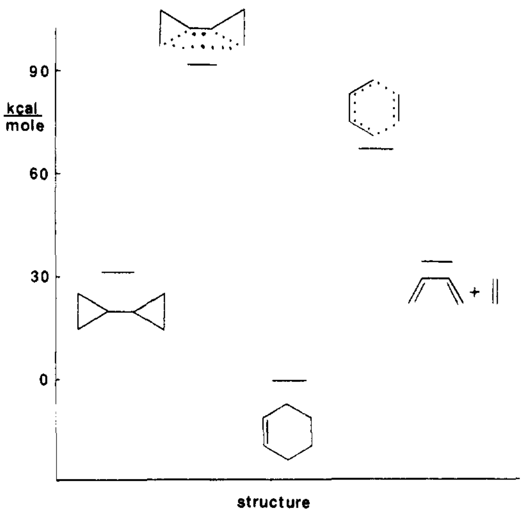

Figure 1. Relative enthalpies of bicyclopropyl, cyclohexene, and ethylene + butadiene and the transition states for their interconversion: ΔH_f for bicyclopropyl from ref 7a, ΔH_f for cyclohexene, butadiene and ethylene from ref 7b, $\Delta H^{\ddagger}$ from bicyclopropyl from ref 3, and $\Delta H^{\ddagger}$ from cyclohexene from ref 14.

primary pathways to allylcyclopropane and ethylene and butadiene were proposed, and these products are among the major ones in laser photolysis as well. Both activation techniques led to the formation of a variety of C_6 dienes. The major surprise in the laser chemistry was the absence of cyclohexene among the products under any conditions. Cyclohexene was obtained as a primary thermal product by Flowers and Frey and was reported to be a principal product in the chemically activated (:CH_2 + vinylcyclopropane) decomposition of bcp by Doering and Gilbert.[5] The absence of cyclohexene in the infrared photochemical reaction mixture suggested that at the high average excitation energies and low pressures characteristic of this activation method, cyclohexene undergoes further reaction.[6] Specifically, we felt our data could best be explained by a retro-Diels–Alder pathway to ethylene and butadiene from "hot" cyclohexene formed in a primary step. This pathway should also exist in the thermal experiment. Accordingly, the pyrolysis of bcp was reexamined with a particular eye toward two aspects of the Flowers and Frey mechanism that seemed at odds with the IR photochemistry. These were: (1) the existence of parallel reaction channels requiring either C(1)–C(2) or C(2)–C(3) bond cleavage, and (2) the origin of ethylene and butadiene in a direct reaction channel from bcp.

Figure 1 shows a schematic potential energy surface for the proposed chemical activation pathway to ethylene and butadiene. In the thermal reaction, cyclohexene, at the instant of its formation, would contain internal energy equal to $\Delta H_1 + \Delta H_1^{\ddagger} + E(T)_{\text{internal}}$, where ΔH_1 is the exothermicity of the bcp to cyclohexene reaction (~31 kcal/mol),[7] $\Delta H_1^{\ddagger}$ is the activation enthalpy (~60 kcal/mol),[3] and $E(T)_{\text{internal}}$ is the excess energy of the average reacting bcp above the barrier. Even without excess internal energy, Figure 1 shows that the sum of ΔH_1 and $\Delta H^{\ddagger}$ provides the first-formed cyclohexene with energy well in excess of that required for the retro-Diels–Alder reaction. Thus, chemically activated unimolecular decay of cyclohexene could compete with deactivation by energy transfer to bath gas molecules. If this reaction channel were operative in the pyrolysis experiments, the activation parameters determined by Flowers and Frey for what they presumed to be a "direct" channel from bcp to ethylene and butadiene would be meaningless.

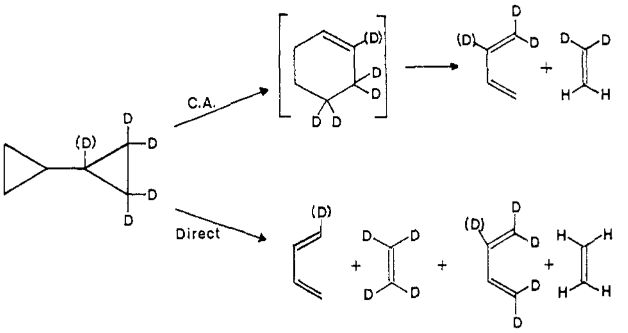

Figure 2. Possible reaction channels to butadiene and ethylene from deuterated bicyclopropyl.

Although no effort has been made to accurately determine the kinetic parameters for the thermal reaction of bcp, our results are in good agreement with previous work. Thus, under static pyrolysis conditions at 394 °C and for a 7.5-h pyrolysis time, 48% reaction occurs. The prediction from published Arrhenius parameters would be 47%.[3] The GC trace for a typical thermal product mixture is similar to that for the IR photochemistry. The principal differences between the infrared photochemical product mixture (Table I) and the thermal product mixture are the appearance of cyclohexene in the pyrolysis accompanied by decreases in butadiene and ethylene and an increase in allylcyclopropane. An interesting feature of the C_6 product mixture in each case is the absence of either branched dienes or of 2-cyclopropylpropene. These products would be expected from cleavage of the 2,3-bond of a cyclopropane ring, and their absence suggests that mechanisms involving cleavage of the 1,2-bond predominate.

The pyrolysis of a sample of bicyclopropyl specifically deuterated on one cyclopropane ring has been carried out to distinguish the direct production and "hot" cyclohexene routes to butadiene and ethylene. The labeled material contained 90% D at carbons 2 and 3 of one ring and 43% D at C-1. The label distribution has been determined by a combination of mass spectroscopy and ^{1}H and ^{2}H NMR.[4,25] The contrasting predictions of the two mechanisms are illustrated in Figure 2. If these products result from splitting out a C_2H_4 or C_2D_4 unit from one cyclopropane ring (direct, Figure 2), then the product pairs ethylene-d_0/butadiene-$d_{4,5}$ and ethylene-$d_{4,3}$/butadiene-$d_{0,1}$ would be expected. However, if ethylene and butadiene result from decomposition of "hot" cyclohexene (C.A., Figure 2), then only ethylene-$d_{1,2}$ and butadiene-$d_{2,3}$ will be produced.

Effluent from the flow pyrolysis of bicyclopropyl-$d_{4,5}$ was trapped at −195 °C and warmed to −78 °C in the side arm of a gas IR cell.[8] The fraction of products with appreciable vapor pressure at this temperature was analyzed by Fourier transform IR spectroscopy and gas chromatography. The infrared spectrum of this vapor-phase mixture (1000–680 cm^{-1}) is shown in Figure 3. Both in this spectrum and in the spectra of IR photolysis mixtures treated similarly the major peaks are at 943 and 752 cm^{-1} in excellent agreement both with literature values[9] and absorptions of authentic

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(5) Doering, W. v. E.; Gilbert, J. C.; Leermakers, P. A. *Tetrahedron* **1968**, *24*, 6863.

(6) Farneth, W. E.; Thomsen, M. W., Schultz, N. L.; Davies, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4001.

(7) (a) Beezer, A. E.; Luttler, W.; de Meijere, A.; Mortimer, C. T. *J. Chem. Soc.* **1966**, 648. (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(8) Conditions: ~10 torr, 723 K, and 17-s residence time. The half-life of cyclohexene at this temperature is approximately 6 h.

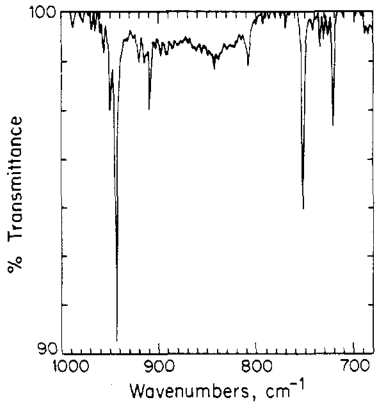

Figure 3. IR spectrum (1000–680 cm^{-1}) of volatile material from bicyclopropyl-$d_{4,5}$ pyrolysis.

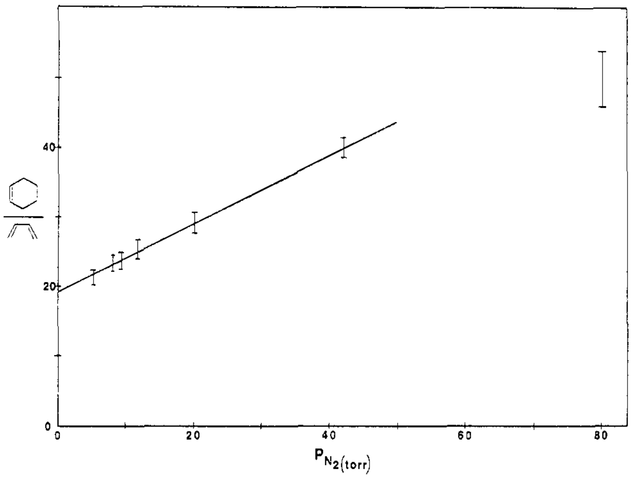

Figure 4. Pressure dependence of the cyclohexene/butadiene ratio.

samples of ethylene-d_2. There is some ambiguity in the assignment of the subsidiary peaks in this spectrum. Butadienes are present as indicated by characteristic butadiene-*1,1*-d_2 absorptions at 940, 910, and 734 cm^{-1}.[10] Butadiene-*1,1,2*-d_3 may also contribute to the peaks at 910 and 720 cm^{-1}.[11] The 720-cm^{-1} peak decreases in intensity with decreasing temperature of the side arm roughly in concert with that at 910 cm^{-1} and more rapidly than the ethylene bands at 943 and 752 cm^{-1}. Small amounts of butadiene-*1,1,4,4*-d_4 (728, 955 cm^{-1}) and undeuterated butadiene (907.8 and 1013 cm^{-1}) are possibly present.[12,13] The peak at 808 cm^{-1} is unambiguous evidence for ethylene-*d*, as expected from starting material incompletely deuterated at C-2.[9] Ethylene-*d* also absorbs at 950 cm^{-1}, and this peak is most likely a combination of ethylene-*d* and undeuterated ethylene. It is possible that some ethylene-d_4 is present since its characteristic absorption in this region is at 720 cm^{-1}.[9] This data constitutes strong evidence that the principal route to ethylene and butadiene under these conditions yields ethylene-$d_{1,2}$ and butadiene-$d_{2,3}$ via an intermediate that has the symmetry of cyclohexene.

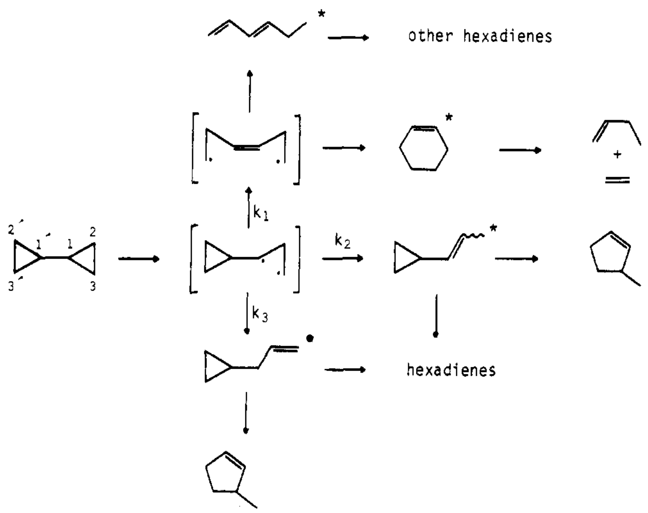

Figure 5. Hypothetical reaction scheme for thermal decomposition of bicyclopropyl.

A relationship between cyclohexene and ethylene and butadiene can be established by examining the pressure dependence of the pyrolysis product mixture.[14] Reactions were carried out in a static reaction vessel at 670 K by using 3.0 torr of bcp and variable pressures of nitrogen as bath gas. The data are plotted in Figure 4 as [cyclohexene]/[1,3-butadiene] vs. P_{N_2}. The increased yield of cyclohexene at the expense of butadiene at higher pressures is consistent with the chemical activation scheme. As expected, ethylene and butadiene change uniformly, and an identical plot could be generated for [cyclohexene]/[ethylene]. The least-squares fit to the data below 50 torr yields a slope of 0.50 torr^{-1} and an intercept of 19 (r = 0.99). There may be a deviation from this line at higher pressures although the limited high-pressure data are not conclusive. On the basis of the presumption that all butadiene arises from hot cyclohexene, the expected ratio of cyclohexene to butadiene is given by eq 1, where

$$\frac{[\text{cyclohexene}]}{[\text{1,3-butadiene}]} = \frac{\displaystyle\int_{E=E_0}^{\infty} \frac{k_d(E)[N_2] + k_d(E)[\text{bcp}]}{k_{UNI}(E) + k_d(E)[N_2] + k_d(E)[\text{bcp}]} f(E)\,dE}{\displaystyle\int_{E=E_0}^{\infty} \frac{k_{UNI}(E)}{k_{UNI}(E) + k_d(E)[N_2] + k_d(E)[\text{bcp}]} f(E)\,dE} \tag{1}$$

$k_{UNI}(E)$ is the first-order rate constant for unimolecular decay of hot cyclohexene, the $k_d(E)$ are second-order rate constants for collisional deactivation via energy transfer to bath gas M, and $f(E)$ is the energy distribution function for "hot" cyclohexene. This expression can be simplified and used to make a semiquantitative determination of the suitability of this mechanism for rationalizing the pressure dependence of the product ratio. Assuming all "hot" cyclohexene molecules react with an identical total energy and that every collision leads to deactivation, eq 1 becomes eq 2, where $k_{UNI}\langle E\rangle$ is the unimolecular decay rate at the

$$\frac{[\text{cyclohexene}]}{[\text{1,3-butadiene}]} = \frac{k_{coll}[\text{bcp}]}{k_{UNI}\langle E\rangle} + \frac{k_{coll}[N_2]}{k_{UNI}\langle E\rangle} \tag{2}$$

average energy $\langle E\rangle$ and k_{coll} are collision rate constants for gas M. Since at constant concentration of bcp the first

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[9] (a) Rochkind, M. M. *Anal. Chem.* **1968**, *40*, 762. (b) Pinchas, S.; Laulicht, I. "Infrared Spectra of Labelled Compounds"; Academic Press: London, 1971; p 85 and references therein.

[10] Hill, E. A. *J. Am. Chem. Soc.* **1972**, *94*, 7462.

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[12] Shimanouchi, T. "NBS Tables of Molecular Vibrational Frequencies"; National Bureau of Standards: Washington, DC, 1980; Vol. 1, pp 205, 207, 208.

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[14] Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: London, 1972; Chapter 8.

term of eq 2 is constant, the slope of the plot in Figure 5 may be interpreted as $k_{\mathrm{coll}}/k_{\mathrm{UNI}}\langle E\rangle$. k_{coll} calculated for collision with N_2 by standard methods is 7.8×10^6 s^{-1} $torr^{-1}$,[15] giving $k\langle E\rangle = 1.6 \times 10^7$ s^{-1}. A consistent value of $k_{\mathrm{UNI}}\langle E\rangle$, 4.1×10^6 s^{-1}, may be obtained from the intercept by using a calculated value of the collision rate for bcp.[15] The difference of a factor of 4 between these two numbers can be understood on the basis of more efficient collisional deactivation by bicyclopropyl than N_2. The strong collision assumption more seriously overestimates the rate of deactivation by N_2 and, therefore, artificially inflates $k_{\mathrm{UNI}}\langle E\rangle$ calculated from the slope. Data for methyl isocyanide deactivation suggest that approximately a factor of 3 might be anticipated in the relative deactivation efficiencies of these two bath gases.[15]

RRKM theory has been shown to predict rate constants for chemical activation processes in excellent agreement with experimental data.[14] We have used quantum RRK (QRRK) theory, a less rigorous but within the constraints of this work more than adequate alternative to RRKM, to calculate a rate of 1.0×10^7 s^{-1} for the chemically activated cyclohexene decomposition. The calculation is based on the QRRK expression in eq 3, where $A = 10^{15.3}$

$$k\langle E\rangle = A\frac{\Gamma(n+1)\,\Gamma(n-m+s)}{\Gamma(n-m+l)\Gamma(n+s)} \tag{3}$$

s^{-1} (the thermal A factor), $s = 42$ (the total number of internal degrees of freedom in cyclohexene), and $m = 19.22 = E_0/h\nu$ (where E_0 is the reaction threshold in kcal/mol[16] and $\nu = 1216$ cm^{-1} is the geometric mean of the cyclohexene vibrational frequencies[17]), and $n = 33.55 = E^*/h\nu$ (where E^* is the total average energy of "hot" cyclohexene reactants: $E^* = \Delta H_1 + \Delta H_1^{*} + E(\mathrm{T})_{\mathrm{internal}}$, as discussed earlier with respect to Figure 1). The internal energy is calculated from the vibrational heat capacity of bicyclopropyl at 675 K, estimated by using group additivity values.[18] The reasonable agreement between experimental and theoretical values for this rate constant provides further evidence that a reaction pathway to butadiene and ethylene via hot cyclohexene is the principal pathway operative under these conditions.

All of our data for both the pyrolysis and the IR photolysis of bicyclopropyl at pressures below 50 torr can be rationalized by the mechanism shown in Figure 5. The important elements of this mechanism are (1) a single first-formed biradical common to all products and (2) the intervention of secondary reaction along all the reaction channels. In the IR photoactivation these secondary reactions are all chemically activated. In reexamining the pyrolysis we have concentrated on the channel leading to ethylene and butadiene and demonstrated that even under thermal activation conditions these products arise predominantly from chemically activated cyclohexene. The evidence for involvement of chemically activated cyclohexene is as follows: (1) isotopic labeling studies implying a symmetric intermediate; (2) a pressure-dependent ratio of cyclohexene to butadiene plus ethylene; (3) good agreement between experimental and calculated values for the unimolecular rate constant for retro-Diels-Alder decay of "hot" cyclohexene.

Experimental Section

Bicyclopropyl was prepared from vinylcyclopropane[19] as follows.

Preparation of 2,2-Dibromobicyclopropyl (2,2-Br_2-BCP). The synthesis of 2,2-Br_2-BCP was accomplished by use of the procedure developed by Roth et al.[20] Potassium *tert*-butoxide (6.72 g, 0.060 mol) was suspended in 25 mL of pentane and cooled to −20 to −10 °C. To this suspension was added 3.4 g (0.050 mol) of vinylcyclopropane. A solution of 13.9 g (0.055 mol) of bromoform in ~10 mL of pentane was then added in a dropwise fashion over a 4–8-h time period so as to prevent the temperature from exceeding −10 °C. After the addition was complete, the reaction mixture was stirred for 20–24 h at room temperature.

Extraction with pentane, drying with magnesium sulfate, and removal of solvent gave combined fractions boiling between 75 and 84 °C at a pressure of 14–20 mmHg (lit. bp 76 °C (14 mmHg).[20] Yields were 51 ± 3%: ^1H NMR ($CDCl_3$) δ 0.50 (5 H, m), 1.5 (3 H, m); IR (liquid) 3110, 3030, 2945, 2870, (3110–2870, C–H stretches), 1475, 1445, 1420, 1390, 1300, 1210, 1180, 1125, 1080, 1060, 1040, 1010 (1080–1010, cyclopropane rings), 925, 865, 700 (CBr), 670 cm^{-1} (CBr); mass spectrum (electron impact, 70 eV), *m/e* (relative intensity) 242 (0.4, M^+), 240 (0.8, M^+), 238 (0.4, M^+), 214 (1.6, $C_4H_4Br_2$, $M^+ - 28$), 212 (4.2, $M^+ - 28$), 210 (1.9, $M^+ - 28$), 201 (18.9, $C_3H_3Br_2^+$), 199 (36.5), 197 (18.4), 188 (0.7, $C_2H_2Br_2^+$), 186 (1.6), 184 (0.7), 161 (2.9, $M^+ - Br$), 160 (0.7, $M^+ - HBr$), 159 (2.6, $M^+ - Br$), 158 (0.6, $M^+ - HBr$), 146 (1.9, $C_5H_5Br^+$), 144 (1.2, $C_5H_5Br^+$), 133 (2.5, $C_4H_4Br^+$), 131 (2.8, $C_4H_4Br^+$), 131 (1.7, $C_3H_4Br^+$), 119 (2.9, $C_3H_4Br^+$), 77 (16.0, $C_6H_5^+$), 67 (2.5, $C_5H_7^+$), 55 (5.0, $C_5H_7^+$), 54 (100.0, $C_4H_6^+$), 53 (5.2).

Preparation of Bicyclopropyl (BCP). A 25 mL flask purged with nitrogen was charged with 8.09 g (0.0278 mol) of tri-*n*-butyltin hydride[21] and then cooled with an ice/water bath. 3.03 g 2,2-Br_2-BCP (3.03 g, 0.0126 mol) was added to the tin hydride over 30 min, the cooling bath was removed, and the reaction mixture was stirred for 6 days. The bcp was removed from the mixture by standard vacuum line transfer techniques and then distilled for purification. The yield was 25% with a purity of 95+%. The crude material was purified by preparative gas chromatography: bp 76 °C (lit. bp 76.0–76.1 °C); ^1H NMR ($CDCl_3$) δ 0.10 (4 H, m), 0.30 (4 H, m), 0.80 (2 H, m); IR (gas phase, 5.0 torr) 3090, 3020, 1470, 1430, 1360, 1300, 1180, 1100, 1025 (cyclopropane ring), 970, 880, 820, 690, 620 cm^{-1}; mass spectrum (electron impact, 70 eV) *m/e* (relative insity) 82 (11.2, M^+), 81 (12.2), 67 (100), 55 (8.4), 54 (95.3), 43 (11.7), 41 (54.4), 39 (38.3).

Deuterated bicyclopropyls were prepared analogously. Deuterium was introduced by successive exchanges of cyclopropyl methyl ketone with 0.1 M sodium carbonate in D_2O. The Bamford–Stevens reaction on the tosylhydrazone of this substrate led to deuterium incorporation at all three olefinic positions in vinylcyclopropane due to the dedeuteration of the starting material by the intermediate vinyl anion. The terminal olefinic position was essentially completely deuterated, and the nonterminal position contained 48.4 ± 8.5% deuterium. Attempted preparation of vinylcyclopropane via the Shapiro modification[23] was not successful. Tri-*n*-butyltin deuteride[24] was used in place of the hydride in the reduction of dibromobicyclopropyl. Deuterium contents and distributions at every stage of the preparation were determined by a combination of ^1H NMR, ^2H NMR, ^{13}C NMR, and mass spectroscopy. Details of the spectral analysis are available.[4,25] The reduced data follow.

Cyclopropyl methyl-d_3 ketone: 96% deuterium at methyl, 0% deuterium elsewhere.

Vinylcyclopropane-d_2 and -d_3: 89% deuterium at C-1, 43% deuterium at C-2.

2,2-Dibromobicyclopropyl-d_2 and -d_3: 86% deuterium at C-3, 41% deuterium at C-1.

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Bicyclopropyl-d_4 and -d_5: 90% deuterium at C-2 and C-3, 43% deuterium at C-1.

Pyrolysis Experiments. The pyrolysis of bcp was carried out under both flow and static conditions. The flow pyrolysis apparatus consisted of a thermostated oven and a quartz tube previously washed with alcoholic potassium hydroxide. The pyrolyses were accomplished by attaching two reservoirs to the ends of the quartz pyrolysis tube. One reservoir served as a collection vessel for the products and the other served to contain the compound to be pyrolyzed. In a typical experiment material was transferred to a reservoir on the vacuum line by using standard techniques. The vessel with the substrate was attached to the pyrolysis tube and the system evacuated while the substrate was kept at a temperature of 77 K. When the pressure was reduced to a desirable level (i.e., 5–10 torr), the liquid nitrogen bath was removed from the reservoir with the material to be pyrolyzed and used to cool the collection reservoir.

Static pyrolyses were accomplished by depositing a known quantity of bcp into a glass tube (previously washed in alcoholic potassium hydroxide and thoroughly dried) by standard vacuum line transfer methods. The compound was condensed with liquid nitrogen and the tube sealed with a torch. If a bath gas, such as nitrogen or argon, was to be used, it was added to the tube just prior to sealing it. To perform the actual pyrolysis, we placed the sealed tubes in a "bomb". The temperature was determined either by using a thermocouple or by pyrolyzing a compound with well-defined Arrhenius parameters (i.e., vinycyclopropane).

Conventional infrared spectra of compounds were obtained by using a Beckman infrared spectrometer. Fourier-transform infrared spectroscopy (FTIR) was accomplished by using either a Digilab FTS-10 or FTS-20 spectrometer.

Nuclear magnetic resonance experiments were done with a Varian CFT-80 NMR spectrometer to obtain proton NMR data. For carbon-13 and deuterium NMR experiments a Varian XL-100 was used.

Mass spectral analyses were done by using a Hitachi RMU6 electron-impact mass spectrometer, a Finnigan 4000 chemical ionization/electron-impact mass spectrometer, or an AEI-MS30 spectrometer. High-resolution mass spectral data were obtained by using the AEI-MS30.

Product distribution and yields were ascertained by flame-ionization gas chromatography with a Varian Model 2400 gas chromatograph equipped with a gas-sample injection valve. The GC column used for these analyses consisted of a 10 ft × $^1/_8$ in. o.d. stainless steel column packed with 10% dinonyl phthalate on Chromosorb W-AWAS (Supelco, Inc.) connected in series with a 20 ft × $^1/_8$ in. o.d. stainless steel column packed with 20% β,β'-oxydipropionitrile. Typically flow rates of 30 ± 1 mL/min and column temperatures of 55–65 °C were employed.

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Registry No. Bicyclopropyl, 5685-46-1; 2,2-dibromobicyclopropyl, 22975-42-4; vinylcyclopropane, 693-86-7; bromoform, 75-25-2; cyclohexene, 110-83-8.

Supplementary Material Available: Complete GC data for the pyrolysis mixture, showing typical resolution and unidentified minor components (1 page). Ordering information is given on any current masthead page.

Unusual Secondary to Primary System Rearrangement via Ring Opening of 1-(3-Halopropylene)-4-methoxybenzenium Ions

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The effect of electron-withdrawing groups on the ring opening of benzenium ions has been investigated by kinetics, equilibrium studies, and product analysis. The use of SnX$_4$ (X = Br or Cl) compounds as highly ionizing solvents and as conveying agents of the X$^-$ nucleophile works quite well. 1,2-Dihalo-3-(4-methoxyphenyl)propanes (**2**; X = Br or Cl) and 1,3-dihalo-2-(4-methoxyphenyl)propanes (**3**; X = Br or Cl) equilibrate at 100 °C in SnX$'_4$ (X$'$ = Br or Cl) when X = X$'$; they undergo halogen exchange with partial rearrangement (**2** → **3** and **3** → **2**) when X $\neq$ X$'$. This **2** → **3** rearrangement is very unusual in benzenium ion chemistry and yields primary halide products. For X = X$'$, the **3** to **2** equilibrium constant K is 10.1, whatever the halogen; the forward rate constants k_{32} are 1.82×10^{-5} and 1.86×10^{-4} s^{-1} for X = Br and Cl, respectively. For X $\neq$ X$'$ (X = Br, X$'$ = Cl), as well as for mixed compounds containing both halogens, the relative proportions of rearranged and unrearranged products have been examined in terms of the evolving reactions. Results indicate a mechanism involving 1-(3-halopropylene)-4-methoxybenzenium ions which, when they react with solvated halide ions, yield a mixture of 1,2- and 1,3-dihalides in equal amounts. This absence of ring-opening regioselectivity which contrasts with that of usual unsubstituted propylenebenzenium ions is attributed mainly to the electron-withdrawing effect of the halogen. Benzenium ion involvement in nucleophilic substitution can bring about significant rearrangement in secondary compounds containing electron-withdrawing groups.

The involvement of an aromatic ring leading to a bridged benzenium ion has been demonstrated in the solvolysis of primary and secondary alkyl tosylates with β-aryl substituents.[1-3] Over the last few years, these reactions have been interpreted in terms of competition between the formation (reversible at times) of these intermediate species and bimolecular solvolysis, and many papers deal with the contributions of these two pathways.[4-12] In one

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