have produced a nonlinear trend of α vs. percentage of **2**.

Acidic workup of the mixture of LPL irradiation, followed by TLC separation, afforded (+)(1*S*)-**7** (Scheme III). According to previous discussions, this leads to the (1*R*,5*R*) configuration for (+)-**2** (Scheme III).

Therefore, the whole body of the above results shows that, for our irradiation times, **1** → **2** is the only process which occurs. This involves chirality transfer from **1** to **2**, resulting in optical rotations and dichroism values of opposite signs for **1** and **2**.[14] As we have measured $\alpha_{total} = 0$ for $c^1/c^2 \simeq 40/60$ (Figure 3), the ratio of specific rotations between enantiomerically enriched **1** and **2**, which has received chirality from **1**, must be ca. 60/40.

III. Conclusions

The successful application of the partial resolution of racemates with CPL presented here owes much to recent innovations in instruments. In fact, the high sensitivity of modern dichrographs, together with the special features of the linearly polarized UV laser light, which is ideally suited to circular polarization, have been indispensable tools. They made possible, in fact, the production of optical activity at a sufficiently high, and strictly controlled level, and to detect it with great accuracy. This was needed in order to carry out our treatment leading to chiroptical data which enabled us to solve stereochemical problems for both molecules (even labile ones) and reactions.

Various alternative modern techniques are available to produce optical activity much more effectively, and to measure the enantiomeric composition of the optically active mixture. However, our technique surpasses all other ones in one respect. In our technique, in fact, the intrinsic molecular spectroscopic dissymmetry (e.g., $\Delta\epsilon$) and the observed dissymmetry of the products (e.g., $\delta\epsilon$) are, conceptually, most directly connected together.

Our technique and the instruments used here are capable to deal with a large variety of compounds. The extension to chromophores absorbing at wavelengths shorter than 300 nm needs to exploit other suitable laser sources, perhaps an excimer laser or a frequency-multiplied neodymium laser.

As a divertissement regarding the n → π^* transitions with enones and ketones, the optical rotation is determined by the n → π^* dichroism totally with compound **8**, only partially with both **1** and **2**, while with **7** there is an overriding contribution by more energetic dichroic bands, probably the $\pi \rightarrow \pi^*$ band. The octant rule[5] can be applied with little confidence to enones.[1] However, in the case of **7**, the use of polarimetric data in combination with the octant rule would lead, in any case, to erroneous results so that either CD or ORD data are required.

IV. Experimental Section

General. UV and IR spectra were taken with respectively Pye-Unicam SP8 150 and Perkin-Elmer 337 spectrometers. ^{1}H NMR spectra were taken with a Varian 360 spectrometer at 60 MHz in CDCl$_3$–(CH$_3$)$_4$Si

and chemical shifts are given in δ (ppm) with respect to internal (C-H$_3$)$_4$Si. Polarimetric measurements were carried out on a Perkin-Elmer 141 polarimeter, with a cell of 10 cm optical-path length. CD spectra are from a Jasco J 500C spectropolarimeter. LPL was obtained from a Spectraphysics 171-19 Ar ion, continuous wave laser, using both the 350- and the 363-nm emission, jointly (0.4–1.5 W). CPL was obtained by polarizing, through a fused silica Fresnel rhomb, the above emissions. The photochemical reactor was made of an Erlenmeyer flask provided with a strain-free optical window. Efficient stirring was ensured by a magnetic bar. LPL and CPL irradiations, as well as CD spectra and polarimetric measurements, were carried out using spectroscopic grade Erba RS methanol as a solvent. Both LPL and CPL irradiations were always carried out under conditions of total absorption.

1-Methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (1). A well-stirred, ca. 2×10^{-2} M solution of 2-methoxytropone[6] in methanol (280 mL) was irradiated with LPL (333, 350, and 363 nm, jointly, 1.5 W) with up to 50–60% conversion of 2-methoxytropone. Under these conditions **1** is the main product, with traces of **2**. The solvent was evaporated at reduced pressure and the oily residue was distilled, using a short, efficient column, at 0.02 torr, bath temperature 60 °C. The central fractions were constituted of pure **1**. **1** was further purified by preparative TLC (Merk Kieselgel 60 PF$_{254}$, 2 mm thick) eluent ethyl ether–*n*-pentane 60:40. **1** was collected from the R$_F$ 0.41 band by extraction with chloroform (0.3 g, yield 39%). Analytical and spectral data agreed with those of the literature.[4a]

Irradiation of (±)-1 with CPL and Isolation of both Methyl 4-Oxo-2-cyclopentene-1-acetate (7) and Methyl 3-Oxocyclopentane-1-acetate (8). A well-stirred solution of (±)-**1** (0.385 g, 2.83 mmol) in 50 mL of methanol was irradiated with right CPL until 40% conversion of **1** into **2** (as shown by ^{1}H NMR analysis of a portion of the mixture, which was evaporated at reduced pressure and the residue was taken with CDCl$_3$), corresponding to α_{436} 0.145°. The solvent was evaporated at reduced pressure, and the residue was added to 3 mL of water acidified with a few drops of 0.75 M sulfuric acid. The aqueous mixture was added to sodium sulfate and then repeatedly extracted with chloroform. The organic layer was evaporated and the residue was subjected to preparative TLC, as above, to give (+)-**1**, 0.143 g (1.05 mmol) from the R_f = 0.41 band. The R_f = 0.27 band gave (+)-**7** which was further purified by TLC to give a pure sample of 0.045 g (0.29 mmol); IR^{4a} ν_{max}^{neat} 1740, 1710, 1580 cm^{-1}; UV λ_{max}^{MeOH} 217 (10 500), 313 (ϵ 33); ^{1}H NMR (CDCl$_3$) δ 7.40 (1 H, dd, $J_{2,3}$ = 5.4, $J_{1,2}$ = 2.4 Hz, H(2)), 5.96 (1 H, dd, $J_{2,3}$ = 5.4, $J_{1,3}$ = 1.8 Hz, H(3)), 3.60 (3 H, s, OCH$_3$), 3.22 (1 H, m, H(1)), 2.8–1.8 (4 H, m, methylene protons). On irradiation at δ 3.22, both the δ 7.40 and 5.96 dd became doublets with $J_{2,3}$ = 5.4 Hz. The above sample of (+)-**7**, 0.038 g (0.25 mmol), in 5 mL of 95% ethanol and 10 mg of 5% Pd–C was hydrogenated at atmospheric pressure for 6 h. Conversion to (−)-**8** was quantitative, as shown by GLC (2 mm × 3 mm column, 15% silicone on Chromosorb W (80 – 100 mesh, N$_2$ 20 mL min^{-1}, 165 °C, retention time 7.5 min): IR ν_{max}^{neat} 1740 cm^{-1}; UV λ_{max}^{EtOH} 285 nm (ϵ 25); the ^{1}H NMR spectrum is in accordance with the literature.[11b]

Infrared Photochemistry of Bicyclopropyl

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Abstract: The decomposition of bicyclopropyl (C$_6$H$_{10}$) induced by multiphoton absorption from an infrared laser has been investigated. The reaction produces a complex product mixture consisting mainly of C$_6$H$_{10}$ isomers. A mechanism is proposed that can rationalize all of the existing infrared photochemical and thermal data on the basis of a single primary step, C–C bond cleavage to a 1,3-biradical. The product mixture results from competitive decay channels of the biradical and successive reactions of the "hot" products. This system provides a striking example of the influence of "hot molecule effects" on the product distributions in infrared multiphoton dissociation.

Polyatomic molecules decompose under the influence of high-power infrared laser radiation. The phenomenon is well characterized[1-3] and theoretical models capable of rationalizing most of the existing data, at least qualitatively, have been developed.[4-6]
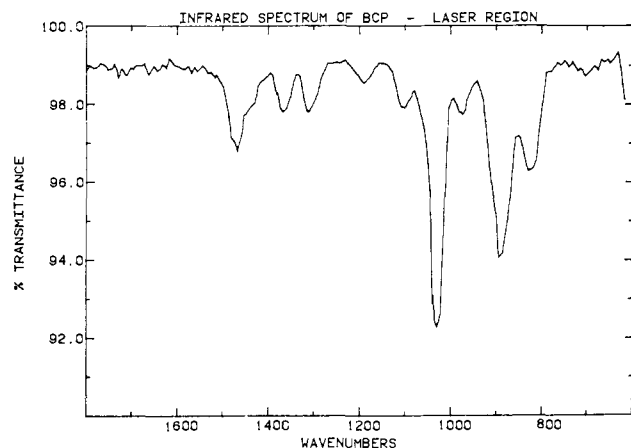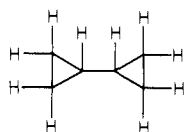
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Figure 1. Infrared spectrum of bicyclopropyl (1800–600 cm⁻¹) taken in a gas cell at ~5 torr (path length = 10 cm).

Figure 2. Representative gas chromatogram of bicyclopropyl photolysis mixture. Peak identification give in Table I.

Figure 3. Fraction of photolysis sample decomposed as a function of the number of laser pulses. Plotted as a first-order decay process.

Most reacting molecules in these experiments absorb more energy than is required to reach the lowest energy reaction threshold, and, in suitable cases, both higher energy primary reaction pathways and secondary reaction pathways can become competitive.[7] It is a question of some importance to applications of infrared photochemistry, for example, in isotope separation[8] or selective isomerization,[9] to determine how much experimental control can be exerted over yields and branching ratios in systems of this kind. We have examined this question in the infrared photochemistry of bicyclopropyl (bcp) (**1**) and analogues spe-

1

cifically deuterated on one ring. Detailed rationale for choosing the bicyclopropyl skeleton and experimental results of the infrared photochemistry of the deuterated derivatives are outlined in a separate paper.[10a]

In this paper we report on the infrared multiphoton photochemistry of the parent all-hydrogen bicyclopropyl. Bicyclopropyl decomposes to give a complex product mixture. Approximately 20 products are observed under standard conditions. This complex product spectrum yields to a remarkably simple mechanistic analysis. On the basis of the proposed mechanism and concepts inherent in rate equation models of infrared photochemistry,[4-6] the relative amounts of the principal products, and the variations in the product mixture with pressure, can be understood. This system provides a rather striking illustration of how "hot molecule effects" influence product distributions in infrared multiphoton dissociation.

Results

The infrared photochemistry of bicyclopropyl was examined in the gas phase at pressures in the range 0.05–0.30 torr. Typically,
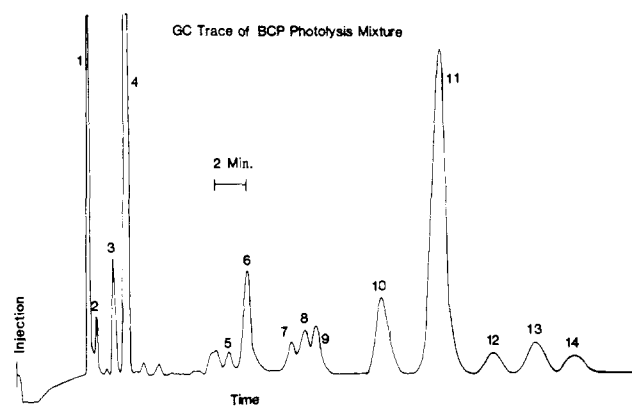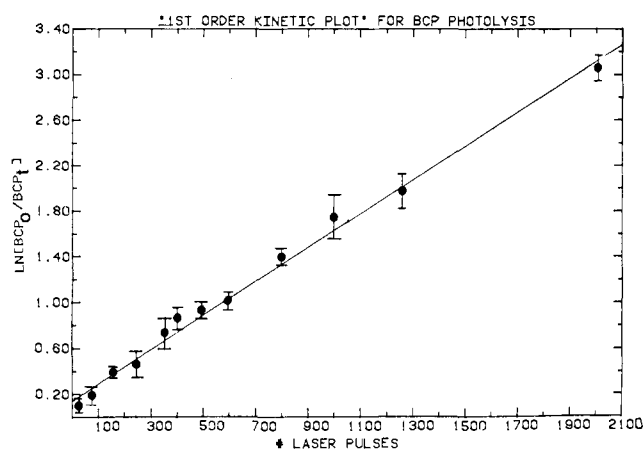
Table I. Product Distribution from Infrared Multiphoton Photochemistry of Bicyclopropyl

peak number from Figure 1	product	approximate percent of product mixtures[a]
1	ethylene	19
2	acetylene	2
3	1-butene	6
4	1,3-butadiene	18
5	1,5-hexadiene	1
6	3-methylcyclopentene	7
7	*trans*-1,4-hexadiene	2
8	*cis*-1,4-hexadiene	2
9	allylcyclopropane	3
10	1,3-hexadienes	14
11	bicyclopropyl	
12	*trans,trans*-2,4-hexadiene	8
13	*cis,trans*-2,4-hexadiene	10
14	*cis,cis*-2,4-hexadiene	7

[a] Reaction carried out at 0.20 torr bcp, 4.79 J/cm² fluence, 1027 cm⁻¹, 1000 pulses at 0.5 Hz.

0.20 torr of bcp was irradiated with 200–1000 pulses of infrared radiation using the P(40) line of the 00°1–02°0 transition of a Lumonics TEA-101 pulsed-CO_2 laser. This infrared frequency is resonant with a bcp absorption centered at 1025 cm⁻¹ (Figure 1). A representative gas chromatogram of the product mixture obtained from an experiment using a laser beam loosely focused to a fluence of ~5.0 J/cm² at the cell center is shown in Figure 2. There are at least 23 products present in the mixture. Each of the numbered peaks has been identified by coinjection of known materials with the product mixture, by GC–FTIR spectroscopy and by GC–MS. In each case, all three techniques are consistent

(1) Danen, W. C.; Jang, J. C. In "Laser-Induced Chemical Processes"; Steinfeld, J. I., Ed.; Plenum Press: New York, 1981; Vol. 1, Chapter 2.

(2) Schultz, P. A.; Sudbo, Aa. S.; Krajnovich, D. J.; Kwok, H. S.; Shen, Y. R.; Lee, Y. T. *Annu. Rev. Phys. Chem.* **1979**, *30*, 379.

(3) Bloembergen, N.; Yablonovitch, E. *Phys. Today* **1978**, *31*, 23.

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(5) Troe, J. *J. Chem. Phys.* **1980**, *73*, 3205.

(6) Baldwin, A. C.; Barker, J. R. *J. Chem. Phys.* **1981**, *74*, 3823.

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

(8) Yogev, A.; Benmair, R. M. *J. Chem. Phys. Lett.* **1979**, *63*, 558 and references therein.

(9) (a) Lewis, F. D.; Oxman, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 7345. (b) Ben-Shaul, A.; Haas, Y. *J. Chem. Phys.* **1980**, *73*, 5107.

(10) (a) Farneth, W. E.; Thomsen, M. W. *J. Phys. Chem.*, in press. (b) Farneth, W. E.; Thomsen, M. W. *J. Org. Chem.*, in press.
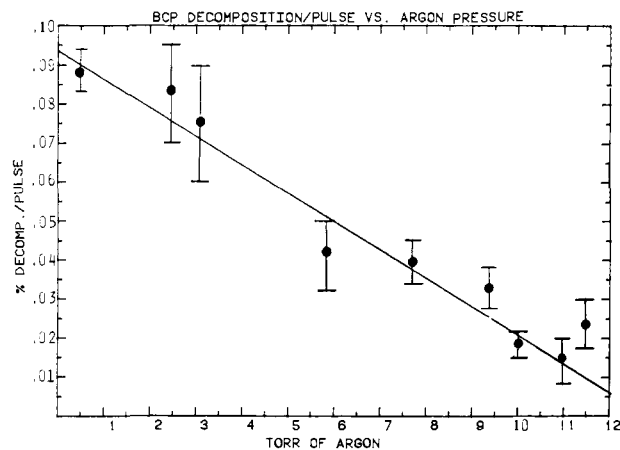
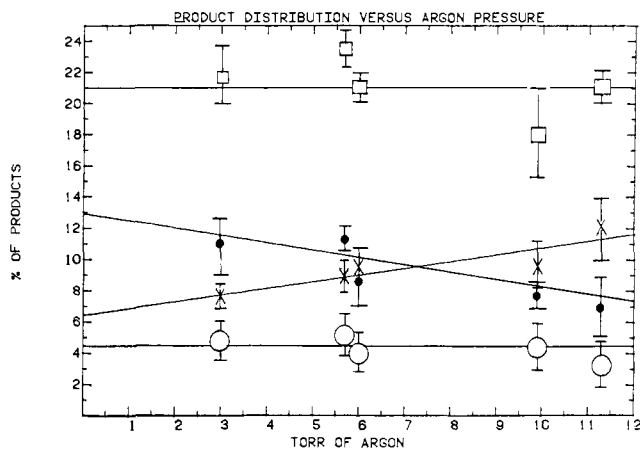**Figure 4.** Fraction of bicyclopropyl decomosed per pulse vs. pressure of Ar bath gas (6.1 J/cm^2).

Figure 5. Partial product distribution vs. pressure of Ar bath gas: (□) butadiene, (●) 3-methylcyclopentene, (×) allylcyclopropane, (O) 1-butene (6.1 J/cm^2).

with the assigned structure. Assignments are shown in Table I. Since product mixtures from bcp pyrolysis are in some respects similar,[10b] gas chromatography data on the thermal product mixtures was useful for comparison during product identification. The principal products from the infrared photodissociation of bcp are ethylene, butadiene, allylcyclopropane, 3-methylcyclopentene, and various unbranched hexadienes. Notably absent are any vinylcyclopropanes, methyl pentadienes, or cyclohexene.

The loss of bcp over 1300 pulses can be treated as a first-order decay, $\ln([\text{bcp}]_0/[\text{bcp}]_t) = kn$, where n is the number of pulses. Figure 3 shows a least-squares fit to data taken at ~7.0 J/cm^2 fluence, $k = 1.5 \times 10^{-3}$/pulse ($r^2 = 0.99$). The product distribution as a function of the number of laser pulses is constant within experimental error even at long irradiation times. Under these conditions, 1300 pulses corresponds to roughly 75% conversion. The major products of the bcp photolysis were independently irradiated under the same conditions. In each case, photoreaction was either nonexistent or too slow to contribute significantly to the bcp product mixture. Five products failed to react: *cis*- and *trans*-1,4-hexadiene, 1,5-hexadiene,[11] ethylene, and butadiene. In addition, cyclohexene and 2-cyclopropylpropene were shown to be unreactive. 1,5-Sigmatropic shifts occur in 1,3-hexadiene and among the 2,4-hexadienes to cause their interconversion.[12] Allylcyclopropane undergoes ring opening to yield chiefly 3-methylcyclopentene. The rate of the allylcyclopropane decomposition was slow relative to its rate of formation from bcp even after 75% conversion of starting material.[13]
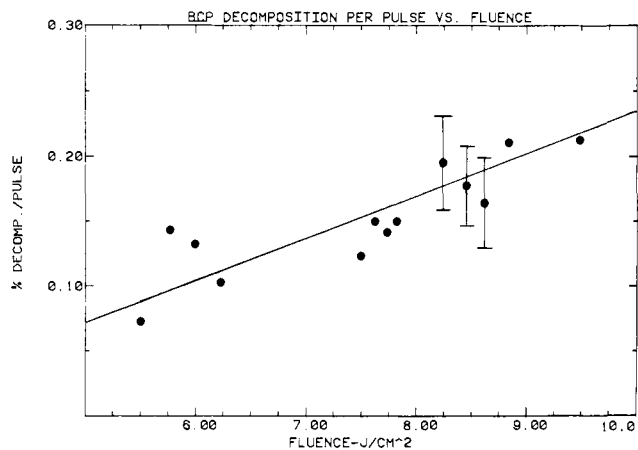
Figure 6. Percent of bicyclopropyl in irradiated volume decomposing per pulse vs. fluence at the focal point.

Scheme I
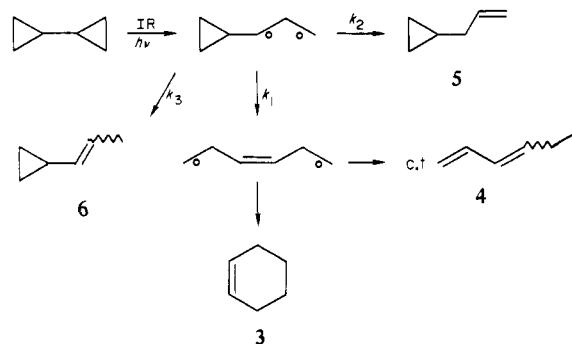
The variations of yield and product distribution with bath gas pressure are shown in Figures 4 and 5, respectively. As shown in Figure 4, the fractional decomposition per pulse decreases as the pressure of argon is increased. The slope of a similar plot using pentane as bath gas is about an order of magnitude larger than that of the argon plot. Bath gas pressure also has some influence on the product distribution as shown in Figure 5. Over this pressure range, allylcyclopropane grows by twofold—principally at the expense of 3-methylcyclopentene. All other products showed little or no change in their fractional contribution to the whole mixture.

The effects of laser fluence on the photodecomposition of bcp were also examined. As expected, increases in fluence were accompanied by increases in the fractional conversion per pulse. The product distribution, however, showed no well-defined trends induced by changes in fluence. Although at the lower fluences (4–5 J/cm^2), the ratio (3-methycyclopentene + allylcyclopropane)/(1,3-hexadiene + 2,4-hexadienes) is significantly smaller than at higher fluences. The yield data are shown in Figure 6.

Discussion

These data indicate that all of the products in the percentages shown in Table I result from chemistry induced by single laser pulses. Products of one pulse do not absorb and react further in subsequent pulses to any appreciable extent. This does not necessarily mean, however, that all products are formed directly from bcp. It has been clearly demonstrated in other systems that consecutive reactions may occur during single laser pulses.[14]

A mechanism that can account for the observed products, the lack of certain others, and trends in the data with pressure or activation conditions is outlined in Scheme I and Table II. All products are postulated to arise from a common elementary step, ring opening to produce a 1,3-biradical. This biradical partitions

(11) This molecule may undergo a degenerate Cope rearrangement under these conditions. Glatt, I.; Yogev, A. *J. Am. Chem. Soc.* **1976**, *98*, 7087.
(12) Buechele, J. L.; Weitz, E.; Lewis, F. D. *J. Am. Chem. Soc.* **1979**, *101*, 3700.

(13) Calculated values give a ratio of rate of formation to rate of decomposition of 3:1 at 75% conversion of bcp.
(14) E.g.: Grimley, A. J.; Stephenson, J. C. *J. Chem. Phys.* **1981**, *74*, 447. See also ref 1 and references therein.

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Table II. Lowest Energy Reaction Channels and Arrhenius Parameters for the Primary Photolysis Products

	$\log A$	$E_a{}^e$	ref
	15.3	67	a
	10.8	33	b
	~14.4	~63	c
	13.5	50	d

a Tsang, W., *Int. J. Chem. Kinet.* 1970, 2, 311. *b* Frey, H. M.; Pope, B. M. *J. Chem. Soc. A* 1966, 1701. *c* Work of Gilbert (Gilbert, J. C. Ph.D. Thesis, Harvard University, 1966) and unpublished work from this laboratory suggest 3-methylcyclopentene as the principal product of the homogeneous reaction. The Arrhenius parameters are taken to be those of methylcyclopropane, ref 19. *d* Arrhenius parameters for vinylcyclopropane: Wellington, C. A. *J. Phys. Chem.* 1962, 66, 1671. *e* kcal/mol.

along three competitive routes: to a 1,6-biradical via cyclopropylcarbinyl rearrangement, k_1, or to allylcyclopropane (**5**) and 1-cyclopropylpropene (**6**) by 1,2-hydrogen shift, k_2 or k_3. The 1,6-biradical yields nonradical products by ring closure to cyclohexene (**3**) or 1,5-hydrogen shift to 1,3-hexadiene (**4**).

These pathways are well-precedented in the thermal chemistry of similar systems. The ring-opening–hydrogen-shift pathway mimics the normal course of reaction for single cyclopropane rings. Methylcyclopropane, for example, yields 1- and 2-butene.[15] The cyclopropylcarbinyl to allylcarbinyl rearrangement has been shown to be very fast in monoradicals.[16] Products analogous to the 1,6-biradical products of Scheme I are the only products obsererved in the pyrolysis of (**2**).[17] The barrier to the cyclo-

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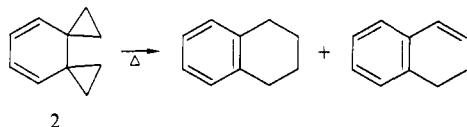
propylcarbinyl rearrangement is ~6 kcal/mol.[16] The barrier to 1,2-H shift in a hypothetical biradical derived from cyclopropane is suggested to be ~10 kcal/mol.[18] Therefore, these processes could be competitive in the intermediate 1,3-biradical of Scheme I, especially at the high internal energies characteristic of infrared multiphoton excitation. While we have no direct evidence for a biradical intermediate and the data could be rationalized by competitive concerted pathways to the primary products shown in Scheme I, the biradical is at least a very useful construct for organizing the data.

In the infrared photochemical experiment each of the four products of Scheme I, **3** → **6**, is formed with excess internal energy. For each product **3** → **6** the total internal energy is given by $\Delta H_0 + \bar{E}_{abs}$ as shown schematically for 1-cyclopropylpropene in Figure 7. $\bar{E}_{abs}$ is the average energy of decomposing bicyclopropyl molecules. $\bar{E}_{abs}$ must be at least as large as the barrier to bicyclopropyl decomposition and in general will be much larger. Since each of these products is exothermic from bicyclopropyl, all four can be formed with considerable internal energy. In fact, in every case, there is enough energy so that secondary reaction channels are accessible. The lowest energy reaction channels for **3** → **6** are shown in Table II, along with their Arrhenius activation energies.

The combination of Scheme I and Table II accounts for all the products of laser-induced reaction except butene. It further suggests that two products not observed, cyclohexene and 1-
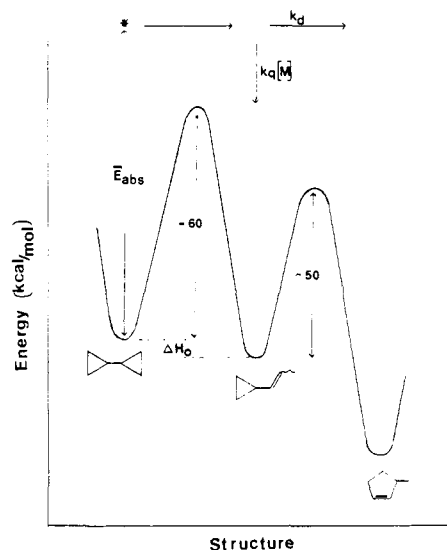

Figure 7. Schematic potential-energy surface for one channel in bicyclopropyl infrared photochemistry.

Table III. RRK Calculations for Lowest Energy Reaction Channels of Primary Products

	$\Delta H°_{298}{}^a$ kcal mol^{-1}	$(E^* - E_0)/E^*$	$k(\bar{E})$,^{b} s^{-1}
	−33	0.46	3.4×10^7
	−14	0.68	2.5×10^7
	−5	0.34	1.9×10^5
	−8	0.49	1.3×10^7

a Heats of formation from: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. $\Delta H°$ = exothermicity for formation of each reactant from bcp. *b* Quantum RRK theory calculations using $s = 42$, A as given in Table II, $h\nu = 1200$ cm^{-1}.

cyclopropylpropene, are intermediates. The absence of these two is the result of rapid secondary decay. Whether or not consecutive reactions occur during single laser pulses depends on the competition between decomposition, k_d, and collisional deactivation, $k_q[M]$, of the "hot" products.

The rates of the "hot" molecule decay reactions can be calculated by using statistical unimolecular rate theories. The simplest version of these theories, classical RRK theory,[19] suggests that these rate constants are proportional to $[(E^* - E_0)/E^*]^{s-1}$ where E^* is the total internal energy of the "hot" reactant, E_0 is the barrier to decomposition, and s is a constant related to the number of vibrational degrees of freedom in the reactant. $E^* \geq \Delta H_0 + \bar{E}_{abs}$ for each pathway.[20] $\bar{E}_{abs}$ may be estimated from a consideration of the requirements imposed on the rate of bcp decomposition by the pressure and the laser pulse width. Absorption continues in a given molecule until an energy is reached at which the rate of unimolecular reaction becomes equal to the rate of further photon absorption. Since the pulse width of the laser is 5×10^{-7} s, this sets a lower limit on the rate constant for molecules reacting during the laser pulse of 2×10^6 s^{-1}. Reaction may also occur after the pulse from partially activated molecules. But, assuming strong collisions, post-pulse reaction will be limited to molecules reacting faster than the collision rate, at these pressures again approximately 2×10^6 s^{-1}. Therefore, the internal energy

(15) Setser, D. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1964**, 86, 564.

(16) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, 98, 7024.

(17) deMeijere, A. *Chem. Ber.* **1974**, 107, 1702.

(18) Berson, J. A. *Annu. Rev. Phys. Chem.* **1977**, 28, 111.

(19) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972.

(20) E^* may be greater than $\Delta H_0 + \bar{E}_{abs}$ if the "hot" product undergoes futher absorption prior to decomposition.

that corresponds to a bcp decomposition rate constant of 2×10^6 s^{-1} should be a lower limit to $\bar{E}_{abs}$. With use of the more accurate quantum version of RRK[19] and published Arrhenius parameters for bcp decomposition, this value is $\bar{E}_{abs} \geq 90$ kcal/mol.

In Table III, the proposed secondary reactions are listed again, along with (1) the value of ΔH° for formation of the reactant from bcp, (2) the ratio $((E^* - E_0)/E^*)$, and (3) the calculated quantum RRK rate constant. Two important conclusions can be drawn from this table. First, the secondary reaction of allylcyclopropane is calculated to be about 2 orders of magnitude slower than secondary reactions in the other three channels. Second, only the allylcyclopropane reaction is slower than the collision rate at 0.20 torr ($\sim 2 \times 10^6$). Therefore, some allylcyclopropane but no cyclohexene or 1-cyclopropylpropene is observed under standard conditions because only for this channel does $k_q[M]$ compete favorably with k_d. As the bath gas pressure is increased, allylcyclopropane grows at the expense of 3-methylcyclopentene because $k_q[M]$ increasingly dominates k_d. On the other hand, the lack of a pressure effect on the proportions of primary and secondary products for the other channels suggests that over the accessible pressure range k_d remains greater than the rate of collisional deactivation. Somewhat higher values of E^* than the minimum we have chosen may be necessary to meet this requirement. Since Ar is a very inefficient deactivator, a pressure of 10 torr, where $k_q[M]$ is $\sim 10^8$, may still produce an effective deactivation rate less than the k_d values of Table III. The 1,3-hexadiene–2,4-hexadiene channel is unique because it is essentially thermoneutral and unimolecular. Therefore, the rate of reverse reaction, 2,4, $\rightarrow$ 1,3, at any E^* is comparable to the rate of the forward reaction. Both are faster than quenching, so that the isolated products represent an effective high-energy equilibrium in this channel.

This mechanism provides a very satisfying explanation for the infrared photochemical product mixtures from bcp. Furthermore, it make some predictions about the thermal chemistry in this system. If the thermal chemistry were carried out in the gas phase at pressures comparable to the laser experiments, one anticipates increases in the first-formed products, cyclohexene, 1-cyclopropylpropene, 3-cyclopropylpropene, and 1,3-hexadiene at the expense of the secondary channels to 3-methylcyclopentene, ethylene, butadiene, and acyclic hexadienes, as a result of lower average energies in the decomposing molecules under thermal conditions. Cyclohexene *is* observed as a major product in the pyrolysis, and allylcyclopropane grows from $\sim 3\%$ of the mixture to $\sim 15\%$. Methylcyclopentene, ethylene, and butadiene correspondingly decrease. 1-Cyclopropylpropene is not observed, and the ratio of 1,3-hexadienes to 2,4-hexadienes is roughly the same as in the infrared photochemistry. However, the channels to 1-cyclopropylpropene and to 1,3-hexadiene have activation barriers to the secondary reaction that are significantly lower than the energy required for the initiating reaction, bcp decomposition. Therefore, although the "hot" molecule channel to consecutive reactions may diminish under thermal conditions, the primary products are simply not thermally stable at the required temperatures. The details of the investigation of the thermal reaction of bcp, including some isotope-labeling studies that are also consistent with this mechanism, are reported elsewhere.[10,21]

In conclusion, it is apparent that secondary reactions of "hot" product molecules are crucial to the understanding of product mixtures from infrared photochemical reactions. To a large degree this secondary chemistry is uncontrollable. The multiphoton activation step itself places serious constraints on the variables that could most obviously be used to control this process. Thus, increasing bath gas pressure reduces consecutive reactions but simultaneously and rapidly attenuates the yield. Decreasing fluence serves principally only to decrease the number of molecules in the reacting population, leaving their average energy and, hence, their rate of secondary reaction, essentially unchanged. Even the use of very low intensity lasers leading to values of $\bar{E}_{abs}$ barely in excess of threshold cannot alleviate the problem.[22] Although

k_d for secondary reaction will be low, multiphoton activation with these lasers is practical only at very low pressures, where $k_q[M]$ is also low and, therefore, the competition between primary and secondary products is not materially affected.

Experimental Section

Photolyses of bcp and related compounds were accomplished by using a grating tuned Lumonics CO$_2$ TEA laser. Typically, 0.200 torr o. bcp or other substrate was loaded into a photolysis cell by using standard vacuum-line transfer techniques. The photolysis cell was then placed in the laser beam and irradiated for measured lengths of time at a pulse frequency of 0.5 Hz. Most photolyses of bcp involved the P(40) line of the 00°1–02°0 transition. The beam was focused with a single 15-in. ZnSe lens or with a telescope consisting of the aforementioned lens and a 5-in. ZnSe lens. Laser power was monitored with a Scientech (Model 38-0102) volume-absorbing calorimeter. An Optical Engineering 16A spectrum analyzer was used to determine the frequency of the laser radiation. The photolysis cell was a Pyrex cylinder 7.5 cm $\times$ 2 cm (i.d.) fitted with polished KCl or NaCl windows. The cell was equipped with two or three side arms to facilitate easy loading of the cell with substrates for photolysis and known materials for coinjection experiments.

Product mixtures were analyzed by flame ionization gas chromatography using a Varian Model 2440 gas chromatograph equipped with a gas sample injection valve. The GC column used for these analyses consisted of a 10-ft-long ($^1/_8$ in. o.d.) stainless steel column packed with 10% dinonylphthalate on Chromosorb W-AWAS (Supelco, Inc.) connected in series with a 20-ft-long ($^1/_8$ in. o.d.) stainless steel column packed with 10% β,β'-oxydiproprionitrile. Typical GC conditions employed a 30 $\pm$ 1 cm^3 of helium per minute flow rate and an oven temperature of 55–65 °C.

Infrared spectra were obtained on a Beckman 4250 infrared spectrometer. Fourier transform infrared spectroscopy (FTIR) was accomplished with either a Digilab FTS-10 or FTS-20 spectrometer. Gas chromatography–Fourier transform infrared spectral analyses were accomplished on a Varian Model 3600 gas chromatograph coupled with a Digilab FTS-10 Fourier transform spectrometer. The effluent from the GC was analyzed by the FTS-10 in the "on the fly" mode. Identities of the products were determined by comparison of infrared spectra of known compounds obtained under identical conditions.

Mass spectrometry was done on a AE1-MS30 or a Hitachi RMU-6 spectrometer. GC-MS was accomplished with a Varian 940 fitted with an appropriate column and coupled to the Hitachi RMU-6. Samples of laser photolysis product mixtures were injected by using a gas sample valve.

Preparative gas chromatography was performed with a Varian Model 1400 thermal conductivity gas chromatograph. For hydrocarbons such as bcp and allylcyclopropane, the column used was a 10-ft-long ($^1/_4$ in. o.d.) copper tube packed with 10% β,β'-oxydiproprionitrile on Chromosorb P. For other compounds the GC column used was either a 10-ft-long ($^1/_4$ in o.d.) stainless steel column packed with 10% OV-101 on Chromasorb G or a similar column packed with 10% Carbowax 1540 on Chromosorb P.

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 and then cooled with an ice/water bath. 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+%: bp 76 °C (lit. bp 76.0–76.1 °C);[23,24] ^{1}H NMR (CDCl$_3$) δ 0.10 (4 H, multiplet), 0.30 (4 H, multiplet), 0.80 (2 H, multiplet); infrared spectrum (gas phase, 5.0 torr) 3090 cm^{-1}, 3020, 1470, 1430, 1360, 1300, 1180, 1100, 1025 (cyclopropane ring), 970, 880, 820, 690 and 620; mass spectrum, electron impact 70 eV, m/e (rel intensity) 82 (11.2, M$^+$), 81 (12.2), 67 (100), 55 (8.4), 54 (95.3), 43 (11.7), 41 (54.4), 39 (38.3).

Preparation of the Br$_2$-bcp was achieved by the addition of dibromocarbene to vinylcyclopropane using the procedure of Roth et al.[25] The tri-*n*-butyltin hydride was prepared by using the procedure of van der Kerk et al.[26]

Preparation of Allylcyclopropane. Cyclopropyl bromide (~ 1.0 g) and 5 mL of THF (dry) were added to a flame-dried three-neck flask containing 1.65 (0.065 mol) of magnesium turnings (the flask was fitted with

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a condenser, addition funnel, and septum). Once the reaction between magnesium and the bromide had started, the remaining cyclopropyl bromide (6.25 g) was dissolved in 50 mL of dry THF and the solution added to the reaction. The total amount of cyclopropyl bromide used was 7.25 g (0.060 mol). Upon completion of addtion of the cyclopropyl bromide/THF solution, the reaction mixture was stirred at room temperature for ~20 min. During this 20-min time period, a suspension of cupric chloride (0.35 g, 2.6 mmol) in 15 mL of THF was prepared in a 250-mL flask. The suspension was cooled with an ice/water bath, and then the previously prepared Grignard was transferred into the same flask by use of a clean, dry cannula and a positive pressure of nitrogen. To this mixture were added 10.75 g (0.06 mol) of HMPA and 7.25 g (0.060 mol) of allyl bromide by syringe. The reaction mixture was then refluxed for 2 h, during which time the color changed from black to red.

After refluxing, the reaction mixture was cooled to room temperature and poured into 150 mL of saturated NH₄Cl solution. This aqueous solution was extracted with 50 mL of ether. The organic phase was separated from the deep blue aqueous phase and extracted with saturated NH₄Cl solution to remove any residual copper species. The organic phase was then washed four times with 100–150 mL of water to remove the HMPA. The ethereal solution was washed three times with saturated sodium chloride solution, dried with anhydrous sodium sulfate/magnesium sulfate, and filtered. The ethereal solution was then fractionally distilled to remove the ether, and the residue was subjected to preparative gas chromatography to yield allylcyclopropane:[27] ^{1}H NMR (CDCl₃) δ −0.1–1.0 (5 H, multiplet), 1.95 (2 H, doublet of doublets (apparent triplet), with fine structure, J = 7 Hz, $J_{allylic}$ ~0.4 Hz), 4.9 (1 H, doublet with much fine structure, J = 10 Hz), 5.1 (1 H, multiplet), 5.7 (1 H, multiplet); infrared spectrum (gas phase, 4.25 torr) 3100 cm⁻¹ (CH, cyclopropane), 3020, 2920, 2850, 1640 (C=C), 1450, 1290, 1175, 1020 (cyclopropane ring), and 920 (C=CH₂, out of plane).

Preparation of *cis*- and *trans*-1-Cyclopropylpropene. Approximately 0.9 mL (0.8 g, 0.008 mol) of 1 cyclopropylpropanol was placed in a 5-mL round-bottom flask and warmed to 100 °C. One drop of concentrated H₂SO₄ was added and the warming continued. A short-path still was attached to the flask, and the products were distilled from the reaction mixture. Analysis of the product mixture by gas chromatography using column A showed two major products produced in equal amounts and two very minor ones. The major products were separated by preparative gas chromatography and determined to be *trans*-1-cyclopropylpropene (first peak) and *cis*-1-cyclopropylpropene (second peak) by NMR spectroscopy. Yield was approximately 50%.

Spectral Data for *trans*-1-Cyclopropylpropene. ^{1}H NMR (CDCl₃) δ 0.1–0.9 (4 H, multiplet), 1.64 (CH₃, 3 H, doublet of doublets, J = 6 Hz, J = 0.5 Hz), 1.70 (1 H, multiplet), 4.93 (1 H, doublet of doublets with fine structure, J = 20 Hz, J = 10 Hz, fine structure $J_{allylic}$ ~ 1 Hz), 5.48 (1 H, doublet of quartets, J = 20 Hz, J = 6 Hz); ^{1}H NMR (CDCl₃, decoupled by irradiating resonant with δ 1.64 (CH₃)) δ 0.1–0.9 (4 H,

multiplet), 4.93 (1 H, doublet of doublets, J = 20 Hz, J = 10 Hz), 5.48 (1 H, doublet, J = 20 Hz); ^{1}H NMR (CDCl₃, decoupled by irradiating resonant with δ 5.48) δ 0.1–0.9 (4 H, multiplet), 1.64 (3 H, singlet with fine structure, J = 0.5 Hz), 1.70 (1 H, multiplet), 4.93 (1 H, doublet with fine structure, J = 10 Hz, J = 1 Hz); infrared spectrum (gas phase, GC-FTIR) 3080 cm⁻¹ (CH), 3000 (CH), 2940 (CH), 1640 (C=C), 1450 (CH₃), 1380 (CH₃), 1200, 1120, 975, and 800.

Spectral Data for *cis*-1-Cyclopropylpropene. ^{1}H NMR (CDCl₃) δ 0.1–0.8 (4 H, multiplet), 1.30 (1 H, multiplet), 1.70 (CH₃, 3 H, doublet of doublets, J = 7 Hz, J = 1.8–2.0 Hz), 4.71 (1 H, doublet of doublets (apparent triplet) with fine structure, J = 10 Hz, J = 10 Hz, J = 1.8 Hz), 5.35 (1 H, doublet of quartets, $J_{doublet}$ = 10 Hz, $J_{quartet}$ = 7 Hz); ^{1}H NMR (CDCl₃, decoupled by irradiating resonant with δ 1.70 (CH₃)) δ 0.1–0.8 (4 H, multiplet), 4.71 (1 H, doublet of doublets—no fine structure, J = 10 Hz, J = 10 Hz), 5.35 (1 H, doublet, J = 10 Hz); ^{1}H NMR (CDCl₃, decoupled by irradiating resonant with δ 5.35) δ 0.1–0.8 (4 H, multiplet), 1.30 (1 H, multiplet), 1.70 (CH₃, 3 H singlet with fine structure), 4.71 (1 H, doublet, J = 10 Hz; infrared spectrum (gas phase, GC-FTIR) 3080 cm⁻¹ (CH), 3030 (CH), 2940 (CH), 1650 (C=C), 1520, 1420, 1375 (CH₃), 1320, 1140, 1025, 960, 920, 820, 720, (cis C=C).

Preparation of 2-Cyclopropylpropene.[28] Sodium hydride (0.05 mol) was placed in a 250-mL three-neck flask and washed several times with petroleum ether. After the system was purged, 25 mL of Me₂SO was added and the suspension stirred while its temperature was raised to approximately 80 °C. At this point 17.9 g (0.05 mol) of methyltriphenylphosphonium bromide dissolved in 50 mL of Me₂SO was added slowly to the Me₂SO anion solution. The color turned from green to brown. Upon completion of the addition, the reaction mixture was stirred for 15 min at a temperature of 0–10 °C. Methyl cyclopropyl ketone (4.62 g, 0.055 mol) was added slowly and the mixtures stirred for 35 min at 0–15 °C, at which time it warmed to room temperature and was stirred for an additional 60 min. Distillation of the mixture provided 2-cyclopropylpropene in a fraction boiling between 70 and 80 °C; yield 35%; ^{1}H NMR (CDCl₃) δ 0.60 (4 H, multiplet), 0.90 (1 H, multiplet), 1.65 (3 H, triplet, $J_{allylic}$ = 2 Hz), 4.70 (2 H, quartet, $J_{allylic}$ = 2 Hz); infrared spectrum (gas phase, GC-FTIR) 3100 cm⁻¹, 3000, 1640 (C=C), 1450 (CH₃), 1375, 1240, 1020, 900. Spectral data consistent with literature values.[29]

Other compounds required for this work were obtained from commercial sources.

Registry No. 1, 5685-46-1; **5,** 4663-23-4; *cis*-**6,** 20479-70-3; *trans*-**6,** 20479-69-0; Br₂bcp, 22975-42-4; cyclopropyl bromide, 4333-56-6; allyl bromide, 106-95-6; 3-cyclopropylpropanol, 5618-01-9; 2-cyclopropylpropene, 4663-22-3; methyl cyclopropyl ketone, 765-43-5; methyltriphenylphosphonium bromide, 1779-49-3.

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^{13}C CP/MAS NMR Study of Molecular Motion in *n*-Alkylsilanes Bonded to the Silica Surface

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Abstract: Motional dynamics in long-chain aliphatic phases bonded to silica gel were studied using CP/MAS ^{13}C relaxation measurements. Differences in cross-polarization rates and proton $T_{1\rho}$ and T_1 values observed for samples prepared by silylation of silica gel with dimethyloctadecylchlorosilane (DMODCS) and dimethyloctylchlorosilane (DMOCS) identified methyl group rotation as a likely principal source of proton spin–lattice relaxation. Cross-polarization rates for carbons located at equidistant positions from the surface-attached silicon atom were similar for DMODCS and DMOCS systems. In general, cross-polarization efficiency was observed to decrease with increasing distance from the surface along the alkyl chain. However, for distances greater than roughly eight carbon units cross-polarization rates are essentially the same.

Introduction

Recent studies of normal and chemically derivitized silica gels using ^{29}Si and ^{13}C cross-polarization (CP)[1] and magic-angle

spinning (MAS) NMR[2–5] have proven highly useful in extracting qualitative and in certain cases quantitative information about

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