Cyclobutene Photochemistry. Identification of the Excited States Responsible for the Ring-Opening and Cycloreversion Reactions of Alkycyclobutenes

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Abstract: Two substituted bicyclic cyclobutene derivatives—7-methyl- and 7-(trifluoromethyl)bicyclo[4.2.0]oct-7-ene—have been prepared. Gas- and solution-phase UV absorption and HeI UV photoelectron spectra have been recorded for the two compounds as well as for the parent hydrocarbon bicyclo[4.2.0]oct-7-ene. The gas-phase spectra suggest that the a,R(3s) state is the lowest energy state in bicycle[4.2.0]octene and the 7-methyl derivative but is raised to higher energies than the π,π* state in the 7-trifluoromethyl derivative. Direct photolysis of the three compounds in hydrocarbon solution with monochromatic far-UV (193 and 214 nm) light leads to competitive ring opening to the corresponding cis,cis- and cis,trans-1,3-cyclooctadiene derivatives, as well as fragmentation to cyclohexene and alkyne in all three cases. Product quantum yields (193-nm excitation) have been measured for both substituted derivatives relative to those for the parent compound. The quantum yields of fragmentation products are highest for the methyl- and unsubstituted compounds, suggesting that these products arise from a Rydberg-like excited state. In contrast, ring opening is most efficient for the trifluoromethyl-substituted compound, although the diene distributions obtained from the series. These results indicate that nonstereospecific ring opening arises largely from the π,π* state of cyclobutene. The contribution to the fragmentation process from a concerted [σ2π + σ2π] cycloreversion pathway is minor, at best. The wavelength dependence of the product distributions from photolysis of the three derivatives is in perfect accord with these assignments.

Introduction

Several recent reports have demonstrated that direct photolysis of alkyl-substituted cyclobutenes in solution results predominantly in nonstereospecific ring opening to the corresponding conjugated dienes, in competition with fragmentation to the corresponding alkene and alkyne. It has been demonstrated that the nonstereospecificity associated with the ring-opening reaction is quite general, in contrast with the general belief that the photochemical electrocyclic ring opening of cyclobutene is governed by orbital symmetry selection rules and should thus proceed stereospecifically and in concerted, disrotatory fashion. In fact, the only example in the literature that supports this view has recently been found to be incorrect. On the other hand, it is well-established that the photofragmentation process is highly stereospecific. The stereochemistry about the adjacent saturated carbons in the cyclobutene moiety is retained in the alkene fragment from the reaction. This is the expected result if fragmentations proceed by concerted [σ2π + σ2π] cycloreversion, but there are alternative pathways that could lead to the same result.

There is good reason to suspect that two or more singlet excited states may play a role in the photochemistry of simple cyclobutenes in solution. Spectroscopic results for alkycyclobutenes, as well as simpler alkenes, indicate that at least three such states are accessible in the far-UV region in the gas phase and in solution. These are the π,π* and σ,π* valence states and the π(R(3s)) state of Rydberg states. The Rydberg transitions may be substantially mixed with valence transitions (such as the σ,π*). In principle, either the valence or Rydberg-like states could be responsible for the major products obtained in the photolysis of cyclobutenes, though via different mechanisms. It is known that alkyl substitution lowers the gas-phase energy of the π(R(3s)) state in simple alkenes while having only small effects on the energy of the valence state. This can be understood most easily by considering that excitation to the Rydberg state involves promotion of a (valence) π-electron to a spatially diffuse 3s (or at higher energies, 3p) orbital. Thus, the electronic character of alkene Rydberg states bears some resemblance to alkene radical cations. As should be expected from this model, the effect of alkyl substituents on alkene Rydberg state energies parallels that on the π-ionization potential (π-IP). Alkenes with lowest Rydberg excited states in the gas phase undergo predominantly alkyl and hydrogen 1,2-migrations upon photolysis in solution, leading to carbon-carbon bond formation intermediates. This behavior has been attributed to alkene Rydberg states due to the analogy with well-known carbocation rearrangements, but the σ,π* state might also be expected to lead to similar rearrangements; the σ-level involved in this transition is localized in the vicinal bonds to the alkene substituents.

In the case of cyclobutene, “Rydberg-derived” alkyl 1,2-migration would lead to cyclopropylcarbenes, which are known to fragment (stereospecifically) to yield the same products as would formal [σ2π + σ2π] cycloreversion. Furthermore, cyclobutene radical cations are known to undergo ring opening in the gas
trifluoromethyl substitution (at the C=C bond) has the effect of raising the gas-phase Rydberg state energies in alkenes such as norbornene, without altering the energy or localized character of the alkene π,π* state.\(^1\) This substituent effect on the gas-phase excited-state manifold is reflected in the solution-phase photobehavior of the alkene. The photochemistry of 2-(trifluoromethyl)norborene\(^2\) is much cleaner (and different) than that observed for norbornene\(^3\) and has been assigned to reaction from the π,π* singlet state exclusively. The effect of trifluoromethyl substitution on the singlet excited state manifold of alkenes should be contrasted to that of π-conjugative substituents, which lower the energy of the π,π* state without substantially altering the energies of states in the Rydberg manifold. In the case of cyclobutenes, phenyl-substituted derivatives do not undergo ring opening on photolysis and fragment with extremely low efficiency;\(^4\) high-energy (and/or highly localized) singlet excited states appear to be a requirement for efficient photochemistry in this system. Thus, trifluoromethyl substitution potentially provides a practical means of investigating pure π,π* photochemistry in simple cyclobutenes, without complication from pathways involving carbene intermediates.

Results

7-Methylbicyclo[4.2.0]oct-7-ene (1) was prepared by the route shown in eq 1\(^5\) and was isolated and purified to >99.9% purity by semipreparative gas chromatography (VPC). 7-(Trifluoromethyl)bicyclo[4.2.0]oct-7-ene (3) was prepared by photochemical addition of trifluoromethyl iodide to bicyclo[4.2.0]oct-7-ene (2), followed by base-catalyzed dehydroiodination with potassium tert-butoxide in dimethyl sulfoxide (eq 2). The intermediates in the syntheses of both 1 and 3 were not fully characterized but

![Figure 1. UV absorption spectra of 1-3 in the gas phase (—) and in deoxygenated pentane solution (—). Gas-phase spectra were recorded at pressures of 1.0–2.0 Torr. The left axes refer to gas-phase spectra, and the right axes refer to solution-phase spectra.](image)

Table 1. Gas-Phase Spectroscopic Properties of Substituted Bicyclo[4.2.0]oct-7-enes 1–3

<table>
<thead>
<tr>
<th>compd</th>
<th>(\pi)-IP (^a)</th>
<th>(E_{\text{g}, \text{R}(\text{eV})} )</th>
<th>(E_{\text{g}, \pi, \pi}(\text{eV}) )</th>
<th>(E_{\text{g}, \pi, \pi}(\text{eV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.5 ± 0.1</td>
<td>5.91 (2.6)</td>
<td>6.40 (2.1)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9.0 ± 0.1</td>
<td>6.37 (2.6)</td>
<td>7.67 (2.3)</td>
<td>≥6.62 (3.1)</td>
</tr>
<tr>
<td>3</td>
<td>9.7 ± 0.2</td>
<td>&gt;6.7 (&lt;3.0)</td>
<td>≥6.62 (3.1)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Lowest vertical ionization potential from photoelectron spectrum (Figure 2). \(^\dagger\) Position of absorption band maximum in gas-phase UV spectrum (Figure 1). \(^\ddagger\) Difference between UV absorption energy and vertical \(\pi\)-IP.

tert-butoxide in dimethyl sulfoxide (eq 2). The intermediates in the syntheses of both 1 and 3 were not fully characterized but
general structures. To conventional scanning UV spectrometer, with samples of pressures exhibited spectral characteristics consistent with their proposed generated n-pentane solution with the same spectrometer and under in eq 3. The products obtained from photolysis of excitation and included minor amounts of 7-methylenebicyclo[4.2.0]oct-7-ene (4c) at temperatures greater than 120–160 °C. In both cases, the trans,cis isomer undergoes thermal cyclization at lower temperatures than the cis,trans isomer does, presumably because of its greater degree of ring strain. With the exception of c,t-4a, these isomers are also extremely sensitive to the presence of acidic impurities (they undergo isomerization to the c,c isomer), particularly at elevated temperatures.

The stereochemical assignments for the three isomers of 4a and 4c were made on the basis of their relative thermodynamic stabilities, UV absorption spectroscopy, and 1H NMR spectroscopy. The positions of the substituents in each exhibit five major NOE enhancements (they undergo isomerization to the c,c isomer), particularly at elevated temperatures.

Relative product yields from the photolyses of 1-3 were determined from the slopes of plots of product concentration vs excitation dose, which were constructed by VPC analysis of photolysis products. These plots were linear in each case throughout this conversion range. In order to obtain a semiquantitative indication of relative product yields, the plots were each carried out concurrently with that of 2 under equivalent conditions and with optically matched solutions (OD193 nm >> 5). Quantum yields for product formation from 1 and 3 were then calculated by using a value of $\phi = 0.14$ for the quantum yield of 5 from photolysis of 2 at 193 nm. Figure 3 shows the concentration vs time plots for product formation from the three compounds in these experiments. Under the VPC conditions used for these analyses, c,t- and t,c-4c were incompletely separated and were thus analyzed together. Independent VPC analyses of mixtures at several conversions, using more stringent conditions, demonstrated that the relative yield of these two products (c,t/c,t-4c = 0.63) did not vary during the course of the experiment. The product quantum yields obtained from the slopes of these plots are collected in Table II.

### Table II. Product Quantum Yields from Photolysis (193 nm) of Deoxygenated Pentane Solutions of 1-3 at 22 °C

<table>
<thead>
<tr>
<th>cyclobutene</th>
<th>c,t-4</th>
<th>(c,t + c,c)-4</th>
<th>5</th>
<th>(c,t-4)/(c,c-4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.049</td>
<td>0.0038</td>
<td>0.13</td>
<td>0.81 • 0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.075</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.186</td>
<td>0.106</td>
<td>0.030</td>
<td>0.63 ± 0.04</td>
</tr>
</tbody>
</table>

*Calculated from the slopes of the concentration vs time plots shown in Figure 3, by using a value of $\phi = 0.14$ for the quantum yield of 5 from photolysis of 2.1 Relative errors are ca. ±5%.

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Photolyses (193 nm) of 1–3 were also carried out by using 0.02 M n-pentane solutions containing a 7/3 mixture of (E)- and (Z)-3-ethylidenecyclohexane (6; 0.001 M), in order to verify that the geometric isomers of 4a–c are stable under our photolysis conditions with respect to secondary cis,trans photoisomerization.

In all cases, the relative amounts of (E)- and (Z)-6 changed by less than 3% after ca. 5% conversion of 1–3, and the relative yields of the photoproducts were similar to those obtained in other runs. These control experiments verify that the product yields listed in Table II are true primary yields and are not distorted due to secondary diene cis,trans photoisomerization.

Photolysis of 0.02–0.1 M pentane solutions of 1–3 with a Zn resonance lamp (214 nm) led to the same products as those obtained in the 193-nm photolyses. Product yields were determined from the slopes of concentration vs time plots. Table III summarizes the relative yields of fragmentation and ring-opening products (i.e., 5/4, [c,c-4]/(c,c-4), and c,c-4/(c,c-4)) obtained from photolysis of the three compounds with the 193- and 214-nm light sources.

Discussion

The gas-phase UV absorption spectra of 1–3 each show a prominent, relatively intense band with an apparent maximum near 185 nm. In the case of 2 and 3, the apparent absorption maxima are so close to the lower wavelength limit of our spectrometer that it is difficult to judge whether they are true maxima or experimental artifacts. Nevertheless, the spectra of 1 and 2 are analogous to those of cyclobutene and 1-methylcyclobutene in this region. In each case, the characteristics of this absorption band are essentially invariant in the corresponding solution-phase spectra, so it can most likely be assigned as due to the σ,π* valence transition. This assignment agrees with that of Pickett and co-workers26 and Robin46 for the analogous transitions in cyclobutene and 1-methylcyclobutene.

The remaining features of the gas-phase spectra vary dramatically with substituent. The spectrum of 2 shows a weak shoulder absorption at 195 nm (6.37 eV), which is shifted to 210 nm (5.91 eV) in that of 3. This absorption is not present in the spectrum of 1, we speculate that it is located at wavelengths shorter than 187 nm (i.e., E ≈ 6.65 eV). The variation in the position of this band throughout the series of compounds parallels the variation in the lowest vertical σ-IP from the PE spectra of 1–3 as a function of substituent (Figure 2 and Table I), as is evident from the near constancy in the term value, and may thus be assigned as due to the π,π* transition. For 1 and 2, these absorptions are reduced substantially in intensity in the solution-phase spectra. This behavior lends additional support to our assignment of these bands as due to Rydberg absorptions.14 The positions of these bands in the spectra of 1 and 2 should be compared to the corresponding ones in the spectra of cyclobutene (6.33 eV) and 1-methylcyclobutene (6.02 eV).26 Robin has assigned these bands as due to π,π* transitions.14

The parallel effects of methyl and trifluoromethyl substitution on the π-IP and position of the gas-phase π,π* transitions in 2 and the lack of a corresponding effect on the π,π* transition energy are analogous to those reported previously for a series of norbornene derivatives (7).19 From the results of a study of the PE, gas- and solution-phase UV absorption and (gas phase) electron energy loss spectra of 7a–c, it was concluded that trifluoromethyl substitution has the effect of substantially raising the energies of states in the Rydberg manifold in alkenes, without appreciably altering the energy or localized character of the π,π* state. The present results show that a similar effect is observed in simple cyclobutene derivatives.

The alteration in the ordering of the singlet excited states in 7c relative to 7b, which is evident in the gas-phase electronic spectra, is reflected in dramatic differences in the solution-phase photochemistry of the two molecules.20 While 7b affords products derived from carbene intermediates formed by alkyl and hydrogen 1,2-migrations predominantly,21 the major product of photolysis of 7c is that of alkyl 1,3-migration. On the whole, the photochemical behavior of 7c is similar to that of 2-cyanonorbornene (7d),27 which has a lowest π,π* singlet state that is substantially lower in energy than that of 7c. On the basis of the behavior observed for 7 and the spectroscopic indication that the lowest energy singlet excited state of 7c, which is accessible in solution, is the π,π* state, we thus expect that the photochemistry of this molecule should cleanly reflect the behavior of this state alone, without possible complications from Rydberg state excitation.

The results summarized in Table II indicate that the photochemistry of 1–3 does indeed show consistent trends with substitution at the double bond. First, it is observed that the quantum yields of isomeric dienes from photochemical ring opening of 1–3 increase systematically throughout the series, while the characteristics of the process with respect to the distribution of isomeric dienes obtained is almost constant. This is consistent with this
aspect of photoreactivity arising exclusively (or at least nearly so) from the \( \pi,\pi^* \) singlet state. The similarities in the distributions of formally allowed and forbidden diene isomers and (for 1 and 3) the relative yields of cis,trans and trans,cis isomers throughout the series of compounds lead to the important conclusion that the nonstereospecificity associated with the photophysical ring opening of alkylicyclobutenes cannot be attributed to some component of the reaction that arises from Rydberg state excitation, as has been suggested previously.\(^3\)

In contrast, the quantum yield of fragmentation (yielding 5) is decreased dramatically in 3 compared to those in 1 and 2, providing a clear indication that the formal cycloreversion reaction is derived largely from the non-Rydberg-like excited singlet state. This assignment of the ring-opening and fragmentation processes to two distinct excited states in solution is precisely that suggested previously by Inoue\(^11\) and Adam\(^15\) and their co-workers, albeit on the basis of very little hard evidence. By analogy with the solution-phase photochemistry of alkenes that exhibit lowest energy \( \pi,\pi^* \) ground-state electronic transition, it is suggested that photoinduced fragmentation in the series of compounds lead to the important conclusion that the nonstereospecific ring opening arises from excitation to the \( \pi,\pi^* \) state. Fragmentation arises largely from the Rydberg-like excited singlet state, presumably via a pathway involving cyclopropylcarbenes formed by alkyl 1,2-migration. The contribution to the latter process from a concerted \( \sigma_2^+\sigma_2^+ \) cycloversion pathway is minor, at best. Further studies, designed to fully delineate the mechanism of the photochemical ring opening of cyclobutene, are in progress.

**Experimental Section**

\(^{1}H\) NMR spectra were recorded on a Varian EM390 (90 MHz) or Bruker AM500 (500 MHz) spectrometers in carbon tetrachloride (or deuteriochloroform where noted). \(^{13}C\) NMR spectra were recorded at 125.6 MHz on the Bruker AM500, and \(^{19}F\) NMR spectra were recorded at 117.7 MHz on a Bruker AM250 spectrometer; all are reported in parts per million downfield from tetramethylsilane (TMS). The \(^{19}F\) NMR spectra were recorded on a VG7070 mass spectrometer interfaced with a Varian 3700 gas chromatograph or on a Hewlett-Packard Model 5971A mass selective detector interfaced with a Hewlett-Packard 5890 gas chromatograph and equipped with DB-1 or DB-1701 (30 m x 0.25 mm; Chromatographic Specialities, Inc.) fused-silica capillary columns. Injector and transfer line temperatures were 250 °C or less. Exact masses were determined on a VGH ZAB-E mass spectrometer and employed a mass of 12.00000 for carbon. Ultraviolet absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 data station. The spectrometer sample compartment was continuously flushed with nitrogen during and for 30 min prior to the acquisition of spectra. Gas-phase absorption spectra were recorded by using samples prepared as described previously.\(^5,9\) For solution-phase experiments, the sample and reference solutions were deoxygenated with argon prior to recording the spectrum. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as the neat liquids or in CCl\(_4\) or CDCl\(_3\) solution; spectra are reported in wavenumbers, calibrated by using the 1601.9 cm\(^{-1}\) polystyrene absorption.

UV photoelectron spectra were recorded in conventional mode with a spectrometer that has been described in detail elsewhere\(^20\) and are the averages of 100–150 scans. The spectra were calibrated relative to the peak at 15.60 eV corresponding to the ionization of nitrogen.

Analytical VPC separations were carried out by using a Hewlett-Packard 5890 gas chromatograph (injector temperature 120 °C) equipped with an electron ionization detector, a Hewlett-Packard HP-3396 recording integrator, and one of the following columns: (a) 1.0-µm SPB-1 wide-bore capillary column (30 m x 0.75 mm i.d.); (b) 0.33-µm HP-17 megabore capillary column (15 m x 0.25 mm i.d.); (c) 0.53-µm HP-17 megabore capillary column (15 m x 0.38 mm i.d.); (d) 1.0-µm SPB-1 wide-bore capillary column; (e) 0.53-µm HP-17 megabore capillary column (15 m x 0.25 mm i.d.).

The injector and column operating temperatures (120 and 80–100 °C, respectively) were kept low enough so as to avoid thermal isomerization of the products of photolysis of 1–3.

**Summary and Conclusions**

Gas- and solution-phase UV absorption spectroscopy indicate that trifluoromethyl substitution substantially raises the energy of the \( \pi,R(3s) \) state in simple cyclobutene derivatives while having little effect on the energy of the \( \pi,\pi^* \) state. The effect is analogous to that observed on the excited-state manifold of simpler alkenes. Product quantum yields from 193-nm photolysis of bicyclo[4.2.0]oct-7-ene (2), the 7-methyl derivative I, and the 7-trifluoromethyl derivative 3 indicate that the two main photoelectron channels (fragmentation and ring opening) arise from population of different singlet excited states in solution. The results indicate that nonstereospecific ring opening arises largely, if not exclusively, from excitation to the \( \pi,\pi^* \) state. Fragmentation arises largely from the Rydberg state or one with substantial Rydberg character, presumably via a pathway involving cyclopropylcarbenes formed by alkyl 1,2-migration. The contribution to the latter process from a concerted \( \sigma_2^+\sigma_2^+ \) cycloreversion pathway is minor, at best. Further studies, designed to fully delineate the mechanism of the photochemical ring opening of cyclobutene, are in progress.
barium oxide. Dimethyl sulfoxide (Fisher reagent) was distilled from calcium hydride. Cyclohexene, citraconic anhydride, c,c-1,3-cyclo- octadiene, acetoephone, 4-methoxyacetoephone, lead tetracetate, and potassium tert-butoxide were all used as received from Aldrich Chemical Co. Trifluoromethyl iodide was used as isolated from Du Pont. Dewar containing dry ice/2-propanol at ca. -30 °C in a Rayonet reactor was used as a source of 

carbon tetrachloride.

Synthetic photoysis employed a Hanovia 450-W medium-pressure mercury lamp with quartz or Pyrex immersion wells (Ace Glass, Inc.) or a Rayonet photochemical reactor fitted with 2-12 253.7- or 300-nm mercury lamps and a mercuric iodide plate, which produced a photostationary state mixture consisting largely of 3 (3.5 g).

After workup, the crude product was bulb-to-bulb distilled and isolated by VPC analysis. Com-
pounds were identified as consisting largely of 7-iodo-8-(trifluoromethyl) cyclooctene (7) by 90-MHz IH NMR spec-
tra, which exhibited the following spectral characteristics:21 IH NMR (90 MHz) δ 1.38 (m, 2 H), 1.55 (br m, 8 H), 1.8 (br s, 1 H); 13C NMR δ 23.36, 23.6, 24.25, 25.01, 24.25, 29.21, 126.57, 129.58, 130.62, 133.84; IR (neat) 3006 (m), 2964 (m), 2927 (m) cm⁻¹; MS (m/e 176.0825) found: 176.0821.

Preparation of Compounds. 7-Methylbicyclo[4.2.0]oct-7-ene (1) was prepared by a sequence starting with the acetoephene-sensitized cyclo-

addition of cyclohexene and citraconic anhydride in ethyl acetate at 20 °C.5 The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate) to give a yellow liquid. The spectral data of the crude product were consistent with those previously published.5 Preparation of 7-Methylbicyclo[4.2.0]oct-7-ene (1).

Dimethyl sulfoxide (110 mL) was placed in a large Pyrex tube and heated at 60 °C for 3 h. The tube was sealed with a septum but was identified as consisting largely of 7-iodo-8-(trifluoromethyl) cyclooctene (7) by 90-MHz IH NMR spec-
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Lumonics TE-861M excimer laser filled with an argon/fluorine/helium mixture and vigorous stirring of the preoxygenated solutions during photolysis to ca. 40% conversion (monitoring by VPC). A preparative scale photolysis of 1 was also carried out by using the 16-W Phillips 9310GE zinc resonance lamp (214 nm) in conjunction with a Suprasil quartz immersion well (60-mL volume). After photolysis, the pentane was carefully distilled from the mixtures on a rotary evaporator. The residue was bulb-to-bulb distilled under vacuum, and the products were separated by preparative VPC (columns e and f).

Photolysis of 1 affords the four products shown in eq 3 in addition to one other in ca. 5% yield and two others in ca. 2% yield that were not isolated. Sufficient quantities of c,c,4a to enable spectral characterization could be obtained from semipreparative photolysis of 1. It was identical with the authentic sample prepared above. The other products (c,c,4a, cis-cis-4c, 5) were identified by co-injection of the photolyzate with authentic samples on two VPC columns and by GC/MSD analysis.

Photolysis of 3 affords the four products shown in eq 3 in addition to one other in ca. 5% yield that was not isolated. The isomeric dienes 4c eluted after 1 on VPC columns a-c. cis-cis-4c was isolated by preparative VPC from large-scale photolyses (193 nm) of 3 (ca. 150 mg) in pentane solution to ca. 30% conversion. Samples of c,c,4c from several such runs were combined. The other two diene isomers were isolated in isolable quantities by direct (254 nm) or 4-methoxyacetophenone separation by preparative VPC (columns e and f).

Photolyses were carried out at ambient temperature (ca. 22 °C) in rectangular cells constructed from (Vitro Dynamics) or in 10 × 25 mm cylindrical Suprasil cells (Hellma). Solutions of 1–3 and isooctane (as internal standard) in n-pentane were deoxygenated with argon prior to irradiation, and the sample was agitated during photolysis with a magnetic stirrer. The course of photolysis was monitored between 0.3 and 5% conversion, with aliquots being removed periodically for VPC analysis. Relative product yields were determined from the slopes of concentration vs laser dose constructed for all components of the mixture relative to the internal standard. The concentration vs time plots were linear up to at least 3% conversion in each case. The response of the VPC detector toward 

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