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Cyclobutene Photochemistry.[1] Identification of the Excited States Responsible for the Ring-Opening and Cycloreversion Reactions of Alkylcyclobutenes

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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 π,R(3s) state is the lowest energy state in bicyclo[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 reaction do not vary throughout 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 $[\sigma_{2s}+\sigma_{2s}]$ 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.[3-6] It has been demonstrated that the nonstereospecificity associated with the ring-opening reaction is quite general, in contrast with the general belief[7] that the photochemical electrocyclic ring opening of cyclobutene is governed by orbital symmetry selection rules[8] and should thus proceed stereospecifically and in concerted, disrotatory fashion. In fact, the only example in the literature that supports this view[9] has recently been found to be incorrect.[10] On the other hand, it is well-established that the photofragmentation process is highly stereospecific.[3-6,9] 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 fragmentation proceeds by concerted $[\sigma_{2s}+\sigma_{2s}]$ cycloreversion,[9] but there are alternative pathways that could lead to the same result.[11-13]

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 alkylcyclobutenes, 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.[4,14] These are the π,π^* and σ,π^* valence states and the π,R(3s) Rydberg state.[14] The Rydberg transitions may be substantially mixed with valence transitions (such as the σ,π^*).[14d] In principle, either the valence or Rydberg-like states could be responsible for the major products obtained in the photolysis of cyclobutenes,[3-6,11-13] though via very 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.[14] 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).[14] Alkenes with lowest Rydberg excited states in the gas phase undergo predominantly alkyl and hydrogen 1,2-migrations upon photolysis *in solution*, leading to carbene intermediates.[15] 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 vinylic bonds to the alkene substituents.

In the case of cyclobutene, "Rydberg-derived" alkyl 1,2-*mi*gration would lead to cyclopropylcarbenes, which are known to fragment (stereospecifically) to yield the same products as would formal $[\sigma_{2s}+\sigma_{2s}]$ cycloreversion.[16] Furthermore, cyclobutene radical cations are known to undergo ring opening in the gas

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(1) Part 5 of the series. For Part 4, see ref 5.

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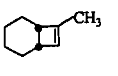
phase[17] (but evidently not in solution, except in special cases[18]); the stereochemistry of the process is not known however. We have previously reported indirect evidence for the formation of cyclopropylcarbenes in the photolysis of cyclobutenes[13] but were unable to define the extent to which they contribute to the formation of formal cycloreversion products. In another paper, we have reported the results of a study of the effects of alkyl substitution on the photochemistry of monocyclic alkylcyclobutenes in solution.[4] While spectroscopic studies showed that increasing alkyl substitution has the same effect on the relative ordering of the valence and Rydberg excited states in the gas phase as is found with simpler alkenes,[14] the product distributions from photolysis in solution show no consistent variations that would help to define how the various excited states that can be populated in solution contribute to the different products observed.

In this paper, we report the results of a study of the spectroscopy and photochemistry of three simple cis-fused bicyclic cyclobutene derivatives (**1–3**), which bear substituents chosen so as to systematically alter the ordering and separation of the π,π^* and Rydberg states in the parent compound. It has been shown that



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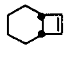

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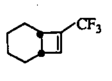
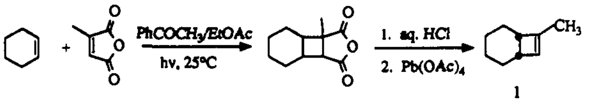


3

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.[19] 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)norbornene[20] is much cleaner (and different) than that observed for norbornene[21] 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;[22] 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[3-5] 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**),



(1)

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

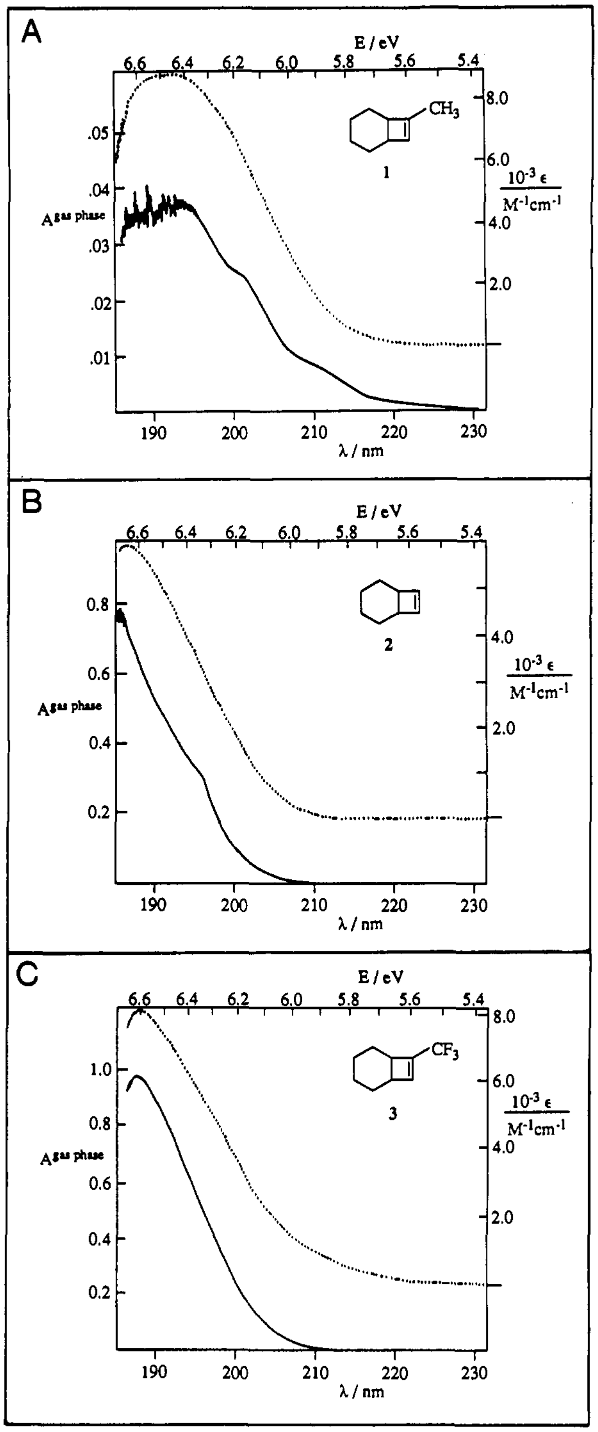


Figure 1. UV absorption spectra of **1–3** in the gas phase (—) and in deoxygenated pentane solution (···). Gas-phase spectra were recorded at pressures of 1.0–2.0 Torr. The left axes refer to gas-phase spectra, and the right axes refer to solution-phase spectra.

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

compd	π-IP[a]	$E_{\pi,R(3s)}$, eV[b] (T, eV)[c]	$E_{\pi,\pi}$, eV[b] (T, eV)[c]
1	8.5 ± 0.1	5.91 (2.6)	6.40 (2.1)
2	9.0 ± 0.1	6.37 (2.6)	≥6.70 (≤2.3)
3	9.7 ± 0.2	>6.7 (<3.0)	≥6.62 (≤3.1)

[a] Lowest vertical ionization potential from photoelectron spectrum (Figure 2). [b] Position of absorption band maximum in gas-phase UV spectrum (Figure 1). [c] Difference between UV absorption energy and vertical π-IP.

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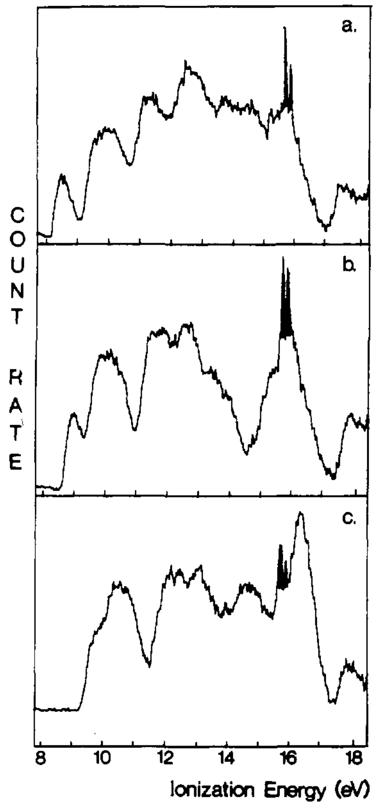
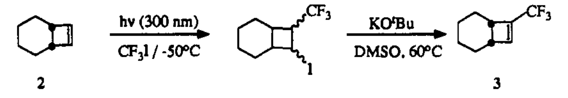


Figure 2. HeI UV photoelectron spectra of (A) 7-methylbicyclo[4.2.0]oct-7-ene (**1**), (B) bicyclo[4.2.0]oct-7-ene (**2**), and (C) 7-(trifluoromethyl)bicyclo[4.2.0]oct-7-ene (**3**). The shaded peaks correspond to N_2 of air, which was used as a calibrant.

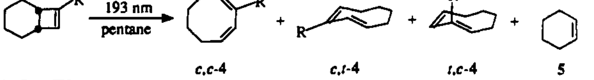
exhibited spectral characteristics consistent with their proposed general structures.



(2)

Gas-phase UV absorption spectra of **1**–**3** were recorded on a conventional scanning UV spectrometer, with samples of pressures in the 1.5–2.0-Torr range, and are presented in Figure 1. Figure 1 also contains spectra recorded for each compound in deoxygenated *n*-pentane solution with the same spectrometer and under the same conditions. HeI UV photoelectron spectra (PES) of **1**–**3** are shown in Figure 2. Table I summarizes the results of these experiments, listing the lowest vertical ionization potentials (from PES) and the positions of the various features in the gas-phase UV absorption spectra of **1**–**3**. The table also includes term values for each absorption feature, calculated as the energy difference between the absorption maximum and the vertical π-IP from the PE spectrum.

Photolysis of deoxygenated, 0.02 M pentane solutions of **1**–**3** with the unfocused pulses (193 nm, ca. 40 mJ, 0.5-Hz repetition rate) from an ArF excimer laser led to mixtures of isomeric 2-substituted 1,3-cyclooctadienes, cyclohexene, and a volatile product presumed to be the corresponding alkyne, as summarized in eq 3. The products obtained from photolysis of **2** were the same as those reported previously for monochromatic 185-nm excitation and included minor amounts of 7-methylenebicyclo[4.1.0]heptane.[3] The photolyses of **1** and **3** each produced one additional product in <5% yield that was not identified in either case. Cyclohexane (**5**), *c,t*-**4a**,**c**, *t,c*-**4c**, and *c,c*-**4a**,**c** were isolated by semipreparative VPC from "large scale" (150–300 mg) runs carried to 10–20% conversion. They were identified on the basis of their ^1H and ^{13}C NMR, infrared, and mass spectra and by comparison to independently synthesized samples in the case of *c,c*- and *c,t*-**4a**. The minor diene isomers *t,c*-**4a**,**c** and *c,t*-**4a**,**c** were prepared in more easily isolable quantities by 4-methoxyacetophenone-sensitized or direct cis,trans photoisomerization of the corresponding cis,cis isomers in deoxygenated pentane solution. The cis,trans and trans,cis isomers undergo thermal isomerization to the cis,cis isomer (**4a**) or to the corresponding bicyclo[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.



(3)

1: R = CH_3
2: R = H
3: R = CF_3

a. R = CH_3
b. R = H
c. R = CF_3

Table II. Product Quantum Yields from Photolysis (193 nm) of Deoxygenated Pentane Solutions of **1**–**3** at 22 °C[a]

cyclobutene	*c,c*-**4**	(*c,t* + *t,c*)-**4**	**5**	(*c,t*-**4**)/(*t,c*-**4**)
1	0.049	0.038	0.13	0.81 ± 0.05
2	0.100	0.075	0.14	
3	0.186	0.106	0.030	0.63 ± 0.04

[a] Calculated from the slopes of the concentration vs time plots shown in Figure 3, by using a value of ϕ = 0.14 for the quantum yield of **5** from photolysis of **2**.[3] Relative errors are ca. ±5%.

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 **4a**,**c** were established by ^1H NMR COSY experiments. The cis,cis isomers were most easily identified on the basis of their higher thermal stability and their UV absorption spectra; the cis,cis isomers absorb at shorter wavelengths ($\lambda_{max} \approx$ 225 nm) than the cis,trans and trans,cis isomers do (λ_{max} = 230–235 nm). Similar differences occur in the UV absorption spectra of *c,c*- and *c,t*-cyclooctadiene.[23] In addition, the most stable isomers of **4a** and **4c** each exhibit $J_{H3-H4} \approx 11.3$ Hz, similar to the vinylic coupling constant in *c,c*-**4b** ($J_{H3-H2} = J_{H3-H4} = 10.5$ Hz).[24] The cis,trans isomers of **4a**,**c** were distinguished from the trans,cis isomers on the basis of their higher thermodynamic stabilities and larger vicinal vinylic coupling constants (J_{H3-H4}) in the ^1H NMR spectra.[25] In addition, the assignments for *c,t*- and *t,c*-**4a** were confirmed by use of proton NOE experiments.

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 photolysates between 0.5 and 4% conversion of starting material. These plots were linear in each case throughout this conversion range. In order to obtain a semiquantitative indication of relative product quantum yields, the photolyses of **1** and **3** were each carried out concurrently with that of **2** under equivalent conditions and with optically matched solutions ($OD^{193 nm} \gg 5$). Quantum yields for product formation from **1** and **3** were then calculated by using a value of ϕ = 0.14 for the quantum yield of **5** from photolysis of **2** at 193 nm.[3] 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** are incompletely separated and were thus analyzed together. Independent VPC analyses of mixtures at several conversions, using more stringent conditons, demonstrated that the relative yield of these two products (*c,t*-/*c*-**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.

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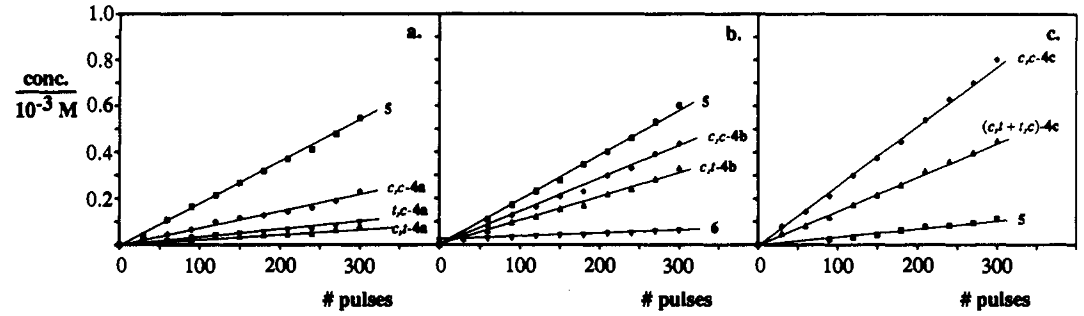


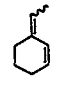
Figure 3. Concentration vs dose plots for the 193-nm photolyses of optically matched, deoxygenated *n*-pentane solutions of (a) **1**, (b) **2**, and (c) **3** at 22 °C.

Table III. Relative Product Yields from Photolysis of Deoxygenated Pentane Solutions of **1–3** at 193[a] and 214[b] nm at 22 °C

cyclobutene	λ, nm	**5**/**4**[c]	(*c*,*t*-**4**)/(*t*,*c*-**4**)	(*c*,*t*-**4**)/(*t*,*c*-**4**)
1	193	1.49	1.29	0.81
	214	2.84	1.69	1.89
2	193	0.80	1.33	
	214	1.10	1.27	
3	193	0.10	1.75	0.63
	214	0.06	2.54	0.86

[a] Ratios calculated from data in Table II. [b] Ratios calculated from slopes of concentration vs time plots from photolysis of 0.1 M solutions. [c] Ratio of yield of **5** to total yield of isomeric dienes.

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.



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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.

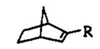
Photolysis of 0.06–0.1 M pentane solutions of **1–3** with a Zn resonance lamp (214 nm) led to the same products as those obtained in the 193-nm photolyses. Product yields were determined from the slopes of concentration vs time plots. Table III summarizes the *relative* yields of fragmentation and ring-opening products (i.e., **5**/**4**, {*c*,*c*-**4**}/{(*c*,*t* + *t*,*c*)-**4**}, and *c*,*t*-**4**/*t*,*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.[26] 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 π,π^* valence transition. This assignment agrees with that of Pickett and coworkers[26] and Robin[14c] 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 **1**. This absorption is not present in the spectrum of **3**; we speculate that it is located at wavelengths shorter than 187 nm (i.e., $E \approx 6.65$ eV). The variation in the position of this band throughout the series of compounds parallels the variation in the lowest vertical π-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,R(3s) 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,R(3s) transitions.[14c]

The parallel effects of methyl and trifluoromethyl substitution on the π-IP and position of the gas-phase π,R(3s) 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.



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a. R = CH_3
b. R = H
c. R = CF_3
d. R = CN

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 **3**, 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

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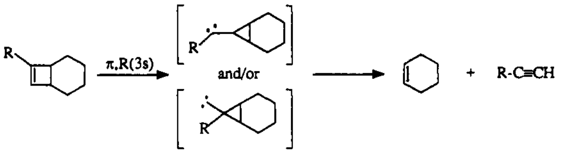
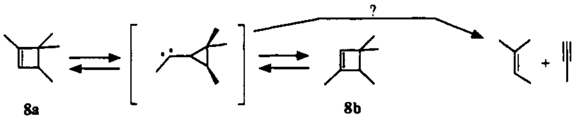
(27) Akhtar, I. A.; McCullough, J. J.; Vaitekunas, S.; Faggiani, R.; Lock, C. J. L. *Can. J. Chem.* **1982**, *60*, 1657.

aspect of photoreactivity arising *exclusively* (or at least nearly so) from the π,π^* 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 photochemical ring opening of alkylcyclobutenes 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 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[12] and their co-workers, albeit on the basis of very little hard evidence. By analogy with the solution-phase photobehavior of alkenes that exhibit lowest Rydberg states in the gas phase, the fragmentation process presumably results from initial alkyl 1,2-migration (ring contraction) to yield the bicyclic cyclopropylcarbene intermediate(s) shown in eq 4. Species of this type, generated from thermolysis or photolysis of the appropriate diazo compound, are well-known to undergo stereospecific fragmentation to the corresponding alkene and alkyne in addition to ring expansion to the corresponding cyclobutene derivative.[16] Our previous report of the photointerconversion of **8a,b** provides indirect evidence for the formation of cyclopropylcarbenes in the photolysis of cyclobutenes (eq 5).[13]



(4)



(5)

8a **8b**

The effects of changing the excitation wavelength on the product distributions from photolysis of **1–3** are also consistent with the above assignments. These data are collected in Table III as product ratios. The trends in the ratio of fragmentation to combined ring-opening products (i.e., **5**/**4**) with substituent at a single excitation wavelength are the result of a decreasing π,R(3s) contribution, accompanied by an increasing π,π^* state contribution, throughout the series of compounds. As expected, increasing the excitation wavelength results in increases in the relative yields of fragmentation products *only* for **1** and **2**, in which the π,R(3s) state is the lower energy state in the gas phase; the opposite wavelength effect is observed for **3**. This rules out the possibility that the variation in fragmentation/ring opening ratios throughout the series is due to a substituent effect on the rate of formation or fragmentation of cyclopropylcarbene intermediates. The small, "residual" yield of fragmentation products that are obtained from photolysis of **3**, at 214 nm in particular, may reflect a minor contribution from a π,π^*-derived $[\sigma_{2s}+\sigma_{2s}]$ cycloreversion pathway for formation of these products.

Variation of the excitation wavelength appears to result in small changes in the distribution of isomeric dienes in the photolyses of **1** and **3**, for reasons that we do not yet understand. The 214-nm photolyses were carried out with solutions of relatively high cyclobutene concentrations (0.06–0.1 M) and analyzed at very low (0.2–4%) conversions in order to minimize secondary diene photolysis. In spite of the fact that concentration vs time plots obtained from these runs showed good linearity over this conversion range in each case, the possibility that the diene distributions from photolysis of **2** and **3** are distorted slightly due to secondary photolysis cannot be rigorously ruled out. The 214-nm data are most reliable for **1**, which has substantially stronger absorption at this wavelength compared to **2** and **3**.

Summary and Conclusions

Gas- and solution-phase UV absorption spectroscopy indicate that trifluoromethyl substitution substantially raises the energy of the π,R(3s) state in simple cyclobutene derivatives while having little effect on the energy of the π,π^* 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 **1**, and the 7-trifluoromethyl derivative **3** indicate that the two main photoreaction 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 π,π^* 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 $[\sigma_{2s}+\sigma_{2s}]$ cycloreversion 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 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 ($CFCl_3$ for the ^{19}F spectra). Mass 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 × 0.25 mm; Chromatographic Specialities, Inc.) fused-silica capillary columns. Injector and transfer line temperatures were 150 °C or less. Exact masses were determined on a VGH ZABE mass spectrometer and employed a mass of 12.000000 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 spectra were recorded by using samples prepared as described previously.[4,19] 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[28] 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 a flame 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 × 0.75 mm i.d. borosilicate; Supelco, Inc.); (b) 0.53-μm HP-17 megabore capillary column (15 m × 0.58 mm i.d. fused silica; Hewlett-Packard, Inc.). 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**.

Semipreparative VPC separations employed a Hewlett-Packard 5750B gas chromatograph equipped with a thermal conductivity detector (detector temperature 110 °C) and one of the following stainless steel columns (Supelco, Inc.): (c) 3.8% UC W982 on 80/100 Supelcoport (24 ft × $^1/_4$ in.); (d) 20% oxybis(dipropionitrile) (ODPN) on Chromosorb 80/100 PNAW (20 ft × $^1/_4$ in.); (e) 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb 80/100 PNAW (12 ft × $^1/_4$ in.); (f) 20% TCEP on Chromosorb 80/100 PNAW (5 ft × $^1/_4$ in.); (g) 15% Carbowax 20M on 60/80 Chromosorb W (5 ft × $^1/_4$ in.). Detector temperatures higher than 110 °C resulted in isomerization of *c,t*-**4a–c** and *t,c*-**4a,c** (especially) to the corresponding bicyclo[4.2.0]oct-7-ene derivative or isomeric *cis,cis*-diene.

n-Pentane, 2,2,4-trimethylpentane (isooctane), and cyclohexane were Baker Photrex grade and used as received from the supplier. Pyridine (Fisher reagent) was dried over potassium hydroxide and distilled from

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(28) Werstiuk, N. H.; Butler, D. N.; Shahid, E. *Can. J. Chem.* **1986**, *65*, 760.

barium oxide. Dimethyl sulfoxide (Fisher reagent) was distilled from calcium hydride. Cyclohexene, citraconic anhydride, *c,c*-1,3-cyclooctadiene, acetophenone, 4-methoxyacetophenone, lead tetraacetate, and potassium *tert*-butoxide were all used as received from Aldrich Chemical Co. Trifluoromethyl iodide was used as received from Columbia Organics. (*E,E*)- and (*E,Z*)-3-ethylidenecyclohexene (**6**) were synthesized as a mixture according to the published procedure[29] and enriched in one of the isomers by semipreparative VPC (column c).

Synthetic photolyses 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 lamps and a merry-go-round apparatus.

Preparation of Compounds. 7-Methylbicyclo[4.2.0]oct-7-ene (1) was prepared by a sequence starting with the acetophenone-sensitized cycloaddition of cyclohexene and citraconic anhydride in ethyl acetate at 20 °C, followed by hydrolysis of the tricyclic anhydride and bisdecarboxylation of the resulting dicarboxylic acid(s) with lead tetraacetate in pyridine.[3–5,30,31] After workup, the crude product was bulb-to-bulb distilled and isolated and purified by VPC (columns c,e) to >99.9% purity: ^{1}H NMR δ = 1.44 (m, 2 H), 1.58 (m, 2 H), 1.62 (s, 3 H), 1.66–1.73 (cplx m, 4 H), 2.72 (m, 1 H), 2.81 (br s, 1 H), 5.86 (m, 1 H); ^{13}C NMR (CCl_4) δ = 15.42, 19.07, 19.34, 23.99, 25.10, 37.86, 42.36, 132.04, 149.28; IR (neat) 3026 (m), 2936 (s), 2902 (s), 2858 (s), 1633 (m), 1443 (s), 1369 (w), 1357 (w), 1283 (w), 1270 (w), 1060 (w), 965 (w), 820 (w), 809 (s), 755 (w) cm^{-1}; MS *m/e* (*I*) = 122 (28), 107 (53), 94 (29), 93 (94), 91 (25), 81 (37), 80 (30), 79 (100), 77 (25), 67 (37), 56 (13), 55 (14), 54 (18). Mass Calcd for C_9H_{14}: 122.1120. Found: 122.1096.

Bicyclo[4.2.0]oct-7-ene (2) was prepared according to the published method[32] and exhibited ^{1}H NMR, IR, and mass spectral characteristics similar to those previously published.

7-(Trifluoromethyl)bicyclo[4.2.0]oct-7-ene (3). In a thick-walled Pyrex tube (6 in. × 1 in. o.d.) fitted at one end with a Rotaflo stopcock was placed **2** (7.3 g, 0.068 mol). The tube was attached to a vacuum line, degassed with two freeze–pump–thaw cycles, and then placed on a balance in a dewar containing liquid nitrogen. Trifluoromethyl iodide (10 g, 0.05 mol) was condensed into the tube through a separate stopcock on the vacuum line. Afer the tube was removed from the vacuum line and the contents were allowed to melt and mix, it was placed in a quartz dewar containing dry ice/2-propanol at ca. −30 °C in a Rayonet reactor. The solution was irradiated with 12 300-nm Rayonet lamps until it turned yellow (ca. 14 h), with periodic addition of dry ice to the dewar to maintain a temperature below ca. −30 °C. After photolysis, the tube was reattached to the vacuum line and the excess trifluoromethyl iodide was separated from the product by distillation. The yellow liquid that remained (16.1 g) was used without further purification in the following step but was identified as consisting largely of 7-iodo-8-(trifluoromethyl)bicyclo[4.2.0]octane on the basis of its 90-MHz ^{1}H NMR spectrum: ($CDCl_3$) δ = 1.5 (cplx m, 8 H), 2.9 (cplx m, 2 H), 4.5 (m, 1 H), 6.2 (m, 1 H).

Dimethyl sulfoxide (110 mL) was placed in a large Pyrex tube and deoxygenated with a stream of dry nitrogen. Potassium *tert*-butoxide (6.6 g) and a portion of the product from above (11.8 g, 0.039 mol) were added, affording a deep yellow solution. The tube was placed in a dry ice/2-propanol bath, evacuated and sealed, and then heated at 60 °C for 12 h. The tube was opened, and the deep red mixture was placed in a separatory funnel containing water (200 mL). The mixture was extracted with *n*-pentane (5 × 30 mL). The combined extracts were washed with brine (3 × 150 mL), 5% aqueous sodium thiosulfate (3 × 100 mL), and water (14 × 150 mL), dried over anhydrous sodium sulfate, and filtered. Careful removal of the solvent by distillation afforded a yellow liquid, which was bulb-to-bulb distilled under vacuum to yield a colorless liquid consisting largely of **3** (3.5 g, ca. 30% yield from **2**) contaminated with a small amount (>7%) of residual pentane (by VPC analysis). Compound **3** was purified (>99.8%) by semipreparative VPC, by using one pass through column f to remove residual DMSO followed by two passes through column c, and has the following spectral properties: ^{1}H NMR ($CDCl_3$) δ = 1.43 (cplx, 2 H), 1.57 (cplx, 3 H), 1.68 (cplx m, 1 H), 1.74 (cplx, 2 H), 2.82 (m, 1 H), 3.06 (m, 1 H), 6.49 (m, 1 H); ^{13}C NMR (C7 not detected) ($CDCl_3$) δ = 17.85, 18.40, 23.44, 38.46, 39.77, 119.71 (q, *J* = 269 Hz), 142.20; ^{19}F NMR ($CDCl_3$) δ = −67.5; IR (neat) 3060 (w), 2940 (s), 2871 (m), 1650 (s), 1450 (m), 1360 (w), 1330 (s), 1300 (m), 1270 (m), 1250 (w), 1220 (m), 1150 (s), 1125 (s), 1050 (m), 1010 (m), 940 (m), 920 (w), 870 (m), 820 (m) cm^{-1}; MS (*m/e* (*I*) = 176 (4), 161 (26), 148 (27), 147 (27), 146 (12), 141 (27), 134 (26), 127 (42), 115 (31), 107 (56), 91 (21), 80 (23), 79 (100), 77 (23), 67 (26), 54 (21). Mass Calcd. for $C_9H_{11}F_3$: 176.0825. Found: 176.0821.

***cis,cis*-, *cis,trans*-, and *trans,cis*-2-Methyl-1,3-cyclooctadiene (4a).** Authentic samples of *c,c*- and *c,t*-**4a** were prepared by iodine-catalyzed dehydration of 1-methyl-2-cyclooctenol (**9**) in refluxing propionic acid (120 °C). Compound **9** was prepared by dropwise addition (over ca. 1.5 h) of a solution of 2-cyclooctenone (4.8 g, 0.039 mol) in anhydrous ether (10 mL) to an ether (50 mL) solution of methylmagnesium iodide (from 1.6 g of Mg and 9.1 g of iodomethane), followed by stirring at room temperature for an additional 1 h. Workup in the normal fashion followed by evaporation of solvent yielded 4.4 g of the crude alcohol, which exhibited the following spectral characteristics:[21] ^{1}H NMR (90 MHz) δ = 1.25 (s, 3 H), 1.55 (br m, 8 H), 1.8 (br s, 2 H), 2.8 (br s, 1 H, exchangeable), 5.2–5.6 (m, 2 H); IR (neat) 3400 (br s), 3020 (w), 2930 (br s), 2860 (w), 1445 (m), 1272 (w), 1045 (s), 1022 (w), 980 (m), 788 (w), 745 (m), 708 (w) cm^{-1}; MS (*m/e* (*I*) = 140 (7), 125 (13), 123 (100), 107 (8), 97 (72), 93 (16), 91 (11), 81 (78), 79 (48), 77 (17), 71 (43), 69 (66), 67 (79).

A portion of the crude sample of **9** (2.0 g, ca. 0.014 mol) was dissolved in propionic acid (10 mL), a grain of iodine was added, and the mixture was refluxed at 120 °C for 1 h. The brown solution was cooled and poured into isooctane (60 mL). The resulting mixture was washed with saturated aqueous bicarbonate (5 × 60 mL) and 5% aqueous sodium thiosulfate (3 × 30 mL) and stirred vigorously with saturated aqueous bicarbonate (60 mL) for 12 h. The organic layer was separated, washed with water (20 mL), and dried over anhydrous sodium sulfate. The volume of the solution was reduced to ca. 3 mL on the rotary evaporator. Gas chromatographic analysis of the crude mixture (after bulb-to-bulb distillation under vacuum) showed it to consist of ca. 12% *c,c*-**4a**, 8% *c,t*-**4a**, and ca. 80% isooctane. The isomeric dienes were collected and purified by semipreparative VPC (column *f*).

The t,c isomer was prepared for isolation by 4-methoxyacetophenone-sensitized photolysis of *c,c*-**4a** (150 mg) in deoxygenated pentane solution, which produced a photostationary state mixture consisting of *c,c/c,t/t,c*-**4a** = 80/8/12. After removal of the solvent on the rotary evaporator and bulb-to-bulb distillation of the residue, the three isomers were separated on column f (injector temperature 100 °C; column temperature 60 °C) and collected as the neat liquids (*c,c*- and *c,t*-**4a**) or in carbon tetrachloride (*t,c*-**4a**). The latter isomer was found to be particulary unstable, undergoing cis,trans isomerization to *c,c*-**4a** in the VPC detector at temperatures higher than 120 °C or more slowly in CCl_4 solution at room temperature (half-life ~8 h). The cis,trans isomer undergoes isomerization to *c,c*-**4a** upon heating in benzene solution at 160 °C (half-life ~2 h).

The three geometric isomers of **4a** elute after **1** on VPC columns a,c–f and are listed below in order of elution from columns a and f.

***cis,cis*-2-Methyl-1,3-cyclooctadiene (*c,c*-4a):**[24] ^{1}H NMR δ = 1.39 (m, 2 H), 1.43 (m, 2 H), 1.70 (s, 3 H), 2.06 (m, 4 H), 5.33 (tq, *J* = 7.8, 1.3 Hz, 1 H), 5.54 (dt, *J* = 11.3, 6.8 Hz, 1 H), 5.62 (d, *J* = 11.3 Hz, 1 H); ^{13}C NMR δ = 23.36, 23.64, 25.01, 28.24, 29.21, 126.57, 129.58, 130.62, 133.84; IR (neat) 3006 (m), 2964 (m), 2927 (s), 2854 (s), 1652 (w), 1445 (s), 1372 (w), 1100 (w), 1050 (w), 912 (m), 844 (w), 822 (m), 755 (w), 734 (s), 720 (m) cm^{-1}; UV λ_{max} = 225 nm (ϵ = 6800); MS *m/e* (*I*) = 122 (41), 107 (32), 94 (22), 93 (73), 91 (33), 81 (24), 80 (25), 79 (100), 77 (35), 67 (18), 53 (21), 41 (32) 39 (56). Mass Calcd. for C_9H_{14}: 122.1120. Found: 122.1100.

***cis,trans*-2-Methyl-1,3-cyclooctadiene (*c,t*-4a):** ^{1}H NMR δ = 1.38 (m, 2 H), 1.42 (m, 2 H), 1.68 (s. 3 H), 2.02 (m, 4 H), 5.40 (dt, *J* = 11.5, 6.6 Hz, 1 H), 5.50 (br s, 1 H), 5.59 (d, *J* = 11.5 Hz, 1 H); ^{13}C NMR (quaternary carbon not detected) δ = 23.66, 23.97, 25.07 (Me), 29.35, 32.97, 122.60, 127.06, 130.72; IR (neat) 3008 (m), 2966 (m), 2928 (s), 2858 (m), 1649 (w), 1444 (s), 1373 (w), 1269 (w), 1199 (w), 1166 (w), 916 (w), 898 (w), 867 (w), 832 (m), 793 (m), 772 (m), 699 (s), 686 (s) cm^{-1}; UV λ_{max} = 231 nm (ϵ = 7800); MS *m/e* (*I*) = 122 (64), 107 (50), 94 (29), 93 (99), 91 (33), 82 (31), 81 (26), 79 (100), 77 (33), 67 (21), 53 (16), 41 (22), 39 (27). Mass Calcd. for C_9H_{14}: 122.1120. Found: 122.1097.

***trans,cis*-2-Methyl-1,3-cyclooctadiene (*t,c*-4a):** ^{1}H NMR δ = 1.59 (cplx m, 4 H), 1.68 (s, 3 H), 2.14 (cplx m, 4 H), 5.37 (d, *J* = 11.1 Hz, 1 H), 5.45 (ddd, *J* = 9.33, 6.76, 1.94 Hz, 1 H), 6.03 (d, *J* = 9.37 Hz, 1 H); ^{13}C NMR (quaternary carbon not detected) δ = 18.53, 27.30, 29.15, 34.48, 35.87, 134.87, 135.33, 136.57; IR (CCl_4) 3010 (m), 2968 (w), 2928 (s), 2857 (m), 1679 (m), 1439 (s), 1370 (w), 1252 (m) 1164 (w), 926 (w), 883 (m) cm^{-1}; UV λ_{max} = 228, 235 ($\epsilon \approx$ 6000); MS *m/e* (*I*) = 122 (80), 107 (85), 93 (73), 91 (29), 81 (28), 79 (100), 77 (40), 67 (44), 66 (48), 53 (30), 51 (17), 41 (40).

Preparative scale (100–300 mg) photolyses of **1** and **3** were carried out in 2 in. × 2 in. cylindrical Suprasil cells (ca. 50-mL volume), by using the pulses (193 nm. ca. 15 ns, ca. 40 mJ; 6-Hz repetition rate) from a

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(30) Owsley, D. C.; Bloomfield, J. J. *J. Org. Chem.* **1971**, *36*, 3768.

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Lumonics TE-861M excimer laser filled with an argon/fluorine/helium mixture and vigorous stirring of the predeoxygenated 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 Philips 93106E 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,t*-**4a**, *t,c*-**4a**, **5**) were identified by coinjection of the photolysate 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,e. *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 prepared in isolable quantities by direct (254 nm) or 4-methoxyacetophenone-sensitized photoisomerization of *c,c*-**4c**. Direct photoisomerization led to a photostationary state mixture consisting of *c,c*-/*t,c*-/*c,t*-**4c** = 86/10/4, while sensitized photolysis afforded a photostationary state mixture of *c,c*-/*t,c*-/*c,t*-**4c** = 89/2/8. Both photolysates also produced small amounts (<5%) of **3**. The spectral characteristics of the three diene isomers are listed below in order of elution from columns a and e.

cis**,*****cis*****-2-(Trifluoromethyl)-1,3-cyclooctadiene (*****c*****,*****c*****-4c)**: ^{1}H NMR ($CDCl_3$) δ = 1.49 (m, 4 H), 2.15 (m, 2 H), 2.22 (m, 2 H), 5.86 (d, J = 11.4 Hz, 1 H), 5.95 (dt, J = 11.4, 7.0 Hz, 1 H), 6.27 (tq, J = 7.9, 1.5 Hz, 1 H); ^{13}C NMR δ = 21.99, 22.66, 27.17, 28.32, 119.64, 123.8 (q, J = 274 Hz), 128.4 (q, J = 32 Hz), 133.49, 136.65; ^{19}F NMR ($CDCl_3$) δ = −67.4; IR (neat) 3030 (w), 2940 (s), 2865 (m), 1660 (m), 1640 (w), 1460 (s), 1422 (m), 1360 (m), 1315 (s), 1270 (m), 1180 (s), 1160 (s), 1120 (s), 1080 (w), 1050 (s), 960 (m), 930 (m), 840 (m), 770 (m), 740 (s) cm^{-1}; UV λ_{max} = 222 nm (ϵ unknown); MS *m/e* (*I*) = 176 (20), 161 (8), 148 (10), 147 (11), 127 (12), 121 (18), 119 (22), 107 (18), 88 (100), 86 (41), 82 (21), 79 (34), 67 (9). Mass Calcd. for $C_9H_{11}F_3$: 176.0825. Found: 176.0815.

trans**,*****cis*****-2-(Trifluoromethyl)-1,3-cyclooctadiene (*****t*****,*****c*****-4c)**: ^{1}H NMR ($CDCl_3$) δ = 1.42 (m, 1 H), 1.65 (m, 1 H), 1.78 (dd, 1 H), 2.13 (cplx d, 1 H), 2.09 (cplx d, 1 H), 2.24 (dt, 1 H), 2.45 (cplx m, 1 H), 2.54 (dt, 1 H), 5.87 (dd, J = 9.3, 8.3 Hz, 1 H), 6.00 (cplx d, J = 14.4 Hz, 1 H), 6.12 (d, J = 9.3 Hz, 1 H); ^{19}F NMR ($CDCl_3$) δ = −61.3; IR ($CDCl_3$) 3015 (w), 2930 (s), 2858 (m), 1637 (w), 1596 (m), 1438 (w), 1392 (w), 1365 (w), 1295 (w), 1270 (s), 1220 (m), 1168 (s), 1139 (s), 1115 (s), 1098 (s), 1006 (w) cm^{-1}; UV λ_{max} = 236 nm (ϵ unknown); MS *m/e* (*I*) = 176 (7), 147 (10), 141 (59), 134 (10), 127 (100), 115 (40), 114 (11), 109 (11), 107 (30), 95 (13), 91 (27), 80 (11), 79 (99), 77 (46), 69 (10), 65 (11), 51 (20), 41 (9), 39 (28).

cis**,*****trans*****-2-(Trifluoromethyl)-1,3-cyclooctadiene (*****c*****,*****t*****-4c)**: ^{1}H NMR ($CDCl_3$) δ = 1.41 (m, 1 H), 1.63 (m, 1 H), 1.82 (m, 1 H), 2.10 (cplx m, 2 H), 2.25 (m, 1 H), 2.42 (m, 1 H), 2.55 (m, 1 H), 5.91 (m, 2 H), 6.22 (m, 1 H), addition of 20% C_6D_6 to the solution caused the 5.91 multiplet to split into two complex doublets with splitting J = 15.8 Hz; ^{13}C NMR (quaternary and CF_3 carbons not detected) ($CDCl_3$) δ = 26.96, 32.34, 32.96, 33.95, 121.47, 140.91, 146.35; ^{19}F NMR ($CDCl_3$) δ = −67.5; IR ($CDCl_3$) 3005 (w), 2935 (s), 2851 (m), 1637 (m), 1597 (m), 1437 (m), 1419 (w), 1374 (w), 1327 (w), 1301 (s), 1275 (s), 1167 (s), 1117 (s), 1040 (s), 977 (m), 962 (m), 824 (m), 809 (m) cm^{-1}; UV λ_{max} = 234 nm (ϵ unknown); MS *m/e* (*I*) = 176 (8), 148 (9), 141 (49), 127 (93), 115 (34), 114 (9), 109 (11), 107 (28), 95 (10), 91 (23), 80 (22), 79 (100), 78 (10), 77 (41), 69 (10), 51 (16), 41 (8), 39 (24).

Analytical photolysis experiments employed the excimer laser (0.5-Hz repetition rate) or the zinc resonance lamp (214 nm). Analytical photolyses were carried out at ambient temperature (ca. 22 °C) in rectangular cells constructed from 10 × 20 mm rectangular Suprasil tubing (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 **1**–**3**, *c,c*-**4a**–**c**, and **5** was calibrated relative to the internal standard with standard solutions.

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