Conrotatory Photochemical Ring Opening of Alkylcyclobutenes in Solution. A Test of the Hot Ground-State Mechanism

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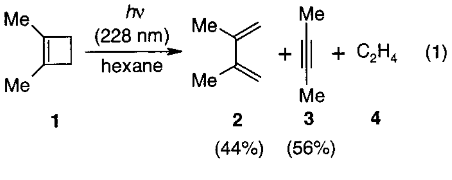
Abstract: Quantum yields for photochemical ring opening of six alkylcyclobutenes have been measured in hexane solution using 228-nm excitation, which selectively populates the lowest π,R(3s) excited singlet states of these molecules and has been shown previously to lead to ring opening with clean *conrotatory* stereochemistry. The compounds studied in this work—1,2-dimethylcyclobutene (**1**), *cis*- and *trans*-1,2,3,4-tetramethylcyclobutene (*cis*- and *trans*-**5**), hexamethylcyclobutene (**8**), and *cis*- and *trans*-tricyclo[6.4.0.0^{2,7}]dodec-1^2-ene (*cis*- and *trans*-**9**)—were selected so as to span a broad range in molecular weight and as broad a range as possible in Arrhenius parameters for thermal (ground-state) ring opening. RRKM calculations have been carried out to provide estimates of the rate constants for ground-state ring opening of each of the compounds over a range of thermal energies from 20 000 to 49 000 cm^{-1}. These have been used to estimate upper limits for the quantum yields of ring opening via a hot ground-state mechanism, assuming a value of $k_{\mathrm{deact}} = 10^{11}$ s^{-1} for the rate constant for collisional deactivation by the solvent, that internal conversion to the ground state from the lowest Rydberg state occurs with close to unit efficiency, and that ergodic behavior is followed. The calculated quantum yields are significantly lower than the experimental values in all cases but one (**1**). This suggests that the Rydberg-derived ring opening of alkylcyclobutenes is a true excited-state process and rules out the hot ground-state mechanism for the reaction.

Introduction

It has been known for some time that the photochemical electrocyclic ring opening of alkylcyclobutenes proceeds nonstereospecifically when these compounds are irradiated in solution with 185- or 193-nm light.[1] In most cases that have been studied, the formation of the corresponding alkyne and alkene by (stereospecific) [2 + 2] photocycloreversion competes with ring opening.[2,3] It has been concluded that the two types of reactions originate from two different excited singlet states: ring opening from the valence π,π^* state and cycloreversion from the π,R(3s) Rydberg state,[4] whose energy is similar to or lower than that of the π,π^* state in alkylcyclobutenes and other nonconjugated olefins.[5]

Despite the overall nonstereospecificity of the ring-opening reaction, time-resolved spectroscopic studies on the parent molecule[6] and steric effects on the quantum yields for 214-nm ring opening of monocyclic cyclobutenes[7] both suggest that the reaction begins with disrotatory stereochemistry on the π,π^* excited-state surface, as orbital symmetry selection rules predict.[8] Other results suggest that the stereospecificity is lost because the reaction proceeds adiabatically, yielding the disrotatory diene isomer in an excited state, from which it decays by *E*,*Z*-isomerization.[9−11]

The precise role of the π,R(3s) Rydberg state in cyclobutene photochemistry has continued to be of concern, particularly with respect to the ring-opening reaction. A recent paper described the results of a more systematic attempt to investigate the Rydberg-state photochemistry of alkylcyclobutenes, through study of three derivatives in which the π,R(3s) excited state is of significantly lower energy than the valence π,π^* singlet state and hence can be populated selectively.[12] It was found that selective excitation at the long-wavelength edge of the Rydberg absorption band of 1,2-dimethylcyclobutene (**1**), both in the gas phase at 1 atm and in hexane solution, results in substantial yields of both ring-opening and cycloreversion products (eq 1), indicating that the Rydberg state is, in fact, active toward ring opening. Furthermore, results obtained for *cis*- and *trans*-1,2,3,4-



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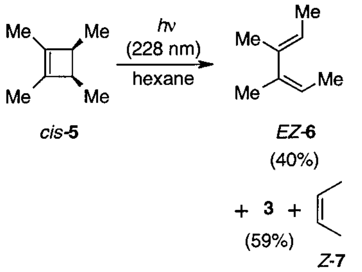
tetramethylcyclobutene (**5**; eqs 2 and 3, respectively) indicate that Rydberg-derived ring opening proceeds with a high degree of *conrotatory* stereospecificity—the stereochemistry associated with the ground-state process. This led to the suggestion of two possible mechanisms for the Rydberg-derived process. The first is as a true excited-state reaction, where the observed conrotatory stereospecificity might be related to the radical cation character associated with the olefinic π,R(3s) state;[13,14] cyclobutene radical cations undergo ring opening in the gas phase,[15,16] and theoretical calculations suggest that the reaction should proceed with preferred conrotatory stereochemistry.[17,18] On the other hand, ring opening of cyclobutene radical cations generally does not occur in condensed phases[19,20] except with photochemical activation,[20−22] but the one known example of solution-phase ring opening proceeds with conrotatory stereochemistry.[23] The second possibility is that it proceeds via a hot ground-state mechanism, with the Rydberg excited state merely providing a conduit for efficient internal conversion to upper vibrational levels of the ground state, from which reaction ensues in competition with collisional deactivation of the thermally activated molecule by the solvent.



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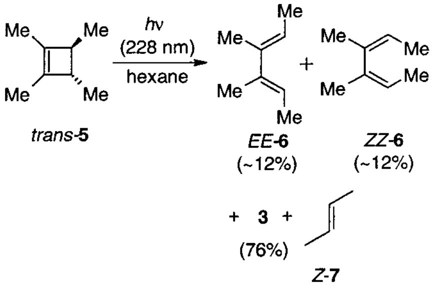

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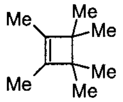
Although photoinduced hot ground-state reactions are common in the gas phase, they are much less so in solution, where collisional deactivation of vibrationally excited molecules occurs on a time scale of approximately 10^{-11} s.[24−28] Thus, for such processes to be observed in significant yields, the rate constant for reaction, at whatever internal thermal energy the molecule possesses when it arrives in the ground state (and after intramolecular vibrational energy redistribution, which occurs on a time scale of 10^{-11}−10^{-12} s[24,25,29,30]) must be on the order of 10^{10} s^{-1} or higher. Such processes are especially viable for small molecules with high excited-state energies, and which are prone to thermal reaction involving low activation barriers. Simple alkylcyclobutene derivatives would appear to be particularly reasonable candidates for this, as they undergo thermal ring opening with Arrhenius activation energies on the order of ~35 kcal/mol (log $A \approx 13.5$)[31] and absorb below ~230 nm. For example, for a molecule such as **1** containing 42 vibrational degrees of freedom and $E_{S1} \approx 120$ kcal/mol, internal conversion from S_1 produces a ground-state molecule that contains excess vibrational energy corresponding to an effective temperature of roughly 2300 K (vide infra); a simple calculation (using this temperature and the published Arrhenius parameters for thermal ring opening of the molecule[32−34]) suggests that it should isomerize with a rate constant on the order of 2×10^{10} s^{-1}. It is thus clear that the possibility of a hot ground-state reaction is a viable one, and so we decided to investigate it in more detail.



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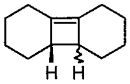

cis-**9**
trans-**9**

The approach we have used involves measurement of quantum yields for ring opening of a series of 1,2-dialkylcyclobutenes (**1**, **5**, **8**, **9**) of varying molecular weights and Arrhenius parameters for thermal ring opening, with the idea of comparing them to "expected" values, calculated with the assumption that ring opening proceeds exclusively via the hot ground-state mechanism. The expected quantum yield for ring opening by this mechanism is given by eq 4, where k_{RO} is the rate constant for ground-state ring opening of the molecule at a total internal energy corresponding to that of a 228-nm photon, k_{deact} is the rate constant for its collisional deactivation by the solvent, and internal conversion is assumed to be the only pathway for excited-state decay other than cycloreversion. The latter assumption maximizes the quantum yield for ring opening that is predicted by this mechanism.

$$\Phi_{calc} = (1 - \Phi_{CR})[k_{RO}/(k_{RO} + k_{deact})] \tag{4}$$

The extensive time-resolved spectroscopic studies of Troe and Luther and their co-workers on the collisional deactivation of vibrationally excited organic molecules, such as cycloheptatriene[28] and azulene,[35] in hydrocarbon solvents allow an

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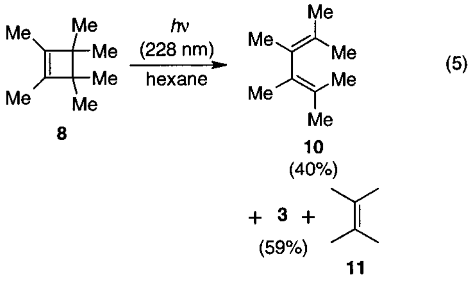
estimate of $k_{\text{deact}} \approx 10^{11}$ s^{-1} for hexane solution, a value which can be assumed to be roughly independent of solute structure and size.[36] The rate constants for thermal ring opening (k_{RO}) have been calculated in one (or both) of two ways. Both calculations required the prior computation of the complete vibrational spectrum for each compound, which was accomplished by quantum mechanical calculation[37] at the DFT/3-21G* or DFT/6-31G*+d levels of theory. In the first method, an effective temperature of the molecule (T), energized by the 228-nm photon, was estimated, and the rate constant $k(T)$ was then calculated from reported[31,33,38] Arrhenius data. This was applied to all six compounds studied. In the second method, the energy-specific, or microcanonical, rate constant $k(E)$ was calculated using RRKM theory.[39] This was applied to four of the compounds studied. The results allow a quantitative assessment to be made of the extent to which the hot ground-state mechanism contributes to the photochemical ring opening of alkylcyclobutenes under conditions of selective Rydberg-state excitation.

Results and Discussion

As we found previously for **1** and **5**,[12] direct irradiation of hexamethylcyclobutene (**8**) and *cis*- and *trans*-tricyclo[6.4.0.0^{2,7}]-dodec-1^2-ene (*cis*- and *trans*-**9**) as 0.05 M solutions in hexane, with the light from a cadmium resonance lamp (228 nm), results in the formation of the corresponding ring-opening and cycloreversion products (eqs 5−7). The photolyses were monitored as a function of irradiation time by capillary gas chromatography, and the products were identified either by co-injection with authentic samples that were prepared by known procedures (**10**, **12**) or obtained commercially (**11**), or after isolation from semi-preparative-scale irradiations and comparison of spectral properties to literature data (*E*- and *Z*-**13**).



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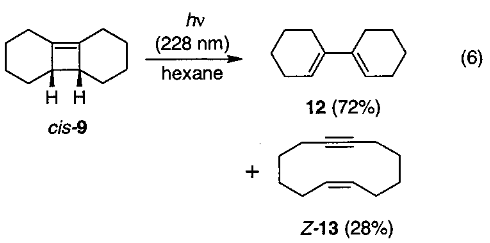

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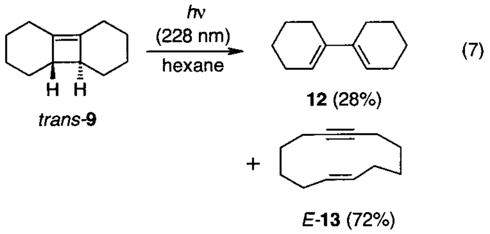

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Table 1. Experimental Quantum Yields for Ring Opening (Φ_{RO}) and RO/CR Ratios from 228-nm Photolysis of Alkylcyclobutenes in Hexane Solution, and Calculated Quantum Yields for Ring Opening Assuming the Hot Ground-State Mechanism (Φ_{Calc})

compound	λ_{ex} (nm)	RO/CR[a]	Φ_{RO}[b]	Φ_{calc}[c]
1	228	0.79 ± 0.07	0.09 ± 0.02	0.17
cis-**5**	228	0.69 ± 0.05	0.08 ± 0.01	0.022
trans-**5**	228	0.25 ± 0.02	0.04 ± 0.01 (*EE*)	0.038 (*EE*)
			0.04 ± 0.01 (*ZZ*)	0.016 (*ZZ*)
8	228	0.70 ± 0.07	0.11 ± 0.02	0.0030
cis-**9**	228	2.6 ± 0.3	0.13 ± 0.02	0.0005
	214	2.7 ± 0.2	0.15 ± 0.02	
trans-**9**	228	0.39 ± 0.04	0.20 ± 0.02	0.022
	214	0.27 ± 0.03	0.06 ± 0.02	

[a] Ratio of the yield of ring-opening products (all isomers) to cycloreversion product. [b] The quantum yield for ring opening of **1** was measured by uranyl oxalate actinometry and is the average of four determinations; those for **5**, **8**, and **9** were measured using **1** as a secondary actinometer and are the averages of two determinations each. [c] Calculated according to eq 4, using RO/CR and Φ_{RO} to estimate Φ_{CR}, and $k(E)$ from Table 2 ($k(T)$ for *cis*- and *trans*-**9**), and $k_{\text{deact}} = 10^{11}$ s^{-1} in each case.

The quantum yield for ring opening of **1** with 228-nm excitation (Φ_{exp}) was determined by uranyl oxalate actinometry. Quantum yields for ring opening of the other five compounds were then determined using **1** as a secondary actinometer, from the relative slopes of concentration vs time plots for product formation between 0.5 and 5% conversion (see Supporting Information). Plots of the relative concentration of ring-opening (RO) and cycloreversion (CR) products ([**10**]/[**3**] for **8** and [**12**]/[**13**] for **9**) versus time yielded straight lines with slopes indistinguishable from zero, showing them to be constant over the conversion ranges monitored in all cases. Quantum yields for ring opening of *cis*- and *trans*-**9** were also determined with 214-nm excitation, again using **1** as a secondary actinometer ($\Phi_2 = 0.06^7$). The quantum yield data and RO/CR ratios are summarized in Table 1. No other products could be detected in any of the systems studied, within the limits of our analytical method over the conversion range monitored.

The quantum yields for 228-nm ring opening of the six cyclobutenes studied in this work vary only slightly throughout the series, and in most cases are similar to those obtained with 214-nm excitation. The one exception is *trans*-**9**, which reacts 3−4 times more efficiently at 228 nm than at 214 nm. Since **12** (as the stable cis,cis-isomer) is the product of conrotatory ring opening of *trans*-**9**, the significantly increased quantum yield for ring opening of this compound at 228 relative to 214 nm is consistent with the behavior of *cis*- and *trans*-**5**, both of which undergo clean conrotatory ring opening with 228-nm excitation.[12] Interestingly, the RO/CR ratios for both isomers of **9** and the quantum yield for ring opening of the cis-isomer change very little as a function of excitation wavelength.

Vibrational spectra for **1**, *cis*- and *trans*-**5**, and **8** were calculated at the B3LYP/6-31G*+d level of theory, while those for *cis*- and *trans*-**9** were calculated at the B3LYP/3-21G* level. A correction factor of 0.98 was applied to the vibrational frequencies.[37]

Estimates of $k(T)$ for the six molecules were calculated from the published Arrhenius parameters for thermal ring opening, using "effective temperatures", T_{eff}, calculated from the statistical thermodynamical expression for the total internal energy of a

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Table 2. Thermal Ring Opening of Alkylcyclobutenes: Arrhenius Parameters,[31,33,38] Effective Temperatures, and Calculated Rate Constants ($E = 43\,860$ cm^{-1})

compound ($3N - 6$)	E_a (kcal/mol)	$\log(A/\mathrm{s}^{-1})$	T_{eff}/K^a	$k(T)$/10^9 s$^{-1\,b}$	$k(E)$/10^9 s$^{-1\,c}$
1 (42)	36.0	13.84	2340	29	21
cis-**5** (60)	37.7	14.2	1970	10	2.2
trans-**5** (60)	33.6 (*EE*)	13.85 (*EE*)	1815	6.2	4.0 (*EE*)
	~38.7 (*ZZ*)	14.2 (*ZZ*)	1815	3.3	1.6 (*ZZ*)
8 (78)	38.7^d	14.5^d	1515	0.8	0.30
cis-**9** (84)	44.2	14.2	1490	0.05	
trans-**9** (84)	28.9	13.6	1495	2.3	

^{a} Interpolated from plots of total internal energy ($\langle E\rangle$; see eq 8) versus temperature. ^{b} Thermal rate constant from Arrhenius equation at T_{eff}. ^{c} RRKM calculated rate constant. ^{d} Changed from the reported values[33] of $E_a = 40.5$ kcal/mol and $\log(A/\mathrm{s}^{-1}) = 15.5$ (see text).

molecule (eq 8), given the computed vibrational spectra and a

$$\langle E\rangle = \sum_{i=1}^{3N-6} \frac{h\nu(i)}{\exp\{h\nu(i)/kT\} - 1} \tag{8}$$

total internal energy corresponding to that of a 228-nm photon ($\langle E\rangle = 43\,860$ cm^{-1}). The reported Arrhenius parameters for thermal ring opening of **8** ($E_a = 40.5$ and $\log(A/\mathrm{s}^{-1}) = 15.5$, based on three data points)[33] seemed unrealistically high, so they were adjusted to values which seemed more reasonable ($E_a = 38.7$ and $\log(A/\mathrm{s}^{-1}) = 14.5$), and which reproduced the rate constants to within 25% of their reported values over the 180−200 °C temperature range. Arrhenius parameters for ring opening of *trans*-**5** to *ZZ*-**6** are unknown, and so they were assumed to be roughly the same as those for ring opening of **8**: $E_a = 38.7$ kcal/mol and $\log A = 14.2$. Table 2 summarizes the published Arrhenius parameters for the six compounds, their effective temperatures, and the values of $k(T)$ estimated by this procedure.

Estimates of $k(E)$ were calculated for **1**, *cis*- and *trans*-**5**, and **8** using RRKM theory.[39] For each compound, the ring C−C stretching mode at ca. 1150 cm^{-1} was chosen as the primary reaction coordinate, and four of the low-frequency modes were chosen as variables for estimation of the vibrational spectrum of the activated complex. The remaining portion of the spectrum was then abbreviated by grouping vibrations of similar frequencies together, to produce spectra containing a maximum of 40 individual frequencies. The spectrum of the activated complex was assumed to be identical to that of the initial substrate, except for the primary reaction coordinate and the four modes chosen as variables; these were adjusted manually so as to reproduce the entropy of activation corresponding to the reported Arrhenius *A* factor for thermal isomerization of the molecule. Values of $k(E)$ were then calculated for internal energies ranging from 20 000 to 49 000 cm^{-1}. The results of these calculations are shown graphically in Figure 1; the $k(E)$ values at an internal energy of 43 860 cm^{-1} were then obtained by interpolation of these data and are listed in Table 2. As can be seen from the table, the RRKM rate constants, $k(E)$, are all quite similar to the more qualitative thermal rate constants, $k(T)$, obtained using the Arrhenius equation and effective temperatures calculated from statistical thermodynamics.

Expected values for the quantum yield of ring opening by the hot ground-state mechanism (Φ_{calc}) were then calculated according to eq 4, using as estimates for k_{RO} either the $k(E)$ values from RRKM theory for **1**, **5**, and **8** or the $k(T)$ values for **9**, together with the value of 10^{11} s^{-1} for k_{deact}. These are listed in Table 1, along with the experimental quantum yield data for these compounds.

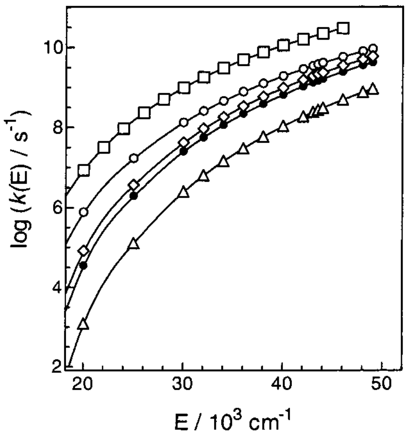

Figure 1. log($k(E)$) (from RRKM theory) vs E for the ring opening of alkylcyclobutenes **1** (□), *cis*-**5** (◇), *trans*-**5** (*EE*, ○; *ZZ*, ●), and **8** (△).

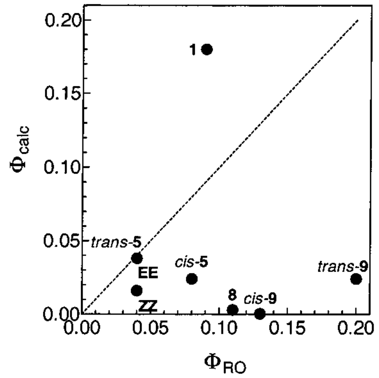

Figure 2. Comparison of calculated (Φ_{calc}) versus experimental (Φ_{RO}) quantum yields for 228-nm photochemical ring opening of alkylcyclobutenes.

While the experimental quantum yields for ring opening vary by less than a factor of 5 throughout within the series, the values calculated from the RRKM data show the expected marked variation with molecular size. Figure 2 shows a plot of calculated vs experimental quantum yields for the six compounds studied in this work, which illustrates the resulting poor fit of the experimental data to the mechanistic model on which the calculated values are based. For the larger molecules in the series (**8** and **9**), the experimental quantum yields are between 10 and ca. 300 times higher than the values predicted on the basis of the hot ground-state model, differences that are well beyond what might be accommodated by the uncertainties associated with the various assumptions used in the calculations. Thus, the results strongly suggest that, in general, Rydberg-derived ring opening does proceeds not via the hot ground-state mechanism but as a true excited-state process in which ring opening is initiated on the π,R(3s) potential energy surface. Unlike π,π^* state ring opening, which orbital symmetry rules predict to proceed in disrotatory fashion, the π,R(3s) process appears to proceed with the preferred conrotatory stereochemistry that is predicted theoretically for the ring opening of cyclobutene radical cations.[17,18] Simple orbital symmetry considerations lead to the prediction that π,R(3s) excited-state ring opening should proceed with the same stereochemistry as the ground-state process, since the highest occupied π-MO of the diene product is the same for ring opening of the π,R(3s) state as it is for ring opening in the ground state. The same is true for ring opening of the radical cation.

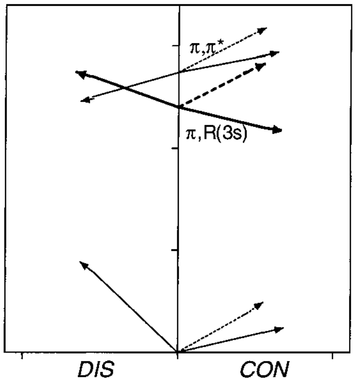

Figure 3. Sketch of ground, π,π^*, and π,R(3s) potential energy surfaces for *con-* and *disrotatory* ring opening in monocyclic cyclobutenes (solid lines; e.g., *cis*-**5**) and in derivatives such as *cis*-**9** (dashed lines), in which the conrotatory pathway is blocked due to structural constraints.

It is interesting to note that *cis*-**9** maintains a high degree of reactivity toward ring opening with 228-nm excitation; one might have expected otherwise on the basis of the fact that conrotatory ring opening must produce the highly strained cis,trans-isomer of the diene **12**. This might be explained by a mechanism in which a pathway for internal conversion to the π,π^* surface is activated by the introduction of a structurally induced barrier to conrotatory ring opening on the π,R(3s) surface, analogous to that which exists on the ground-state surface for ring opening of this molecule.[8,38] This is illustrated in Figure 3. A similar explanation might account for the significant yields of diene obtained from *trans*-**9** upon shorter wavelength (π,π^*) excitation,[40] where structural constraints toward disrotatory ring opening may activate internal conversion to the π,R(3s) excited-state surface and ring opening via the conrotatory pathway. If this explanation is correct, then one might expect to observe pronounced temperature effects on the quantum yields for ring opening of structurally constrained derivatives of this type.

Summary and Conclusions

Selective excitation at the long-wavelength edge of the π,R(3s) absorption band of a series of 1,2-dialkyl-substituted cyclobutenes results in competing electrocyclic ring opening and [2 + 2] cycloreversion. Under these conditions, ring opening proceeds with clean conrotatory stereochemistry and with an efficiency that does not vary systematically with either molecular size or reactivity toward ground-state ring opening. Thus, the experimental quantum yields do not correlate with those expected for ring opening via a hot ground-state mechanism. The latter have been estimated from calculated (RRKM) rate constants for ground-state ring opening at internal thermal energies corresponding to the energy of a 228-nm photon. This lack of a correlation between experimental and calculated quantum yields suggests that Rydberg-derived ring opening occurs as a true excited-state process and does not proceed from upper vibrational levels of the ground state, populated by internal conversion from the Rydberg state.

Previous work[9−11] suggests that the π,π^* ring opening of alkylcyclobutenes proceeds via an adiabatic mechanism, in which a single diene isomer is produced in the π,π^* excited state by the disrotatory ring-opening pathway. The overall nonstereospecificity of the reaction then results from decay of the excited diene product by *E*,*Z*-isomerization. However, there is generally considerable overlap between the valence and Rydberg absorptions in the gas- and solution-phase UV absorption spectra of alkylcyclobutene derivatives, and so it remains to be determined whether competing reaction from the π,π^* (disrotatory) and π,R(3s) (conrotatory) excited states might provide a more likely explanation for the overall nonstereospecificity observed upon shorter wavelength excitation. This possibility will be addressed in a forthcoming paper.

Experimental Section

The cyclobutenes studied in this work were prepared and purified as previously reported,[7,40] while photoproducts were identified by GC co-injection with authentic samples or after isolation from semipreparative-scale photolyses of the corresponding cyclobutene derivative. The cyclobutenes were purified to >99% purity by semipreparative gas chromatography, using stainless steel columns ([a] 20% ODPN on 80/100 Chromosorb PNAW, 0.25 in. × 20 ft (compound **1**); [b] 3.8% UCW-982 on 80/100 Supelcoport, 0.25 in. × 24 ft (*cis*- and *trans*-**5** and **8**); [c] 15% Carbowax on 80/100 Chromosorb PNAW, 0.25 in. × 12 ft (*cis*- and *trans*-**9**)). Cyclohexane, hexanes, isooctane, and decane (BDH Omnisolv) were used as received from the supplier. UV absorption spectra were recorded using a Cary 50 UV/vis spectrophotometer in 1-cm Suprasil cells. Analytical gas chromatographic separations were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 0.53-mm × 30-m DB-1 fused silica column (Chromatographic Specialties, Inc.) for compounds **1**, *cis*- and *trans*-**5**, and **8**, or a 0.22-mm × 15-m DB-17 fused silica column (Chromatographic Specialities, Inc.) for *cis*- and *trans*-**9**. FID response factors were determined for all compounds by construction of standard working curves in the usual way.

Samples for photolysis contained the cyclobutene (ca. 0.05 M) and cyclohexane or decane (0.001 M) in isooctane (**1**) or hexanes (**5**, **8**, **9**) solution. Aliquots (ca. 0.3 mL) were placed in 5-mm-o.d. Suprasil tubes, sealed with rubber septa, and deoxygenated with a stream of dry argon. Photolyses were carried out in a merry-go-round apparatus, using 16-W Philips 93106E zinc or 16-W Philips 93107E cadmium resonance lamps for irradiation at 214 or 228 nm, respectively, and irradiating solutions of **1** and one of the other cyclobutenes simultaneously. Aliquots were removed at suitable time intervals and analyzed by GC. Product yields were determined from the slopes of product concentration vs time plots (see Supporting Information) and compared to the slope of the analogous plot for the formation of **2** from **1** for the determination of relative quantum yields.

The quantum yield for ring opening of **1** at 228 nm was determined in isooctane solution using uranyl oxalate as the actinometer, following the analytical procedure outlined by Kuhn et al.[41] The sample and actinometer solutions were placed in 4-mL cylindrical Suprasil cells, deoxygenated with argon, mounted on a merry-go-round apparatus, and irradiated with the Cd resonance lamp for ca. 30 min. The yield of **2** was measured by GC (as the average of three determinations), while the conversion of uranyl oxalate was measured by UV spectroscopy. A sample of uranyl oxalate was also photolyzed in a Pyrex cuvette for a similar period of time in order to check for the effects of the longer wavelength Cd emission bands on the photolyses. Conversion of the actinometer was found to be negligible.

Compound **1** was also used as the actinometer for determination of the quantum yields for ring opening of *cis*- and *trans*-**9** with 214-nm light, using the previously determined value of $\Phi_2 = 0.06 \pm 0.01$.[7]

Theoretical calculations were performed on a Silicon Graphics Octane computer using Gaussian 94.[42] RRKM calculations of the

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microcanonical rate constants, $k(E)$, were performed on a Sun E250 workstation using the Marcus expression,[39]

$$k(E) = L^{+}W(E_v^{+})/N(E^{*})$$

where L^{+} is the path degeneracy, $W(E_v^{+})$ is the sum of vibrational states of the complex, and $N(E^{*})$ is the density of states of the energized molecule. This assumes that adiabatic rotational effects are unimportant. Sums and densities of states were calculated by standard procedures (direct count/Whitten−Rabinovitch approximation).[39]

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Supporting Information Available: Representative concentration vs time plots showing the formation of diene products, from merry-go-round irradiation (228 nm) of alkylcyclobutenes **1**, *cis*- and *trans*-**5**, **8**, and *cis*- and *trans*-**9** in deoxygenated hexane solution at 25 °C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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