# Cyclobutene Photochemistry. Steric Effects on the Photochemical Ring Opening of Alkylcyclobutenes

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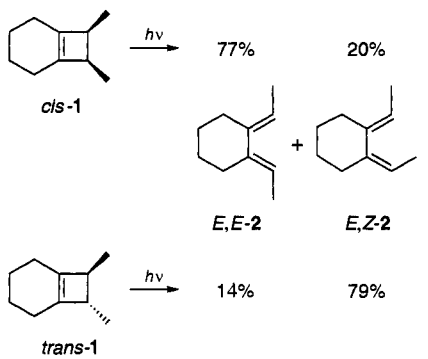
**Abstract:** Quantum yields for photochemical ring opening and cycloreversion in hydrocarbon solution have been determined for the direct photolysis (214 nm) of six 1,2-dimethylcyclobutene derivatives which contain methyl groups at $C_3$ and $C_4$ in numbers varying from zero to four. As the hydrogens on $C_3/C_4$ of the parent compound (1,2-dimethylcyclobutene) are replaced with increasing numbers of methyl groups, the total quantum yield for ring opening increases to a maximum of ~0.3 and then decreases with further methyl substitution. The quantum yields for ring opening ($\phi_{total}$) of hexamethylcyclobutene and 1,2-dimethylcyclobutene are nearly the same, and the lowest in the series. The maximum occurs with *trans*-1,2,3,4-tetramethylcyclobutene; $\phi_{total}$ for the *cis*-isomer is significantly lower, but both yield an approximate 1:1 mixture of formally allowed and forbidden diene isomers. A similar trend is observed in the relative quantum yields for ring opening and cycloreversion throughout the series. The results are interpreted in terms of a combination of bond strength and steric effects on the efficiency of the ring-opening process. Increasing methyl substitution causes an increase in $\phi_{total}$ through the first three members of the series owing to progressive weakening of the $C_3-C_4$ bond. Compounds containing *cis*-dimethyl substitution exhibit substantially reduced quantum yields for ring opening, relative to what would be expected based on bond strength effects alone. This is proposed to be due to steric effects on the efficiency of the process, suggesting that the initial stages of the photochemical ring opening of cyclobutene involve disrotatory motions on the excited singlet state potential energy surface.

## Introduction

Direct irradiation of alkylcyclobutenes in solution results in competitive ring opening and formal $[\sigma_{2s} + \sigma_{2s}]$ cycloreversion[1,2] along with the formation of minor amounts of rearrangement products in some cases.[3-5] In apparent violation of orbital symmetry selection rules,[6] ring opening proceeds nonstereospecifically. Cycloreversion, on the other hand, proceeds with complete retention of the stereochemistry at the $C_3$ and $C_4$ carbons of the cyclobutenyl system. We have recently shown that the two reaction pathways originate from singlet excited states of different configurations;[7] cycloreversion results from population of a Rydberg-like ($\pi$,R(3s)) excited state and may involve cyclopropyl carbene intermediates,[8] while ring opening ensues from the $\pi,\pi^*$ state.

While the nonstereospecificity of the ring-opening reaction appears to be quite general, isolated examples for which a high degree of disrotatory stereospecificity is observed have been reported.[9-11] One example is the photochemical ring opening of *cis*- and *trans*-7,8-dimethylbicyclo[4.2.0]oct-1[6]-ene (**1**; eq 1).

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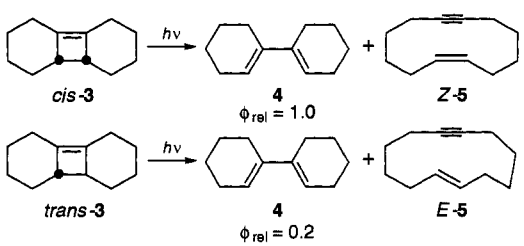
Ring opening of these compounds proceeds nonstereospecifically, but in both cases the formally-allowed isomer of diene **2** is formed in highest (>75%) chemical yield.[11] Most of the other systems which have been studied yield roughly equal distributions of formally-allowed and forbidden diene isomers.[1,2] A second example is provided by the photochemistry of *cis*- and *trans*-tricyclo[6.4.0.0$^{2,7}$]dodec-1$^2$-ene (**3**; eq 2),[10] which was first

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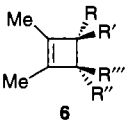
reported over 25 years ago by Saltiel and Ng Lim.[9] Photolysis of both of these compounds in hydrocarbon solution results in the formation of 1,1′-bicyclohexenyl (**4**) in addition to the cyclic enynes (**5**) resulting from cycloreversion, but *trans*-**3** undergoes ring opening with roughly five times lower efficiency than the *cis* isomer. We have interpreted this difference as suggesting that ring opening *initiates* with disrotatory motions on the excited state reaction coordinate;[1,2,11] ring opening of *trans*-**1** proceeds with relatively low efficiency because the disrotatory pathway involves incipient formation of the thermodynamically unstable *cis,trans* isomer of 1,1′-bicyclohexenyl.[9]

The suggestion that orbital symmetry does play a role in the reaction, in spite of its overall nonstereospecificity, is also supported by recent spectroscopic studies. Mathies and coworkers have recently reported the results of a study of cyclobutene ring opening by UV resonance Raman spectroscopy,[12] a technique which allows elucidation of the dynamics of photochemical reactions within the first 50 fs after electronic excitation.[13] These experiments indicate that the initial stages of ring opening on the lowest excited singlet state surface involve simultaneous disrotation about the $C_1-C_4$ and $C_2-C_3$ bonds, in addition to the expected structural changes involved in the process (i.e. lengthening of the $C_1-C_2$ and $C_3-C_4$ bonds and rehybridization of $C_3/C_4$). It was suggested that the nonstereospecificity observed in the ring opening of substituted systems is due either to substituent-induced perturbation of the ordering and/or interactions of the low-lying excited singlet states in the parent compound or to the loss in disrotatory stereospecificity occurring over a time scale longer than can be probed by resonance Raman intensities.[12]

If photochemical ring opening does indeed involve initial disrotatory motions on the excited state potential energy surface, then one might expect the overall efficiency of the reaction to be affected by steric interactions between substituents at $C_3$ and $C_4$. The importance of steric factors (of this type) in ground state disrotatory electrocycloreversions evidently has not been extensively documented, presumably because six-electron thermal electrocycloreversions are relatively uncommon as a result of the greater thermodynamic stability of 1,3-cyclohexadienes relative to their 1,3,5-hexatriene isomers.[14] Nevertheless, there is evidence to suggest that increasing the steric bulk of substituents at $C_5/C_6$ of a cyclohexadienyl system does result in an increase in the activation energy for thermal ring opening.[15] Secondary deuterium kinetic isotope effects on the thermal electrocyclization of 1,3,5-hexatriene suggest that steric factors play a dominant role in the reverse (electrocyclization) process.[16] One might expect that the effects of such interactions should be even more acutely exerted on the rates of excited state disrotatory electrocyclic processes, since excited state pericyclic reactions are normally subject to quite small activation barriers. All else being equal, the result should be a reduction in the quantum yield for cyclobutene excited state ring opening when one or both of the two possible disrotatory electrocyclic modes are blocked by *syn*-dialkyl substitution, provided that such motions are involved in the evolution of the process on the excited state potential energy surface.

In this paper, we describe the results of a study which was designed to evaluate the importance of steric factors on the excited state ring opening of alkylcyclobutene derivatives. We report the photochemistry of the series of 1,2-dimethylcyclobutene derivatives **6a**–**e**

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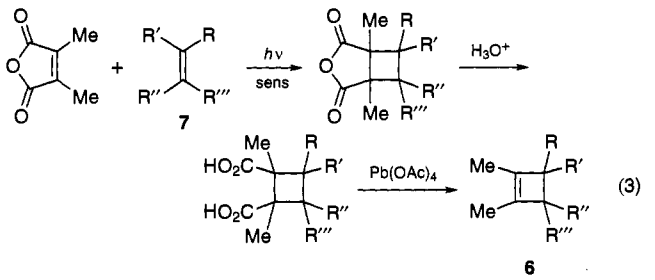
**a**: R = R′ = R″ = R‴ = H
**b**: R = R′ = R″ = H; R‴ = Me
**c** (*trans*): R = R‴ = H; R′ = R″ = Me
**c** (*cis*): R = R″ = H; R′ = R‴ = Me
**d**: R = H; R′ = R″ = R‴ = Me
**e**: R = R′ = R″ = R‴ = Me

in hydrocarbon solution upon 214-nm excitation, including quantum yields for the formation of ring opening and cycloreversion products. The possible role of orbital symmetry in the early stages of this prototypical photoelectrocyclic reaction are discussed in light of our results.

## Results

Cyclobutenes **6b**–**d** were synthesized by a general route consisting of triplet-photosensitized [2 + 2] cycloaddition of dimethylmaleic anhydride with the appropriate alkene (**7b**–**d**), acid hydrolysis of the resulting bicyclic anhydride, and oxidative decarboxylation of the resulting cyclobutanedicarboxylic acid with lead tetraacetate (eq 3).[8,11,17] In the case of **6e**, oxidative




(3)

decarboxylation was carried out directly on the anhydride, without prior hydrolysis to the dicarboxylic acid. The isomeric compounds *cis*- and *trans*-**6c** were synthesized as a mixture and were separated by semipreparative gas chromatography (GC).[17] 1,2-Dimethylcyclobutene (**6a**) was synthesized by photochemical electrocyclization of 2,3-dimethyl-1,3-butadiene (**8a**).[18] All six compounds in the series were purified to >99% purity (as determined by GC) by semipreparative GC.

Ultraviolet absorption spectra of the six compounds were recorded in deoxygenated hexadecane solution at 23 °C. Those of *cis*- and *trans*-**6c** were similar to the previously reported spectra in isooctane solution.[17] The spectra of the other four compounds are similar to one another, showing only edge absorption extending to *ca.* 225 nm in the spectral region above 185 nm. The molar extinction coefficient at 214 nm is in the range 1000–2000 $M^{-1}$ $cm^{-1}$ for all compounds in the series.

Direct photolysis of deoxygenated, 0.02–0.05 M solutions of **6a**–**e** in hexadecane with the unfiltered light from a Zn resonance lamp (214 nm) yields the isomeric dienes **8a**–**e** as mixtures of geometric isomers, the alkenes **7a**–**e**, and 2-butyne (**9**) (see eqs 4–6). The dienes were identified after isolation from preparative scale photolyses by semipreparative GC or by GC coinjection of the crude photolysatees with authentic samples. 2-Butyne and **7a**–**e** were identified by GC/MS and by coinjection with authentic samples. No other products were detected in any case, within the detection limits of our analytical technique (<2% of the major product). The relative yields of *E,E*-, *E,Z*-, and *Z,Z*-**8c** from photolysis of *cis*- and *trans*-**6c** under

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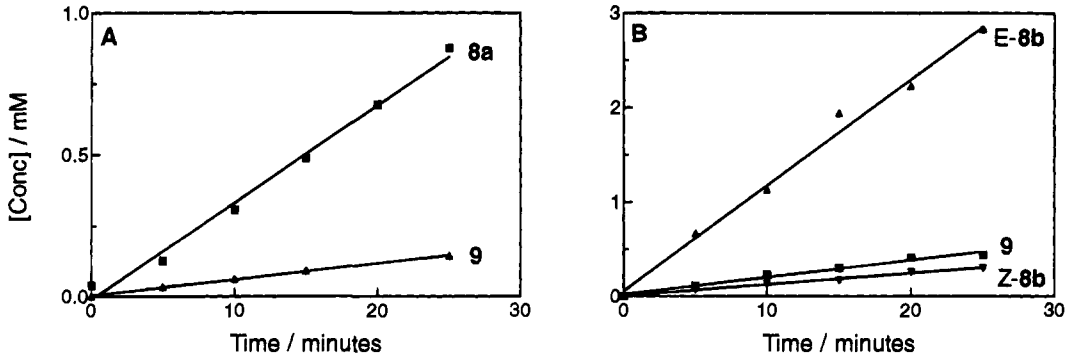
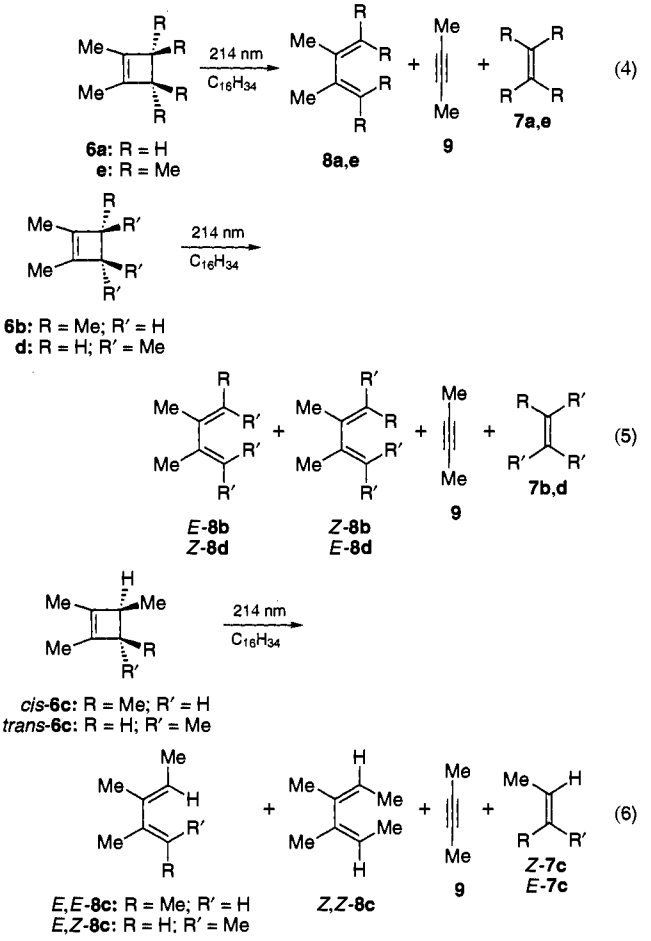



**Figure 1.** Concentration *vs* time plots for product formation from 214-nm photolysis of deoxygenated 0.05 M solutions of **6a** (A) and **6b** (B) in hexadecane at 23 °C.

these conditions are identical to those reported previously from photolysis in isooctane solution.[17]




The quantum yield for formation of **8a** from the photolysis (214 nm) of 1,2-dimethylcyclobutene (**6a**) in deoxygenated hexadecane solution was determined by uranyl oxalate actinometry and is the average of triplicate determinations. Quantum yields for 2-butyne formation from **8a** and for diene and 2-butyne formation from **6b**–**e** in hexadecane solution were determined by merry-go-round photolyses relative to the quantum yield for formation of **8a** from **6a** in the same solvent, over conversion ranges of 5–10%. Product quantum yields were determined for each compound from the slopes of concentration vs time plots, examples of which are shown in Figure 1 for product formation from the photolysis of **6a** and **6b** in hexadecane solution. The quantum yield data are collected in Table 1.

**Table 1.** Quantum Yields for Ring Opening and Cycloreversion from Direct Photolysis (214 nm) of Cyclobutenes **6** in Deoxygenated Hexadecane Solution at 23 °C[a]

| compd | $\phi_8$ | $\phi_8^{total}$ | $\phi_9$ |
|---|---|---|---|
| **6a** | 0.060 ± 0.008[b] | 0.060 ± 0.008 | 0.010 ± 0.002 |
| **6b** | *E*-**8b**: 0.20 ± 0.04<br>*Z*-**8b**: 0.021 ± 0.004 | 0.22 ± 0.05 | 0.032 ± 0.007 |
| *cis*-**6c** | *E,E*-**8c**: 0.069 ± 0.015<br>*E,Z*-**8c**: 0.10 ± 0.02<br>*Z,Z*-**8c**: 0.0004 ± 0.0001 | 0.17 ± 0.04 | 0.015 ± 0.003 |
| *trans*-**6c** | *E,E*-**8c**: 0.089 ± 0.015<br>*E,Z*-**8c**: 0.14 ± 0.03<br>*Z,Z*-**8c**: 0.029 ± 0.006 | 0.26 ± 0.05 | 0.014 ± 0.003 |
| **6d** | *E*-**8d**: 0.16 ± 0.03<br>*Z*-**8d**: 0.005 ± 0.002 | 0.17 ± 0.03 | 0.021 ± 0.005 |
| **6e** | 0.05 ± 0.02 | 0.05 ± 0.02 | 0.010 ± 0.002 |

[a] Determined relative to that of the formation of **8a** from photolysis of **6a**,[b] using the slopes of concentration *vs* time plots from merry-go-round irradiations of **6b**–**e** and **6a**. [b] Determined by uranyl oxalate actinometry.

## Discussion

The series of monocyclic alkylcyclobutenes (**6a**–**e**) studied in the present work all have lowest Rydberg-like ($\pi$,R(3s)) excited singlet states, but the valence ($\pi,\pi^*$) state is reasonably close in energy and accessible upon irradiation with 214-nm light.[17] All six compounds contain identical substitution on the cyclobutenyl C=C bond, so the relative energies of the two low-lying singlet states should be approximately constant throughout the series. This is verified by the solution-phase UV absorption spectra of the compounds; the spectra of all six compounds show weak, diffuse absorptions superimposed on the more intense $\pi,\pi^*$ absorption band centered at shorter wavelengths.

The Rydberg-like excited singlet state is thought to be responsible for the formal [2 + 2] photocycloreversion reaction of alkylcyclobutenes,[7] leading in the present cases to the formation of the corresponding alkenes (**7**) and 2-butyne (**9**). Alkene Rydberg states commonly undergo 1,2-alkyl and -hydrogen migrations leading to carbenes,[19] and we have shown that cyclopropylcarbenes are formed to at least a small extent in the photolysis of alkylcyclobutene derivatives.[8] However, whether or not cyclopropylcarbenes are true intermediates in the cycloreversion reaction is difficult to determine; these species, when generated by thermolysis or photolysis of diazo- or diazirine-precursors, usually yield relatively small amounts of fragmentation products, the major products being cy-

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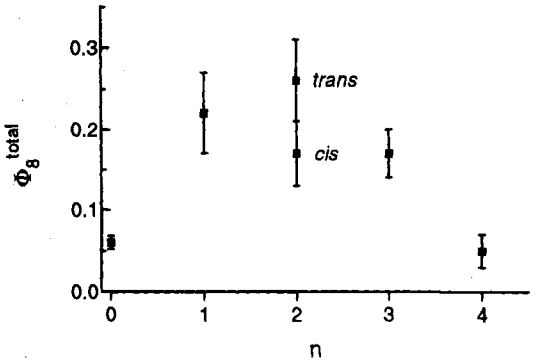


**Figure 2.** The total quantum yield for diene formation ($\Phi_8^{total}$) *vs* the number of $C_3/C_4$ methyl groups ($n$) in 1,2-dimethylcyclobutene derivatives **6a**–**e**.

clobutenes derived from ring expansion.[20-22] In contrast, ring expansion products are formed in much lower yield than cycloreversion products in the photolysis of unsymmetrically-substituted alkylcyclobutenes for which isomerization via the cyclopropyl carbene route can be detected.[8]

The quantum yields for formation of **7** and **9** vary irregularly throughout the series of cyclobutenes **6a**–**e** (Table 1) but are relatively small (0.01–0.03) in all cases. The quantum yields for photocycloreversion of *cis*- and *trans*-**6c** are identical within experimental error, and as noted previously,[17] the reaction proceeds stereospecifically. There is no apparent trend in the variation in cycloreversion efficiency with substitution at $C_3$ and $C_4$ of the cyclobutene ring in **6**.

The quantum yields for ring opening, on the other hand, do show a regular variation with $C_3/C_4$ substitution. Figure 2 shows a plot of the total quantum yield for diene formation from **6** ($\Phi_8^{total}$) *versus* the number of methyl groups at $C_3/C_4$ ($n$). The maximum occurs with *trans*-**6c** ($n$ = 2) and falls off as the degree of methyl substitution is increased or decreased from this value. The quantum yield for ring opening of *cis*-**6c** is roughly 2/3 of that observed for the *trans* isomer.

We ascribe the increase in $\Phi_8^{total}$ between $n$ = 0 and $2_{trans}$ to a progressive weakening of the $C_3$–$C_4$ bond as a result of increasing methyl substitution. Such effects have been noted previously[1,2] and result in increased yields of dienes relative to cycloreversion products as the cyclobutenyl $C_3$–$C_4$ bond is weakened through appropriate substitution.[23] The same trend is observed here for **6a**, **6b**, and *trans*-**6c**, which exhibit $\Phi_8^{total}/\Phi_9$ ratios of ~6, 7, and 18, respectively. The quantum yield ratios fall off again in compounds *cis*-**6c** (11), **6d** (8), and **6e** (5). From the point of view of bond-strength arguments alone, one might expect these values to continue to increase with increasing methyl substitution at $C_3/C_4$; in the case of *cis*-**6c**, the $C_3$–$C_4$ bond strength might in fact be expected to be smaller than that in the *trans* isomer owing to eclipsing of the methyl groups. *syn*-Dimethyl substitution clearly causes a reduction in both the absolute and relative quantum yields for ring opening compared to what might be expected on the basis of bond strength arguments alone. Thus, the present data allow us to rule out a simple biradical mechanism for the process, in which ring opening occurs by linear $C_3$–$C_4$ bond rupture to yield a 1,4-biradical, which then relaxes to yield a mixture of diene isomers.[4]

A reasonable explanation for the reduced absolute and relative yields of dienes obtained from those compounds containing *syn*-

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(21) White, W. R. I.; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841.
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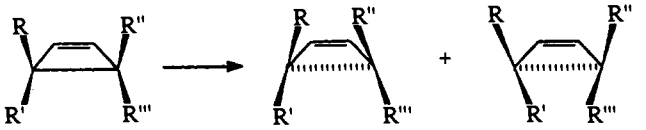
**Scheme 1.** Disrotatory Modes in Cyclobutene Ring Opening




dimethyl substitution (*cis*-**6c**, **6d**, and **6e**) is that the rate of excited state ring opening (relative to the rates of other excited state decay pathways) is altered by steric effects between *syn* substituents at $C_3/C_4$. Such effects would be expected if ring opening involves disrotatory motions in its early stages on the excited state reaction coordinate. Ring opening involving disrotatory twisting about the $C_1$–$C_4$ and $C_2$–$C_3$ bonds as the $C_3$–$C_4$ bond cleaves can occur by two pathways, as is illustrated in Scheme 1. Each of these pathways involves buttressing of one set of the *syn* substituents at $C_3/C_4$ (R/R″ or R′/R‴). Both pathways for ring opening of *trans*-**6c** involve methyl–hydrogen buttressing, while those for *cis*-**6c** involve methyl–methyl and hydrogen–hydrogen interactions. The increase in $\Phi_8^{total}$ throughout the initial three members of the series (**6a**, **6b**, and *trans*-**6c**) suggests that no appreciable loss in efficiency results from replacing one pathway involving a hydrogen–hydrogen interaction with one involving a methyl–hydrogen interaction. Thus, the reduced $\Phi_{8c}^{total}$ observed for *cis*-**6c** compared to that for the *trans* isomer can be ascribed to the fact that there is available to the *cis* isomer only one ring-opening pathway which does not involve an unfavorable methyl–methyl interaction. The similarity in the quantum yields of ring opening of *cis*-**6c** and **6d** is consistent with the trend established by the earlier members of the series, *i.e*, that replacing a hydrogen-hydrogen interaction with a methyl–hydrogen interaction does not result in an appreciable loss in overall efficiency. The fact that *both* ring-opening pathways involve methyl–methyl interactions in the case of **6e** results in a substantial reduction in $\Phi_8^{total}$ compared to those observed for *cis*-**6c** and **6d**. It is noteworthy that the quantum yields for ring opening of 1,2-dimethylcyclobutene (**6a**) and hexamethylcyclobutene (**6e**) are the same within experimental error.

If steric factors do have an effect on the rate of disrotatory excited state ring opening, then one would also expect to observe some discrimination in product distribution in cases where disrotatory ring opening can lead to two diene isomers. This *is* observed in the three compounds in the series to which this applies: *cis*-**6c** (*E,E/Z,Z*-**8c** ~ 170), **6d** (*E/Z*-**8d** ~ 30), and **6b** (*E/Z*-**8b** ~ 10). The behavior of *cis*-**6c** should be contrasted with that of the *trans* isomer, from which *E,E*-**8c** is formed in only three times the yield of *Z,Z*-**8c**. It is interesting that the degree of steric discrimination observed in the ring opening of the three compounds (*cis*-**6c** > **6d** > **6b**) follows the *difference* in the severity of the steric interactions involved in the two possible disrotatory ring-opening pathways for each compound (i.e., Me/Me *vs* H/H > Me/Me *vs* Me/H > Me/H *vs* H/H). However, the significance of this trend must be tempered by the fact that for **6b** and **6d**, both diene isomers can be formed by either dis- or conrotatory ring-opening pathways.

While the trends noted above are consistent with other indications[10-12] that, in spite of the overall nonstereospecificity of the photochemical ring opening of alkylcyclobutenes, disrotatory motions *are* involved in the initial stages of the process on the excited state potential energy surface, there are clearly other possible explanations that must be considered. One is that the observed substituent effect on the quantum yield of ring opening of **6** might be due to an effect on some other excited state decay process besides ring opening. This could be explicitly addressed if the excited singlet state lifetimes of **6a**–**e**

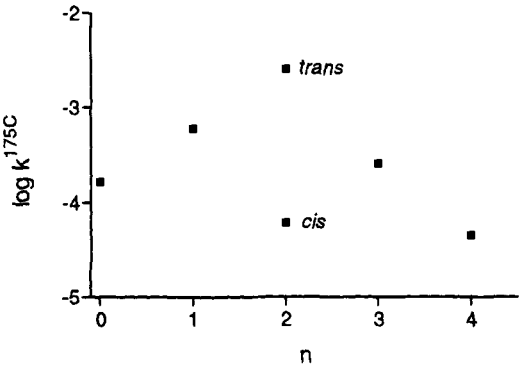



**Figure 3.** Rate constants for thermal ring opening of 1,2-dimethylcyclobutene derivatives **6a**−**e** in the gas ($n = 0$−2) and solution ($n =$ 3, 4) phase at 175 °C[27] *vs* the number of $C_3/C_4$ methyl groups ($n$).

could be determined, since this would allow calculation of absolute rate constants for excited state ring opening. At the very least, however, the fact that the *relative* quantum yields for ring opening and fragmentation (which equal the relative rates of the two processes) vary with substituent in similar fashion to the absolute values for ring opening (*vide supra*) allows the conclusion that *syn*-dimethyl substitution at $C_3/C_4$ affects the rates of the two *reactive* excited state decay processes in different ways: it either decreases the rate of ring opening or increases the rate of cycloreversion. The former seems the more reasonable possibility.

It is interesting to compare the trends in the quantum yields for photochemical ring opening of **6a**−**e** as a function of $C_3/C_4$ methyl substitution with those in the free energies of activation for the thermal ring opening of the same compounds. The latter is illustrated in Figure 3, which shows a plot of calculated (from published data[24-27]) rate constants for the thermal ring opening of **6a**−**e** *versus n*. The rate constants for **6a**−**c** are gas-phase values,[24-26] while those for **6d,e** are solution-phase values.[25] As can be seen from comparison of Figures 2 and 3, the trends as a function of degree of methyl substitution at $C_3/C_4$ of the cyclobutene ring are similar for the photochemical and thermal ring-opening processes of these compounds. The trend in $\Delta G^{\ddagger}$ with methyl substitution in these compounds has been explained as being due to a combination of steric and electronic effects on the energetics of the ground state (conrotatory) process;[27-29] the combination of these effects results in a strong preference for formation of diene isomer(s) arising from (conrotatory) outward rotation of methyl substituents on $C_3/C_4$ and rate retardations when both conrotatory modes involve inward rotation of methyl substituents. Thus for the present series of compounds, similar substituent effects on the rates of disrotatory and conrotatory ring opening are, in fact, expected. In order to demonstrate more precisely the role of steric effects on the quantum yields of excited state ring opening, it will clearly be necessary to study systems for which steric effects play a subordinate role to electronic effects in thermal ring opening.

The most attractive mechanism to explain the general features of cyclobutene photochemical ring opening is one which involves initial disrotatory motions on the excited state surface, but decay to the ground state surface occurs in such a way that more than one isomeric diene is obtained. This would be the case if the excited-to-ground state funnel geometry for ring opening is similar to that for excited state *cis,trans* isomerization of the diene. In terms of the conventional avoided surface crossing mechanism for excited state reactions,[30] this could occur if disrotatory ring opening proceeds to completion on the excited state surface to yield fully open excited *s-cis* diene (i.e., adiabatically). In terms of more recent theoretical views of photopericyclic reactions,[31] this would occur if internal conversion to the ground state surface occurs at the same *conical intersection* as would be involved in the photochemistry of the corresponding *s-cis* diene. *Ab initio* (MC-SCF) calculations for 1,3-butadiene indicate that the geometry of the conical intersection accessible from the $^2A_g$ state of the *s-cis* conformer is one in which the $C_1-C_2$ and $C_3-C_4$ bonds are twisted (in the disrotatory sense) and the central bond ($C_2-C_3$ in 1,3-butadiene; $C_1-C_2$ in cyclobutene) is twisted by about 50°.[32] Recent experimental results for both cyclobutene[11,12] and constrained *s-cis* dienes[33] support the notion that central bond twisting is involved in the photochemistry of cyclobutene and 1,3-butadiene.[1,2]

Another mechanism that has been suggested to explain the nonstereospecificity of cyclobutene ring opening attributes the formation of formally forbidden diene isomers to (conrotatory) reaction from upper vibrational levels of the ground state, which are populated by internal conversion in competition with disrotatory ring opening.[1-3] It is possible that such a mechanism could explain the similarities between the substituent effects on the thermal and photochemical ring opening of **6a**−**e** which were noted earlier. However, for this to be true, the average effective temperature of the ground state species undergoing reaction would have to be such that the thermal energy available is of a similar magnitude to the average thermal activation barrier for conrotatory ring opening of alkylcyclobutenes (~35 kcal/mol[27]). This being the case, it is then difficult to explain the substantial yield of *Z,Z*-**8c** obtained from photolysis of *trans*-**6c** (*Z,Z/E,E* ~ 0.3); the *Z,Z*-diene is not formed in detectable yields (i.e., <1% of that of *E,E*-**8c**) in the thermal ring opening of this compound.[25]

The similarity in the trends in the quantum yields for photochemical ring opening and free energy of activation for thermal ring opening of **6a**−**e** thwart any attempt to distinguish between preferred con- and disrotatory ring-opening modes in the photochemical ring opening of these compounds. At the very least, however, the present results are consistent with other indications[10-12] that the photochemical process initiates with preferred disrotatory twisting of the $C_1-C_4/C_2-C_3$ bonds on the excited state potential energy surface for ring opening. Further work is in progress to fully elucidate the mechanism and molecular factors responsible for its apparent deviation from orbital symmetry selection rules.

## Experimental Section

Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396 integrator, and (a) a HP-1 megabore capillary column (12 m × 0.53 mm; Hewlett-Packard, Inc.) or (b) a SPB-1 microbore capillary column (15 m × 0.2 mm; Supelco, Inc.).

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Semipreparative GC separations employed a Varian 3300 gas chromatograph and one of the following stainless steel columns: (c) 20% $\beta,\beta$-oxybis(dipropionitrile) (ODPN) on 80/100 Chromosorb PNAW (20 ft × 0.25 in.) or (d) 3.8% UC W982 on 80/100 Supelcort (24 ft × 0.25 in.).

2,3-Dimethyl-1,3-butadiene, 2,3-dimethylmaleic anhydride, acetophenone, propene, 2-butene (*cis* + *trans*), 2-methyl-2-butene, 2,3-dimethyl-2-butene, 2-butyne, and *n*-heptane were all used as received from Aldrich Chemical Co. Ethyl acetate was Baker Analyzed (HPLC grade). Tetrahydrofuran and ethyl ether were purchased from Fisher Chemical Co., dried over sodium/benzophenone and distilled prior to use. Pentane and cyclohexane were Baker Analyzed (Photrex grade) and used as received from the supplier. Lithium perchlorite and uranyl sulfate were purchased from Alfa Inorganics and used as received. Oxalic acid (BDH) was recrystallized three times from water. Uranyl oxalate was prepared and purified according to the published method.[34] *n*-Hexadecane was purchased from Aldrich and purified by stirring several times with concentrated sulfuric acid for 12 h, followed by several washings with aqueous sodium bicarbonate and water. It was then dried with anhydrous sodium sulfate, refluxed for 12 h over calcium hydride, and then distilled under reduced pressure using a Vigreux fractionating column. The material obtained showed a UV absorbance of <0.05 at 200 nm (1 cm pathlength).

**1,2-Dimethylcyclobutene (6a).**[18] A solution of 2,3-dimethyl-1,3-butadiene (**8a**, 3.63 g, 0.044 mol) in pentane (15 mL) was placed in a 25.0 mL quartz tube which was sealed with a rubber septum, deoxygenated with a stream of dry nitrogen for 15 min, and irradiated with seven 254-nm light lamps in a Rayonet reactor to a conversion of ca. 50% (6 h; estimated by GC using column c). The solution was reduced to a volume of ca. 7 mL by distillation at atmospheric pressure, and the residue was bulb-to-bulb distilled under vacuum. 1,2-Dimethylcyclobutene (**6a**) was isolated from the crude mixture by semipreparative gas chromatography on column c and exhibited spectral data similar to those previously published.[18]

Compounds **6b–d** were synthesized in 20–30% overall yield in three steps consisting of acetophenone-sensitized photocycloaddition of 2,3-dimethylmaleic anhydride to the corresponding alkene **7**, hydrolysis of the resulting bicyclic anhydride to the corresponding cyclobutanedicarboxylic acid, and oxidative decarboxylation of the dicarboxylic acid(s). The procedures employed varied only slightly from those published previously for *cis*- and *trans*-**6c**[17] and other alkylcyclobutene derivatives.[3,4,8] Compound **6e** was synthesized by an analogous procedure, except the lead tetraacetate oxidation was carried out directly on the bicyclic anhydride without prior hydrolysis to the dicarboxylic acid. The cyclobutenes were purified to >99% purity by preparative GC using columns c or d and exhibited $^1$H NMR spectra which were similar to the published spectra in each case. Those of *cis*- and *trans*-**6c** have been reported by us previously.[17] $^1$H NMR, mass, and UV spectral data for **6b**, **6c**, and **6e** are given below. **1,2,3-Trimethylcyclobutene (6b)**:[26] $^1$H NMR $\delta$ 0.91 (d, 3 H), 1.07 (s, 6 H), 2.45 (m, 2 H), 3.21 (m, 1 H); MS *m/e* (*I*) 96 (45), 95 (12), 81 (100), 80 (75), 79 (51), 68 (61), 55 (65), 54 (66), 42 (39), 41 (29); UV (hexadecane) $\lambda_{max}$ ($\epsilon$) 186 (12 100). **1,2,3,4-Pentamethylcyclobutene (6d)**:[35] $^1$H NMR ($CCl_4$) $\delta$ 1.02 (d, $J$ = 6.8 Hz, 3H), 1.21 (s, 6H), 1.37 (s, 6H), 2.71 (m, 1H); MS *m/e* (*I*) 124 (32), 123 (5), 109 (54), 108 (23), 96 (31), 82 (52), 70 (100), 69 (67), 68 (32), 55 (47), 54 (43), 53 (32), 37 (21), 27 (12); UV (hexadecane) $\lambda_{max}$ ($\epsilon$) 187 (7700). **Hexamethylcyclobutene (6e)**:[35–37] $^1$H NMR ($CDCl_3$) $\delta$ 1.02 (s, 12H), 1.44 (s, 6H); MS *m/e* (*I*) 138 (29), 137 (9), 123 (67), 97 (35), 96 (100), 95 (54) 93 (21), 80 (13), 79 (56), 78 (50), 77 (12), 54 (47), 37 (41), 27 (15); UV (hexadecane) $\lambda_{max}$ ($\epsilon$) 185 (6900).

2-Butyne, 2,3-dimethyl-1,3-butadiene (**8a**), and (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-3,4-dimethyl-2,4-hexadiene (**8c**) from photolysis of **6a** and **6c**, respectively, were identified by GC coinjection of photolysates with authentic samples. The latter were available from a previous study.[17] (*E*)- and (*Z*)-2,3-dimethyl-1,3-pentadiene (**8b**), (*E*)- and (*Z*)-2,3,4-trimethyl-2,4-hexadiene (**8d**), and 2,3,4,5-tetramethyl-2,4-hexadiene (**8e**) were isolated by semipreparative scale photolyses of deoxygenated, 0.05 M pentane solutions of **6b**, **6d**, and **6e**, respectively. These photolyses employed a 16-W Philips 93106E zinc resonance lamp, placed in the center of a merry-go-round apparatus. Solutions (*ca.* 6 mL) were contained in 12 × 120 mm quartz tubes sealed with rubber septa and were deoxygenated with a slow stream of dry nitrogen prior to photolysis. After photolysis to *ca.* 50% conversion, the solutions were concentrated by careful distillation at atmospheric pressure and bulb-to-bulb distilled under vacuum, and the dienes were isolated by semipreparative GC. The dienes were identified on the basis of their $^1$H NMR, mass, and UV absorption spectra. **(*E*)-2,3-Dimethyl-1,3-pentadiene (E-8b)**:[38,39] $^1$H NMR ($CCl_4$) $\delta$ 1.55 (d, $J$ = 6.5 Hz, 3H), 1.73 (s, 6H), 4.83 (s, 2H), 5.31 (q, $J$ = 6.5 Hz, 1H); MS *m/e* (*I*) 96 (35), 95 (24), 81 (100), 80 (51), 79 (22), 68 (57), 55 (81), 54 (66), 42 (45), 41 (31), 37 (25), 27 (41); UV (cyclohexane) $\lambda_{max}$ ($\epsilon$) 235-nm (21 000). **(*Z*)-2,3-Dimethyl-1,3-pentadiene (Z-8b)**:[38] $^1$H NMR ($CCl_4$) $\delta$ 1.67 (d, $J$ = 6.8 Hz, 3H), 1.75 (s, 6H), 4.83 (s, 1H), 4.93 (s, 1H), 5.65 (q, $J$ = 6.5 Hz, 1H); MS *m/e* (*I*) 96 (31), 95 (25), 81 (100), 80 (61), 79 (25), 68 (60), 55 (80), 54 (65), 42 (54), 41 (30), 37 (25), 27 (45); UV (cyclohexane) $\lambda_{max}$ ($\epsilon$) 239 nm (15 900). **(*E*)-2,3,4-Trimethyl-2,4-hexadiene (E-8d)**:[35,40] $^1$H NMR ($CCl_4$) $\delta$ 1.54 (d, $J$ = 6.7 Hz, 3H), 1.70 (s, 6H), 1.72 (s, 6H), 5.37 (q, $J$ = 6.5 Hz, 1H); MS *m/e* (*I*) 124 (35), 123 (11), 109 (59), 108 (29), 96 (42), 82 (55), 70 (100), 69 (61), 68 (35), 55 (42), 54 (45), 53 (30), 37 (29), 27 (19); UV (cyclohexane) $\lambda_{max}$ ($\epsilon$) 207 nm (9500). **(*Z*)-2,3,4-Trimethyl-2,4-hexadiene (Z-8d)**:[35,40] $^1$H NMR ($CCl_4$) $\delta$ 1.61 (d, $J$ = 6.8 Hz, 3H), 1.72 (s, 6H), 1.76 (s, 6H), 5.79 (q, $J$ = 6.5 Hz, 1H); MS *m/e* (*I*) 124 (36), 123 (11), 109, (55), 108 (25), 96 (42), 82 (54), 70 (100), 69 (62), 68 (36), 55 (45), 54 (45), 53 (39), 37 (29), 27 (21); UV (cyclohexane) $\lambda_{max}$ ($\epsilon$) 218 nm (9650). **2,3,4,5-Tetramethyl-2,4-hexadiene (8e)**:[35,39,41] $^1$H NMR ($CCl_4$) $\delta$ 1.47 (s, 6H), 1.63 (s, 12H); MS *m/e* (*I*) 138 (31), 137 (10), 123 (57), 97 (41), 96 (100), 95 (55), 93 (24), 80 (18), 79 (50), 78 (55), 77 (15), 54 (49), 37 (45), 27 (18); UV (cyclohexane) $\lambda_{max}$ ($\epsilon$) 202 nm (10 200).

Quantitative photolyses were carried out at ambient temperature (*ca.* 23 °C) in 5 × 80 mm quartz tubes which contained *ca.* 0.5 mL of solution and were sealed with rubber septa, and employed the unfiltered zinc resonance lamp and merry-go-round apparatus. Hexadecane solutions containing the cyclobutenes (*ca.* 0.05 M) and *n*-heptane as internal standard (*ca.* 5 × $10^{-4}$ M) were placed in the tubes and deoxygenated with a slow stream of dry nitrogen for *ca.* 30 min prior to photolysis. Typically, three samples were irradiated simultaneously: a solution of 1,2-dimethylcyclobutene (**6a**) along with solutions of two of the other five compounds. Aliquots were removed every 5 min for GC analysis on columns a or b to a total conversion of ca. 10% of **6a**. Relative (to internal standard) photoproduct GC peak areas were converted to absolute concentrations using the internal standard concentration and GC response factors, which were determined for each compound from standard solutions. Absolute product yields per unit time were calculated from the slopes of product concentration *vs* time plots, examples of which are shown in Figure 2.

These were converted to absolute quantum yields using the formation of 2,3-dimethyl-1,3-butadiene (**6a**) from photolysis (214 nm) of 1,2-dimethylcyclobutene (**8a**) in isooctane solution, determined by uranyl oxalate actinometry.[42–44] The procedure employed involves consecutive irradiation of solutions of the substrate (0.02 M) and the actinometer (0.001 M) in identical 2.5 × 1 cm round Suprasil UV cells, which were contained in a merry-go-round apparatus surrounding the unfiltered Zn resonance lamp. Control experiments, in which the actinometer solution was irradiated with and without a Vycor filter surrounding the lamp, showed that the longer-wavelength emission lines from the lamp (between 275 and 350 nm) are at least 50 times weaker than the

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214-nm line, and thus have no detectable effect on the conversion of the actinometer within the time it takes to photolyze the substrate to ca. 10% conversion (~45 min). *It is therefore unnecessary to employ an interference filter to isolate the 214-nm Zn resonance line for uranyl oxalate actinometry with the Zn resonance lamp.* This is a significant advantage over our previous procedure, which incorporated an interference filter to eliminate the long-wavelength Zn lines[2] and requires much longer (by almost an order of magnitude) irradiation times.

The solutions containing **8a** and the actinometer were then irradiated for 10–30 min, the absolute yield of **8a** was determined by GC, and the conversion of the actinometer was determined according to the published method.[34,44,45] A value of 0.50 ± 0.02 was used for the quantum yield of the actinometer at 214 nm.[45] The value obtained (Table 1) is the average of triplicate determinations; the error is given as the standard deviation from the mean of the three values. The errors quoted for the quantum yields for formation of **9** and **8b–e** were calculated from the standard deviations of the slopes from the concentration *vs* time plots.

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