Orbital Symmetry and the Photochemical Ring Opening of Cyclobutene

William J. Leigh,* J. Alberto Postigo, and Paul C. Venneri

Department of Chemistry, McMaster University
Hamilton, Ontario, Canada L8S 4M1

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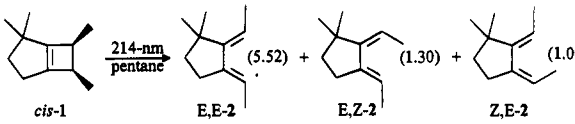
Unlike most excited state pericyclic reactions, the photochemical electrocycloreversion of substituted cyclobutene derivatives proceeds non-stereoselectively.[1] Orbital symmetry selection rules[2] and numerous computational studies[3–9] predict that, for a four-electron system such as cyclobutene/1,3-butadiene, photochemical interconversion should proceed in disrotatory fashion. While substituted 1,3-butadienes do indeed undergo photochemical ring closure with predominant disrotatory stereochemistry,[10–12] direct irradiation of alkyl-substituted cyclobutenes results in the formation of mixtures of both the formally-allowed and -forbidden diene isomers, in relative yields that vary substantially from system to system.[11–13] There are a number of possible mechanistic explanations for this, but the one that is most compatible with orbital symmetry selection rules involves stereospecific, disrotatory ring opening entirely on the excited singlet state surface to yield a single, *electronically excited* diene isomer which decays to the ground state by cis,trans-isomerization. It is well established that the photochemical ring opening of Dewar aromatics follows an analogous pathway.[14,15] Furthermore, spectroscopic results[16] and an analysis of the effects of steric factors on the quantum yields for ring opening of monocyclic cyclobutenes[17] both support the suggestion that, as this mechanism demands, orbital symmetry *is* obeyed in the early stages of the reaction on the excited singlet state surface.

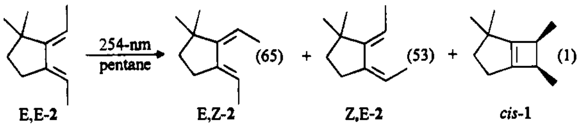
We have published results which are consistent with the adiabatic ring opening mechanism, but within a rather large margin of error owing to the necessity of comparing product ratios from cyclobutene ring opening with ratios calculated from absolute quantum yields for diene cis,trans-photoisomerization.[18] This comparison is valid only with systems whose isomeric dienes exist exclusively in the s-cis conformation (the conformation in which they would be formed during ring opening), since the excited singlet state decay characteristics of conjugated dienes are conformation-dependent.[11,12] We now report the results of a study which was designed to provide a much more precise indication of the validity of the adiabatic ring opening mechanism than is possible with systems based on absolute quantum yield determinations.

Direct irradiation (214-nm) of a deoxygenated, 0.005 M solution of *cis*-4,4,6,7-tetramethylbicyclo[3.2.0]hept-1^5-ene (*cis*-**1**) in pentane containing 5×10^{-4} M (*E,E*)-1,2-bis(ethylidene)-cyclopentane [(*E,E*)-**3**)] and *n*-decane as internal standards results in the formation of (*E,E*)-, (*E,Z*)-, and (*Z,E*)-1,2-bis-(ethylidene)-3,3-dimethylcyclopentane (**2**)[19a] as shown in eq 1. Relative yields of the three diene isomers were determined from concentration vs time plots constructed after capillary GC and GC/MS analysis of the photolysis mixture between 1 and ca. 5% conversion of *cis*-**1** and are included in eq 1.[19b] The diene (*E,E*)-**3** was included in order to determine whether the products are susceptible to secondary photointerconversion under the conditions employed; after 5% conversion of *cis*-**1**, (*E,Z*)-**3** [the main product of photolysis of (*E,E*)-**3**[20]] was undetectable in the photolysis mixture (limits of detection ~10^{-6} M). We thus conclude that the relative yields of (*E,E*)-, (*E,Z*)-, and (*Z,E*)-**2** reported in eq 1 are the true primary relative yields of the three isomers from photochemical ring opening of *cis*-**1**.



[1]

Direct irradiation (254-nm) of a deoxygenated 0.029 M pentane solution of (*E,E*)-**2** affords (*E,Z*)- and (*Z,E*)-**2** as the major products, along with smaller amounts of *cis*-**1**, at conversions less than 5%. Capillary GC analysis of the product mixture at conversions between 0.1 and 5% affords the relative product distributions shown in eq 2; these were determined from the slopes of concentration vs time plots for the three products, which were linear in each case.



[2]

The distribution of allowed and forbidden diene isomers obtained in the ring opening of *cis*-**1** ([*EE*]:[*EZ* + *ZE*] = 2.4 ± 0.3) is similar to that obtained from photolysis of the related compound *cis*-**4** ([(*EE*)-**3**]/[(*EZ*)-**3**] = 2.0 ± 0.3) at the same wavelength (eq 3). In the latter case, the (*EE*)/(*EZ*)-**3** ratio is identical to the ratio predicted ([(*EE*)-**3**]/[(*EZ*)-**3**] = 2.2 ± 0.4) on the basis of a calculation employing the absolute quantum yields for $EE \rightarrow EZ$ isomerization and formation of other products from direct photolysis of (*E,E*)-**3**,[20] within experimental error.[21]

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(1) Clark, K. B.; Leigh, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 6086.

(2) Woodward, R. B.; Hoffmann, R. *The conservation of orbital symmetry*; Verlag-Chemie: Weinheim, 1970.

(3) Van der Lugt, W. T. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042.

(4) Grimbert, D.; Segal, G.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 6629.

(5) Morihashi, K.; Kikuchi, O. *Theor. Chim. Acta* **1985**, *67*, 293.

(6) Aoyagi, M.; Osamura, Y. *J. Am. Chem. Soc.* **1989**, *111*, 470.

(7) Bernardi, F.; De, S.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 1737.

(8) (a) Olivucci, M.; Ragazos, I. N.; Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 3710. (b) Celani, P.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Chem. Phys.* **1995**, *102*, 5733.

(9) Pichko, V. A.; Simkin, B. Y.; Minkin, V. I. *J. Mol. Struct. (THEOCHEM)* **1991**, *235*, 107.

(10) Srinivasan, R. *J. Am. Chem. Soc.* **1968**, *90*, 4498.

(11) Leigh, W. J. *Chem. Rev.* **1993**, *93*, 487 and references cited therein.

(12) Leigh, W. J. In *Handbook of organic photochemistry and photobiology*; Horspool, W. G., Ed.; CRC Press, Inc.: Boca Raton, in press, and references cited therein.

(13) Leigh, W. J. *Can. J. Chem.* **1993**, *71*, 147.

(14) Yang, N. C.; Carr, R. V.; Li, E.; McVey, J. K.; Rice, S. A. *J. Am. Chem. Soc.* **1974**, *96*, 2297.

(15) Carr, R. V.; Kim, B.; McVey, J. K.; Yang, N. C.; Gerhartz, W.; Michl, J. *Chem. Phys. Lett.* **1976**, *39*, 57.

(16) Lawless, M. K.; Wickham, S. D.; Mathies, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 1593.

(17) Leigh, W. J.; Postigo, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 1688.

(18) Leigh, W. J.; Zheng, K. *J. Am. Chem. Soc.* **1991**, *113*, 4019.

(19) (a) The syntheses of *cis*-**1** and authentic samples of (*E,Z*)- and (*Z,E*)-**2** were carried out by exhaustive photolysis (254-nm) of (*E,E*)-**2**. The compounds were isolated and purified by semipreparative GC, and they were identified on the basis of their ^{1}H NMR, IR, and mass spectra. Stereochemical assignments for the various isomers of **2** were made on the basis of ^{1}H NMR NOE experiments. Several other isomers were also produced in the photolysis, including *trans*-**1** and (*Z,Z*)-**2**. We could not obtain sufficient quantities of pure *trans*-**1** to enable its photochemistry to be studied, however. The synthesis of (*E,E*)-**2** was achieved by zirconocene-mediated cyclization of 4,4-dimethyl-2,7-nonadiyne. Complete descriptions of the synthesis and spectroscopic characterization of **1** and **2** are available as supporting information. (b) Diene (*Z,Z*)-**2** could not be detected as a product of photolysis of *cis*-**1**; the maximum yield is estimated as ~10% of that of (*Z,E*)-**2**.

(20) Leigh, W. J.; Postigo, J. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1836.

(21) The predicted (*EE*)/(*EZ*)-**3** ratio is calculated from the quantum yields for photoisomerization of (*EE*)-**3**[20] as $(EE/EZ)_{\mathrm{calc}} = (1 - \Phi_{EE-EZ} - \Sigma\Phi_{EE\rightarrow \mathrm{other\ products}})/\Phi_{EE\rightarrow EZ}$.[11,13,18]

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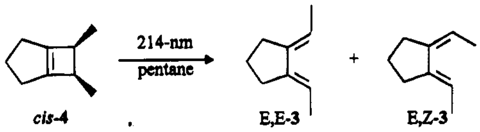

cis-4 E,E-3 E,Z-3 [3]

The correspondence between the relative yields of (*E,Z*)- and (*Z,E*)-**2** obtained from ring opening of *cis*-**1** ([*E,Z*]/[*Z,E*] = 1.30 ± 0.12) and from direct cis,trans-photoisomerization of (*E,E*)-**2** ([*E,Z*]/[*Z,E*] = 1.25 ± 0.11) indicates that productive excited state decay of *cis*-**1** yields the same products *in the same relative yields* as are obtained from direct irradiation of (*E,E*)-**2**. This would be the case if ring opening proceeds in exclusively disrotatory fashion to yield the fully open (*E,E*)-diene in the same electronic excited state as that populated by its direct excitation, that which leads to *E,Z*-isomerization. The minimum requirement is that the geometry at which funneling to the ground state surface occurs is *the same* for both the cyclobutene and the specific diene isomer that would be formed by disrotatory ring opening. The same mechanistic conclusion is afforded by the behavior of *cis*-**4**, but in this case, the analysis requires comparison of the isomeric diene distribution with that predicted on the basis of a calculation involving absolute quantum yields for photoisomerization of *E,E*-**3**. Since productive excited state decay of *E,E*-**2** results in the formation of *two* distinct isomers in determinable yields, a comparable analysis can be carried out in this case simply on the basis of product ratio determinations.

These results suggest that, in spite of the fact that photochemical ring opening of alkylcyclobutenes yields non-stereoselective mixtures of dienes, it is likely that (at least in the present systems) orbital symmetry selection rules are actually fully obeyed. Thus, the ultimate formation of a mixture of diene geometric isomers can be understood in terms of a mechanism in which ring opening occurs in stereospecific, disrotatory fashion on the excited state surface to yield a single, electronically excited diene. The overall non-stereoselectivity results from the manner in which the excited product decays to the ground state, primarily by *E,Z*-isomerization. In conventional terms, our results suggest that ring opening follows the excited state pathway predicted by orbital symmetry rules, but the avoided crossing for disrotatory cyclobutene/butadiene interconversion[3,4] is bypassed to allow access to the same region of the excited state potential energy surface that is accessed predominantly when the single diene isomer is itself excited directly. Similar behavior is observed for a series of bicyclo[*n*.2.0]alk-1-enes related to *cis*-**4**, whose isomeric 1,3-dienes are structurally locked in the s-cis conformation.[22]

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Supporting Information Available: Experimental details of the preparation and characterization of compounds (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[22] Leigh, W. J.; Postigo, J. A.; Zheng, K. To be published.