(H, s), 10.9 (H, s), 11.7 (H, s). Anal. ($C_{11}H_{14}ClNO_2$) C, H, N.

2f: 86% from aldehyde;[13] mp 156–157.5 °C; ^{1}H NMR δ 1.25 (9 H, s), 7.486 (H, d, J = 2.3 Hz), 7.694 (H, d, J = 2.3 Hz), 8.37 (H, s), 10.8 (H, br s), 11.25 (H, br s). Anal. ($C_{11}H_{14}INO_2$) C, H, N.

Synthesis of 1,2-Benzisoxazoles. To a solution of **2** (10 mmol) in dry THF (10 mL) was added **1** (10.5 mmol) in dry THF (5 mL) at room temperature (very slight exotherm). After 10 min K_2CO_3 (11 mmol) was added and the mixture was stirred for an additional 30 min before it was poured into H_2O (400 mL) with vigorous stirring. The solid products were treated as indicated in Table I, while the liquids (**3d**,**h**, **7h**) were extracted into Et_2O, washed with H_2O and staturated brine, dried ($MgSO_4$), and distilled.

Acknowledgment. We extend our thanks to K. B. Streeter and his staff for elemental analysis, to Y. C. Lee for pK_a determinations, to Dr. D. W. Cochran for helpful discussions on the NMR data, and to Kevin Stokker and Mary Zook for assistance in manuscript preparation.

Registry No. 1, 3019-71-4; **2a**, 38730-67-5; **2b**, 71253-52-6; **2b** (aldehyde), 708-76-9; **2c**, 5331-93-1; **2d**, 94-67-7; **2e**, 71064-05-6; **2e** (aldehyde), 71730-43-3; **2f**, 71064-04-5; **2f** (aldehyde), 71064-03-4; **2g**, 1595-15-9; **2h**, 1196-29-8; **2i**, 54758-73-5; **3a**, 71064-06-7; **3b**, 71064-07-8; **3c**, 86013-72-1; **3d**, 271-95-4; **3e**, 86013-73-2; **3f**, 71097-36-4; **3g**, 39835-28-4; **3h**, 4825-75-6; **3i**, 86013-74-3; **7h**, 95-21-6; **7i**, 835-64-3; **5**, 86013-75-4; **6**, 611-20-1; C_6H_5NCO, 103-71-9.

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(13) Stokker, G. E.; Deana, A. A.; deSolms, S. J.; Schultz, E. M.; Smith, R. L.; Cragoe, E. J., Jr.; Baer, J. E.; Russo, H. F.; Watson, L. S. *J. Med. Chem.* **1982**, *25*, 735.

(14) **3a**: ^{1}H NMR ($CDCl_3$) δ 4.0 (3 H, s), 4.2 (3 H, s), 8.8 (H, s). **3b**: ^{1}H NMR ($CDCl_3$) δ 3.8 (3 H, s), 3.83 (3 H, s), 6.23 (H, d, J = 1 Hz), 6.62 (H, d, J = 1 Hz), 8.6 (H, s). **3e**: ^{1}H NMR ($CDCl_3$) δ 1.33 (9 H, s), 7.55 (2 H, s), 8.72 (H, s). **3f**: ^{1}H NMR ($CDCl_3$) δ 1.4 (9 H, s), 7.7 (H, d, J = 1 Hz), 8.0 (H, d, J = 1 Hz), 8.85 (H, s). **3i**: ^{1}H NMR ($CDCl_3$) δ 6.93–8.27 (8 H, m), 9.73 (H, s).

Identification of the Reactive Electronic Excited State in the Photocycloaddition of Alkenes to Cyclic Enones[1,2]

David I. Schuster,* Marc M. Greenberg, Ivan M. Nuñez, and Philip C. Tucker

Department of Chemistry, New York University, New York, New York 10003

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Photocycloaddition of alkenes to cyclic enones has become an important tool in the arsenal of synthetic organic chemists,[3] stimulated by the pioneering studies of Corey nearly 20 years ago.[4] Various aspects of the mechanism of this reaction are understood,[3,5] although a fully precise mechanistic description has yet to be presented. Corey[4] suggested that the reaction involves a triplet excited state of the enone, which forms an "oriented π complex" with the alkene. This species, an exciplex in modern parlance,[6,7] is thought to proceed to give a 1,4-diradical on formation of a covalent bond between C-3 of the enone and one of the olefinic carbons. This biradical was subsequently[5,6] suggested to be a relatively long-lived triplet species. Closure to a four-membered ring completes the sequence, in competion with H transfer and reversion to ground states of the starting materials.[6] The exciplex and diradical are needed to account for the regioselectivity of the reaction and the failure to preserve the stereochemistry of the olefinic moiety in the cycloadduct.[3-5] It has also been observed that the major adduct formed from electron-rich alkenes and 2-cyclohexenones usually has a trans fusion of the four- and six-membered rings.[3-5]

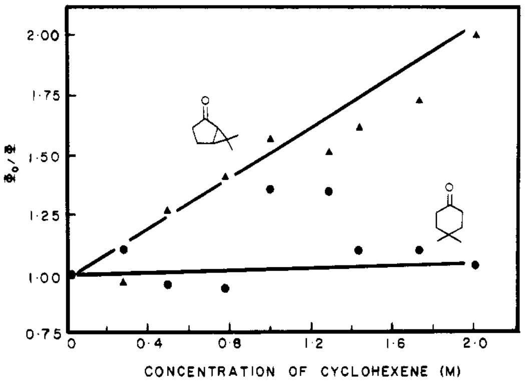

Figure 1. Quenching by cyclohexene of the formation of photoproducts 2 and 4 on irradiation of enone 1 in IPA (run I).

The enone excited state responsible for this reaction has not been precisely identified. Corey[3] implicitly assumed that the reactive state in the case of cyclohexenone was a triplet n,π* state, although there was no direct evidence to support that proposal. In his studies of photocycloaddition of 1,1-dimethoxyethylene to 4,4-dimethylcyclohex-2-en-1-one (**1**), Chapman[8] concluded that trans-fused cycloadducts and oxetanes arose from n,π* triplet excited states of the enone while cis-fused adducts arose from π,π* triplets. McCullough[9] later concluded that cycloaddition of cyclopentene to enone **1** involved the same excited state (which was not explicitly identified) as that responsible for photorearrangement of **1**,[10] on the basis of the observation that the ratio of adducts to rearrangement products (**2** and **3**) was unchanged in the presence of 0.05 M naphthalene, a well-known triplet quencher. He also argued cogently that it was likely that the reactive enone excited state was twisted about the C=C bond, in order to account for the high yield of trans-fused cycloadducts. A mechanism (see Scheme I) was presented involving initial complexation of the olefin and a twisted enone triplet, leading to a twisted 1,4-diradical in which formation of trans-fused adducts by ring closure was competitive with relaxation of the diradical to a more stable geometry, which in turn afforded only cis-fused products on ring closure.[9]

Taking advantage of our knowledge of the detailed mechanisms of photorearrangement and photoreduction of **1** in isopropyl alcohol (IPA) to give **2**, **3**, and **4**[11-13] and

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(1) Photochemistry of Ketones in Solution. 70. Part 69: Brisimitzakis, A. C.; Schuster, D. I., submitted for publication in *Tetrahedron Lett.*

(2) Taken in part from the B.S. Honors Thesis of M.M.G. and the Ph.D. Dissertation of I.M.N., 1982.

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(4) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

(5) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41.

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(7) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45.

(8) Chapman, O. L.; Koch, T. H.; Klein, F.; Nelson, P. J.; Brown, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 1657.

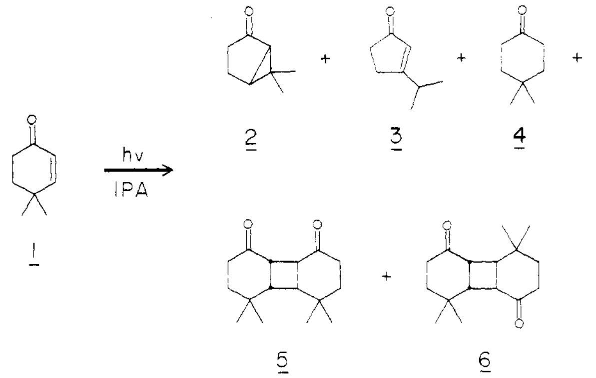
(9) Bowman, R. M.; Calvo, C.; McCullough, J. J.; Rasmussen, P. W.; Snyder, F. F. *J. Org. Chem.* **1972**, *37*, 2084.

(10) For a recent review of the literature on photorearrangement of enones, see: Schuster, D. I. In "Rearrangements of Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

(11) Schuster, D. I.; Brown, R. H.; Resnick, B. M. *J. Am. Chem. Soc.* **1978**, *100*, 4505.

(12) Schuster, D. I.; Nuñez, I. M.; Chan, C. B. *Tetrahedron Lett.* **1981**, *22*, 1187.

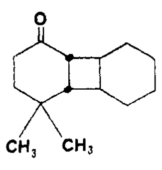
0022-3263/83/1948-2615$01.50/0



the ability to establish conditions where cycloaddition of alkenes to 1 could compete with these processes, we can now specify more precisely the nature of the enone excited state responsible for these reactions. In the presence of increasing concentrations of cyclohexene or 1,1-diethoxyethylene (DEE), it was found that photorearrangement of 1 was quenched in a kinetically first-order process, while reduction was not affected within the limits of experimental uncertainty (see Figure 1 for graphical presentation of the results of a typical run). Also, in a run using a higher concentration of 1 sufficient to allow formation of photodimers 5 and 6,[13] it was found that quenching of the photodimerization by cyclohexene occurred, with Stern–Volmer slopes for both dimers the same (within experimental uncertainty) as that for quenching of formation of lumiketone 2. Characterization of the dimers is described in the Experimental Section. The slopes and intercepts of these Stern–Volmer plots of relative quantum yield vs. olefin concentration are given in Table I.

To test the possibility that a change in solvent polarity as a result of dilution of IPA by cyclohexene might be responsible for the above results, we carried out an experiment (suggested by a referee) in which the amount of IPA in the system was held constant and the total amount of cyclohexene + cyclohexane was also kept constant as the concentration of cyclohexene was varied. The results, shown in Figure 2, again demonstrate selective quenching by cyclohexene of photorearrangement of 1 but not of photoreduction. The curvature in the quenching plot is interesting but will not be discussed further until additional data are collected.

When the photoaddition of 1 to cyclohexene was carried out on a preparative scale, analysis by gas chromatography/mass spectrometry (GC/MS) indicated the formation of a major and a minor cycloadduct, which were separated by column chromatography. Neither of these adducts was affected by treatment with 15% NaOH in methanol for up to 72 h, according to spectral and GC analysis, indicating they both have cis-fused structures, as in 7 and 8.



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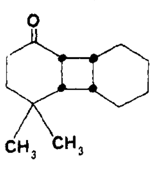

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Spectral data do not allow differentiation of these structures at this time. According to ^{1}H NMR data, there is a minor contaminant in the isolated major cycloadduct which disappears on treatment with base, and this may represent a trans-fused isomer of the major adduct.

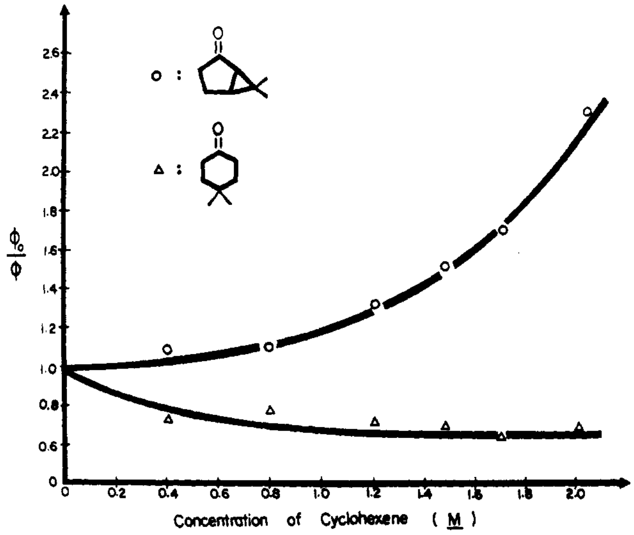

Figure 2. Quenching by cyclohexene of the formation of photoproducts 2 and 4 on irradiation of enone 1 in mixtures of isopropyl alcohol, cyclohexane, and cyclohexene in which the alcohol concentration was held constant.

We therefore conclude that photorearrangement, photodimerization, and photocycloaddition to electron-rich olefins are competitive reactions of 1 involving a common intermediate, while photoreduction of 1 is mechanistically distinct. We have previously argued that photorearrangement of 4,4-disubstituted cyclohexenones to lumiketones proceeds via a twisted π,π^* excited state.[10,11,14,15] Such twisted excited states of several cyclohexenones, including 1, have been identified tentatively as transient intermediates in laser flash studies,[16] with absorption spectra and lifetimes analogous to those found with cyclohexenone and other simple cyclic enones.[11] The product of the lifetime of the transient observed[16] on flash excitation of 1 in IPA (28 ns) and the rate constant for transfer of triplet excitation from this species to naphthalene (5.5×10^8 M^{-1} s^{-1}) is in excellent agreement with the slope of the linear Stern–Volmer plot for quenching by naphthalene of formation of 2 on steady-state irradiation of 1 in IPA (15.4 vs. 13.6 M^{-1}, respectively). This agreement provides strong support for the assignment of the structure of such transients as the twisted π,π^* triplet excited state given originally by Bonneau[17] and for the role of such states in photorearrangement of cyclohexenones to lumiketones.[10] The slopes of the plots demonstrating quenching by cyclohexene and DEE of formation of 2 in IPA, as typified by Figure 1, are equal to $k_{ir}\tau_T$ according to eq 1, where k_{ir}

$$\Phi_0/\Phi = 1 + k_{ir}\tau_T[\text{alkene}] \quad (1)$$

is the rate constant for interaction of the olefin with the reactive enone triplet whose lifetime is τ_T. Using the triplet state lifetime of 1 derived from the flash data of 28 ns, absolute values of k_{ir} are now directly available, and these are shown in Table I. Mechanistically, these rate constants should represent the rate constants for exciplex formation in Scheme I.[6,7] These are the first values for such rate constants to have been directly determined. As expected, the value of k_{ir} for DEE is slightly larger than for cyclohexene, consistent with the observation that electron-rich alkenes add to cyclohexenones more readily than electron-deficient alkenes,[3–5] although quantum efficiencies as a function of alkene substituents have not been reported.

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[13] Schuster, D. I.; Nuñez, I. M., unpublished results. Nuñez, I. M. Ph.D. Dissertation, New York University, 1982.

[14] Schuster, D. I.; Hussain, S. *J. Am. Chem. Soc.* **1980**, *102*, 409.

[15] Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928.

[16] Schuster, D. I.; Rao, J. M.; Bonneau, R., unpublished results.

[17] Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816.

Scheme I

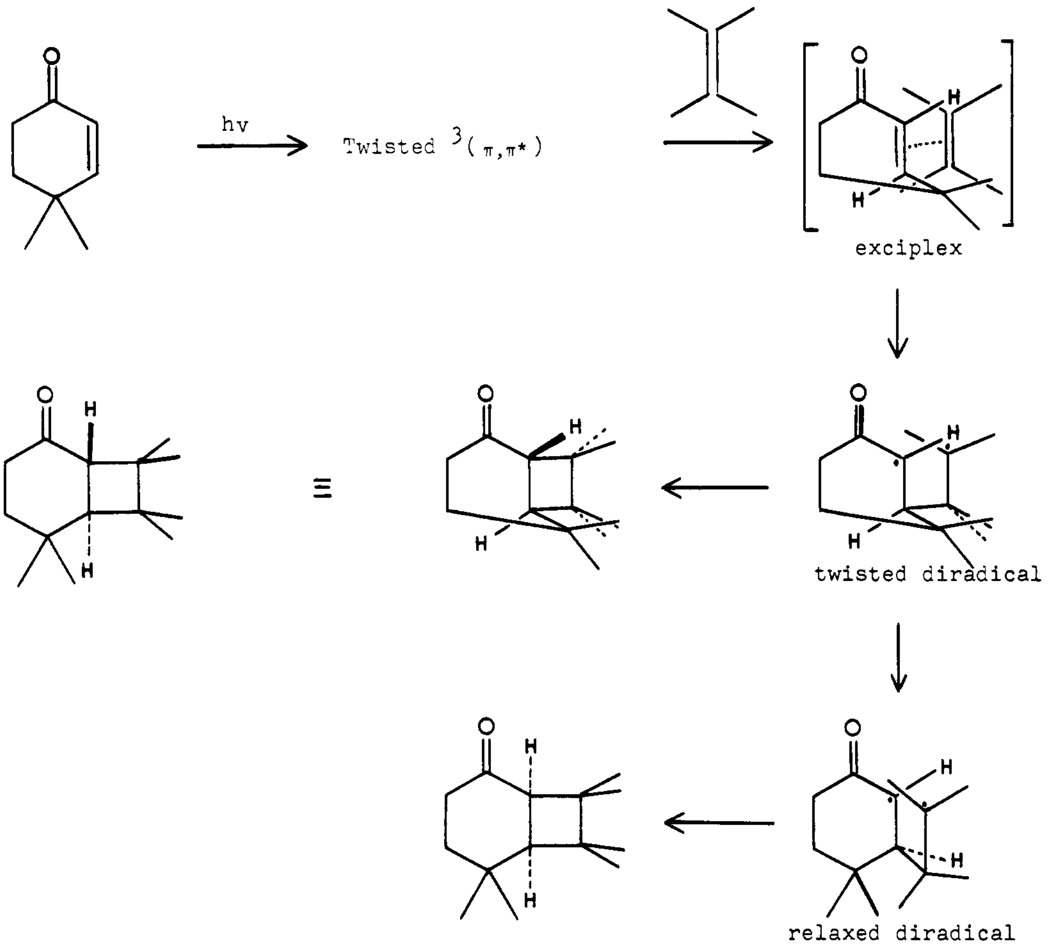

Table I. Statistical Analysis of Quenching Plots[a]

parameter	product 2	4	5	6
		cyclohexene I[b]		
slope, M^{-1}	0.446 ± 0.084	0.061 ± 0.149		
y intercent	0.99	1.05		
r^c	0.969			
k_{ir}, M^{-1} s^{-1} ^{d}	1.6×10^7			
		cyclohexene II		
slope	0.333 ± 0.055	−0.138		
y intercept	1.09	0.972		
r^c	0.950			
k_{ir}, M^{-1} s^{-1} ^{d}	1.2×10^7			
		cyclohexene III		
slope			0.312 ± 0.042	0.301 ± 0.071
y			0.99	0.96
r^c			0.975	0.932
k_{ir}, M^{-1} s^{-1} ^{e}			1.1×10^7	1.1×10^7
		DEE I		
slope	0.808 ± 0.038	0.202 ± 0.041		
y intercept	0.98	1.00		
r^c	0.985	0.794		
k_{ir}, M^{-1} s^{-1} ^{d}	2.9×10^7			
		DEE II		
slope	0.907 ± 0.095	0.059 ± 0.086		
y intercept	0.98	0.98		
r^c	0.931			
k_{ir}, M^{-1} s^{-1} ^{d}	3.2×10^7			

[a] Plots of relative quantum yield of product formation vs. olefin concentration. [b] Data from Figure 1. [c] Correlation coefficient. This parameter is without meaning for lines of negative or zero slope. [d] Calculated from the slope by assuming τ_T is 28 ns (see text). [e] Although the value of τ_T may be less than 28 ns at the high enone concentration (2.5 M) used in this experiment, the value of k_{ir} has been calculated by using this lifetime for illustrative proposes only.

Values of reaction rate constants for addition of alkenes to enones have been calculated previously[6,9,18] from enone triplet lifetimes which were not directly determined but rather were calculated from quenching data by assuming that triplet quenching occurs at diffusion-controlled rates. It should be noted, however, that quenching by naphthalene of the reactive triplet of 1, which we find to be identical with the transient species observed in the flash studies, actually occurs with a rate constant approximately one order of magnitude less than the diffusion-controlled limit of $(0.5–1.0) \times 10^{10}$ M^{-1} s^{-1}.[19] This is consistent with a triplet excitation energy of the enone donor similar to that (61 kcal/mol) of the acceptor (naphthalene), as expected for a relaxed (twisted) enone triplet but not for a planar enone triplet.[17] A similar rate constant was found for cyclohexenone.[16]

We have presented evidence elsewhere[12,13,15] to support the conclusion that photoreduction of 1 to 4 in IPA does not involve a triplet n,π^* state but rather involves a π,π^* triplet state. On the basis of the present data, we would argue that this state is a planar π,π^* triplet state, whose lifetime may be so short that thus far it has not been detected in flash experiments.[16] Quenching by naphthalene of photorearrangement and photoreduction of 1 in IPA are characterized by very similar but not identical Stern–Volmer slopes;[13] we now conclude that this similarity is entirely coincidental since it is clear that these reactions involve different reactive excited states. This is confirmed by the finding that in a 1:1 mixture of *t*-BuOH and toluene, photoreduction is barely affected by naphthalene while formation of 2 is readily quenched with a Stern–Volmer slope of 10.2 M^{-1}, very similar to that measured in IPA.[13] Differential quenching by naphthalene of photorearrangement and photoreduction of 2,4,4-trimethylcyclohex-2-en-1-one in IPA has also been observed.[13]

With respect to the photocycloaddition mechanism, these observations in conjunction with our other studies on 1 and related enones demonstrate that the reactive excited state of the enone that is captured by cyclohexene and DEE is a twisted triplet π,π^* state. This, of course, readily accounts for the formation of both trans-fused and cis-fused cycloadducts, as noted by McCullough.[9] The formation of mainly cis-fused cycloadducts from electron-deficient olefins[3,4] and cycloalkenes could be rationalized if these alkenes also react with twisted enone π,π^* triplets as shown in Scheme I and if the 1,4-diradicals undergo geometric relaxation prior to final ring closure. Additional experiments of the type presented here utilizing a larger variety of alkenes and cyclic enones should settle a number of mechanistic questions and hopefully will add to the usefulness of these reactions as synthetic tools.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 735 spectrophotometer with either neat liquids on polished sodium chloride plates or solutions in matched sodium chloride cells (pathlength 0.1 mm). All spectra were calibrated against the 1601-cm^{-1} band of polystyrene film. Mass spectra were recorded by Mr. C. Strom on a Du Pont Model 21-492 double-focusing mass spectrometer. Analyses by gas chromatography/mass spectrometry (GC/MS) were done on a Hewlett-Packard Model 5992 instrument with the assistance of Mr. Angelo Brisimitzakis. Proton magnetic resonance spectra were recorded on a Varian Associates Model EM-360A 60 MHz spectrometer as dilute solutions in either CCl$_4$ (spectrophotometric grade) or CDCl$_3$ (99.8 D, Aldrich Gold Label) with tetramethylsilane as an internal standard. For thin-layer chromatography, Baker silica gel plates (2.5 × 7.5 cm) were used, with hexane–ether mixtures as the developer. All irradiations were carried out in a Rayonet reactor (Southern New England Ultraviolet Co.) equipped with 16 lamps with an emission maximum of 350 nm (40-nm half-width) with tubes in a Model MGR-100 "merry-go-round". Analysis by gas–liquid partition chromatography (GLC) were done on one of the following: (a) a Hewlett-Packard Model 5750 gas chromatography with either a Model 1753A or model 7123A strip-chart recorder and a flame-ionization detection, with integrations by the cut and weigh method; (b) a Hewlett-Packard Model 5702A gas chromatograph with a Model 3390A electronic integrator/recorder and flame-ionization detector; (c) a Hewlett-Packard Model 5710A gas chromatograph with flame-ionization detector, Model 5702A oven temperature programmer, Model 7123A strip-chart recorder, and Model 3373B electronic integrator.

4,4-Dimethylcyclohex-2-en-1-one (1) was prepared by the condensation of methyl vinyl ketone and isobutyraldehyde as described previously.[21] Fractional distillation gave a clear liquid in 35–41% overall yield based on methyl vinyl ketone. The product was at least 99% pure according to GLC analysis and had spectra as described previously in full accord with the assigned structure.

1,1-Diethoxyethylene (DEE) was prepared by treatment of bromoacetaldehyde diethyl acetal with potassium *tert*-butoxide as described previously. The yields were very poor, on the order of only 10%. An impurity of approximately 10% was evident in the ^{1}H NMR spectrum of the product, and this impurity could not be totally removed even by several vacuum distillations.

Procedure for Quenching Experiments Using Cyclohexene and DEE. A stock solution of enone 1 in isopropyl alcohol (Baker, distilled over magnesium prior to use) was prepared (1.75 M), and 1 mL of this was added to each of several 5-mL volumetric flasks. Varying amounts of either cyclohexene (Baker, distilled prior to use) or DEE (above) were added dropwise to the above volumetric flasks, the amounts being determined by weight. A 1-mL aliquot of a 0.05 M solution of *n*-dodecane (internal standard for GLC) in IPA was added to each tube, and the tubes were then diluted with IPA to a volume of 5 mL, giving a final enone concentration of 0.35 M, cyclohexene concentrations of 0.0–2.0 M, and DEE concentrations of 0.0–0.5 M. Six different concentrations of cyclohexene were utilized in addition to two tubes with no alkene added, while experiments with DEE utilized four different DEE concentrations. Two milliliters of each of these solutions was placed in 10 × 75 mm Pyrex test tubes, which were sealed with rubber septa and the seals covered with aluminum foil. Copper wire was used around each septum to ensure tightness of the seal. Each tube was purged with nitrogen for 10 min before the tubes were inserted in the irradiation apparatus previously described. The irradiations were carried out at 34–37 °C for 9–17 h, depending on the individual run. Product analysis for 2 and 4[23] by GLC was carried out on a 20% XE-60 column on 80/100-mesh Chromasorb W in a 6 ft × $^1/_8$ in. steel column at an oven temperature of 80–90 °C and a detector temperature of 250 °C. Multiple 1.0–1.5-mL injections were made of the contents of each tube, three or four in runs using an electronic integrator and five or six in runs using the cut and weigh method. The data were analyzed by a standard least-squares method, involving computation of correlation coefficients and standard deviations of the relative quantum yield about the slope.

For the experiment in which the effect of cyclohexene on photodimerization of 1 was determined, the procedure was altered

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[18] For a compilation, see ref 5.

[19] Lamola, A. A.; Turro, N. J. "Energy Transfer and Organic Photochemistry"; Wiley-Interscience: New York, 1969.

[20] The effects of temperature on stereochemistry and efficiency of photoaddictions of enones to olefins have been rationalized in terms of the dynamics of the competitive pathways of the intermediate 1,4-diradicals.[6]

[21] Dauben, W. G.; Shaffer, G. W.; Vietmeyer, N. D. *J. Org. Chem.* **1968**, *33*, 4060.

[22] McElvain, S. M.; Kundiger, D. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 506.

[23] These products were isolated from preparative-scale irradiations of enone 1 in IPA and were identified[13] unequivocally on basis of their spectra, as well as by comparisons with samples of 2 prepared previously[24] and of 4 prepared by hydrogenation of 1.

[24] Chapman, O. L.; Rettig, T. A.; Griswold, A. A.; Dutton, A. I.; Fitton, P. *Tetrahedron Lett.* **1963**, 2049.

[25] See: Singh, P. *J. Org. Chem.* **1971**, *36*, 3334.

J. Org. Chem. **1983**, *48*, 2619–2621

in that an enone concentration of 2.5 M in IPA was utilized, and the internal standard for GLC analysis, 0.0127 M 2-acetonaphthone, was added following irradiation. The photodimers **5** and **6** had been isolated and identified previously by Nũnez.[13] The GLC analysis for **5** and **6** was done on a 6 ft $\times$ $^1/_8$ in. aluminum column of 5% QF-1 and 1% Carbowax 20M on Chromasorb G (AW/DMCS treated) at an oven temperature of 160 °C and with the detector set at 250 °C.

Preparation of Photoadducts of Enone 1 and Cyclohexene. In these experiments, 2.3 g of **1** and 24 g of cyclohexene in 125 mL of hexane was irradiated for 24 h by using the Rayonet apparatus without the merry go round. The crude mixture was analyzed by GC/MS, which indicated two components of mass 206, corresponding to adducts of **1** and cyclohexene. The mixture was chromatographed on Davison silica gel (60–200 mesh) with 0–8% ether in hexane as the eluent. The collected fractions were analyzed by gas chromatography (GC), and those showing only a single component were also analyzed by GC/MS. Two different fractions, representing major and minor products, were found which possessed a molecular ion of mass 206 but which otherwise had different mass spectra. The ^{1}H NMR and IR spectra of both fractions and the ^{13}C NMR spectrum of the major product were taken. The IR spectra showed carbonyl absorption at 1710 cm^{-1} for the minor component and at 1705 cm^{-1} for the major component; neither spectrum showed C═C absorption. Both components showed complex ^{1}H NMR spectra in the range 0.5–2.6 ppm. The major product had methyl resonances at 0.89 and 1.05 ppm in addition to two much smaller peaks (<10% of the above) at 0.94 and 1.00 ppm, while the minor product had methyl resonances at 0.85 and 0.95 ppm. The ^{13}C NMR spectrum of the major component in $CDCl_3$ (chemical shifts relative to Me_4Si) was as follows: 214.7 (s), 49.1 (d), 47.8 (d), 37.3 (d of t), 34.8 (d), 34.5 (t), 34.2 (d), 31.0 (s), 28.5 (t), 26.8 (d of q), 23.4 (t), 21.8 ppm (t).

Both adducts were treated with 15% NaOH in methanol at room temperature for 72 h to see if they would undergo isomerization, under conditions previously used to isomerize trans-fused to cis-fused cycloadducts. The NMR spectrum of the major component after base treatment showed that the small peaks at 0.94 and 1.00 ppm had disappeared, suggesting that a small amount of a trans-fused adduct may have been present and was converted by base to the corresponding cis-fused cycloadduct. Similar treatment of the minor component produced no change in its IR spectrum and its GC retention time.

Synthesis and Characterization of Photodimers of 4,4-Dimethylcyclohex-2-en-1-one (1). Irradiation of neat enone **1** with 350-nm lamps in a Rayonet Reactor for 17 h yielded a yellow oil containing suspended crystalline material. This mixture was chromatographed on silica gel by elution with mixtures of ether and hexane. In addition to pure enone **1**, a white crystalline material (dimer A, mp 154–156 °C) was eluted with 5% ether. A second dimeric product, present in trace amounts in later fractions, was detected by GC analysis. The amount did not allow structural studies, except that it was noted that upon standing in acetonitrile for prolonged periods of time, this material isomerized to dimer A. A third product was eluted with 40% ether, and this material also crystallized (dimer C, mp 96–98 °C). The mass spectra of A and C, as well as their IR, UV, ^{1}H NMR, and ^{13}C NMR spectra, indicated they were [2 + 2] dimers of enone **1**.[13] Since their ^{13}C NMR spectra showed only eight signals, unsymmetrical structures for dimers A and C can be ruled out. On steric as well as mechanistic grounds, structures with two trans cyclobutane ring junctions can also be eliminated. On the basis of the crowding seen in models, cis–syn–cis dimers also appear to be unlikely. Dimer A is assigned the anti head-to-tail structure **6** and dimer C the anti head-to-head structure **5** on the following grounds. A downfield signal at 3.01 ppm (d, J = 9 Hz) seen for C is not present in the spectrum of A and is assigned to bridgehead protons α to the carbonyl; a head-to-tail structure would not be expected to give a sharp doublet. The more polar dimer **5** would be expected to be retained on a silica gel column compared with the less polar structure **6**,[26] while the lower melting point of C compared to that of A is consistent with a less symmetrical structure (note that structure **6** has a center of symmetry, allowing tighter packing in the crystalline state). Other arguments to support these assignments are given in ref 13. Dimer B is tentatively concluded to be epimeric to **6** at one of the carbons α to the carbonyls, i.e., it may be a trans-fused cyclo dimer.

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Registry No. **1**, 1073-13-8; **5**, 37402-51-0; **6**, 37165-47-2; **7**, 57166-80-0; **8**, 86118-06-1; DEE, 2678-54-8; cyclohexene, 110-83-8; methyl vinyl ketone, 78-94-4; isobutyraldehyde, 78-84-2; bromoacetaldehyde diethyl acetal, 2032-35-1; naphthalene, 91-20-3.

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Chemiluminescence from the Reaction of 2-Methylene-3-acetyloxazoline-4,5-dione with Hydrogen Peroxide

Daniel Steffek, Robert C. Mebane, and Gary B. Schuster*

Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

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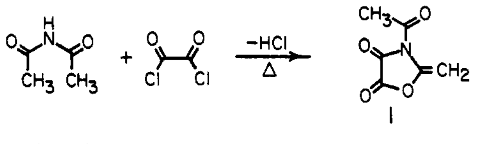
Chemical reactions that generate visible light have been actively investigated for the past 50 years.[1] Recent research has revealed important details of the chemical and physical transformations required for efficient light generation from these processes.[2] Typically these reactions involve, as the starting material or as a key intermediate, an organic peroxide. Conversion of the weak oxygen–oxygen bond of the peroxide to a much stronger carbon–oxygen double bond in a product carbonyl group in most cases supplies much of the energy required to form the requisite electronically excited state. The mechanism for conversion of the chemical potential energy of the peroxide to visible light depends on the details of the structure of the peroxide. One of the most efficient chemiluminescent systems yet discovered is based on the reaction of hydrogen peroxide with certain derivatives of oxalic acid in the presence of a suitable fluorescer.[3,4] This reaction can generate light with an efficiency approaching 35%[5] and forms the basis for the popular Cyalume light sticks. For these reasons we were attracted to the recent report by Richter and Temme[6] of a new reaction of aliphatic imides with oxalyl chloride to give oxazolidinediones (eq 1). We have examined the chemiluminescent reaction of this "derivative" of oxalic acid with hydrogen peroxide.



(1)

Oxazolidinedione **1** was prepared according to the published procedure[6]. When a solution of dione **1** in dimethyl phthalate containing 9,10-diphenylanthracene (DPA) is treated with hydrogen peroxide, the blue chemilumines-

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