(d, ^1J(CH) = 131 Hz, C(6)), 33.9 (t, ^1J(CH) = ca. 120 Hz, C(5)), 24.8 (t, ^1J(CH) = ca. 132 Hz, C(3)**), 24.4 (t, ^1J(CH) = 127 Hz, C(4)**); MS, *m/z* (relative intensity) 164 (10) M•$^+$, 121 (100) [M − C_3H_7]$^+$, 108 (7), 91 (18); HRMS calcd for $C_{11}H_{15}O$ 164.1201, found 164.1203.

Treatment of 1a in THF with CF_3COOH. Under exclusion of light, a solution of **1a** (10 mg, 0.067 mmol) and CF_3COOH (0.33 mmol) in THF (1 mL) was kept for 3 h at −20 °C. According to GCMS, no **6** and **7** had been formed and **1a** appeared to be unchanged.

Irradiation of 1a in [D_8]THF in the Absence of Acid. A solution of **1a** (5 mg, 0.04 mmol) in [D_8]THF (0.5 mL) was irradiated at −50 °C with a low-pressure mercury lamp (254 nm). Polymer formation occurred almost instantaneously; signals of **1a** decreased in the ^{1}H NMR spectrum. After 3 h of irradiation **1a** was completely consumed and signals of **4** (3%) and **5** (2%) were found ([D_7]THF as internal standard).

The Unexpected Regioselectivity in the Singlet Oxygen Cycloadditions to Electron-Rich 1,3-Butadienes

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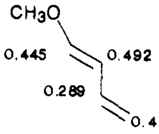
Abstract: The reactions of singlet oxygen with (*E*)- and (*Z*)-1-*tert*-butoxy-1,3-butadiene are compared to the reactions of these substrates with tetracyanoethylene and diphenylketene. Singlet oxygen unlike the other reagents exhibits an affinity for the most highly substituted olefinic linkage in these dienes. The reason for this unusual regiochemical preference of singlet oxygen is discussed. It is suggested that the relative stabilities of the two possible perepoxide regioisomers play a major role in determining the product distribution.

Frontier molecular orbital theory (FMO) has been utilized successfully to predict the regiochemistry of many cycloaddition reactions.[1] These exothermic reactions are ideally suited to such analyses because the interactions in their early transition states can still be justifiably described as perturbations of the HOMOs and LUMOs of the reaction partners.[2] The potent electrophilic nature of singlet oxygen[3] and the exothermicities of its cycloaddition reactions would at first glance appear to fulfill the requirements for the successful application of this powerful theory. We report here, however, that FMO theory fails to predict the regiochemistry of the singlet oxygen 2 + 2 cycloaddition. We also suggest possible explanations for this unexpected behavior.

Results

The isomeric (*E*)- (**1**) and (*Z*)-1-*tert*-butoxy-1,3-butadiene (**2**)[4] reacted rapidly with singlet oxygen at −78 °C in CD_2Cl_2 to give the dioxetane and endoperoxide products shown in Scheme I. In the reactions of both dienes the more highly substituted cis dioxetanes were the major products of the reactions. This is the opposite regiochemistry from that predicted from an analysis of the absolute values of the P_z coefficients[5] or of the proton reactivity surface[5b] of 1-methoxy-1,3-butadiene. Analysis of the electrostatic



potentials[5b] for the four carbon atoms in this diene suggests that reaction at C_3C_4 is 4.9 kcal/mol more favorable than reaction at C_1C_2.

Table I. NMR Data for the Oxidation Products

^{1}H NMR[a]	**3**	**4**	**6**	^{1}H NMR[a]	**3**	**4**	**6**
δ_{H_1}[c]	6.56	6.57	6.24	J_{12}	5.9	5.9	10.1
δ_{H_2}	5.64	5.94	5.88	J_{23}	9.3	9.9	2.2
δ_{H_3}	6.34	6.47	5.57	J_{34}	10.1	9.9	1.8
δ_{H_4}	5.51	5.48	4.66	J_{35}	17.2	17.2	1.8
δ_{H_5}	5.63	b	4.34	J_{45}	1.8		17.0
δ_{CH_3}	1.15	1.16	1.21	J_{13}			1.5
				J_{14}			1.5
				J_{15}			4.4
				J_{24}			4.0
				J_{25}			1.8

[a] All NMR were taken at −80 °C in acetone-d_6 immediately after photolysis. [b] Not observed buried under another peak. [c] ppm.

Table II. Product Distributions as a Function of Solvent in the Reactions of Dienes **1** and **2** with Singlet Oxygen[a]

		products, %				
diene	solvent[b]	**3**	**4**	**5**[c]	**6**	A[d]
***E*-1**	$(CD_3)_2CO$	23	10	2	54	11
	$(CD_3)_2CO/CD_2Cl_2$ (4)	32	13	1	43	9
	$(CD_3)_2CO/CD_2Cl_2$ (1)	32	13	3	41	9
	$(CD_3)_2CO/CD_2Cl_2$ (0.25)	36[e]	15[e]	3	35	11
	CD_2Cl_2	44[e]	18[e]	3	35	0
***Z*-2**	$(CD_3)_2CO$	8	5	0	83	4
	$(CD_3)_2CO/CD_2Cl_2$ (4)	11	7	0	79	3
	$(CD_3)_2CO/CD_2Cl_2$ (1)	13	8	0	77	2
	$(CD_3)_2CO/CD_2Cl_2$ (0.25)	16[f]	10[f]	0	74	g
	CD_2Cl_2	18	12	0	70	0

[a] Distributions measured by integration and cut and weighing of the proton NMR spectrum and are only good to ±5%. [b] The number in the parentheses after the solvent is the volume/volume ratio of the solvents in the mixture. [c] Detected by observing 3-*tert*-butoxyacrolein after reaction mixture decompostion. [d] Directly formed acrolein. [e] Estimate from a seriously overlapped NMR spectrum. [f] Not adjusted for directly formed acrolein. [g] Not determined.

The regiochemical assignments in both reactions were based on analyses of the proton NMR spectra of the dioxetanes taken at −78 °C. The spectral assignments (Table I) were made with the aid of single frequency decoupling experiments and computer simulations. The stereochemical arrangement of the vinyl and *tert*-butoxy groups on the dioxetane rings were established by using the previous observation[6] that δ_{H_2} in cis-substituted dioxetanes are significantly upfield of δ_{H_2} in their trans isomers.

The regiochemical preference for the 2 + 2 cycloaddition was also corroborated by the observation that decomposition of the dioxetanes produced acrolein and *tert*-butyl formate. Only in the decomposition of the reaction mixture from photooxidation of the *E* isomer **1** was a small amount of 3-*tert*-butoxyacrolein observed.

The reactions of **1** and **2** were also investigated in CD_2Cl_2/

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Scheme I

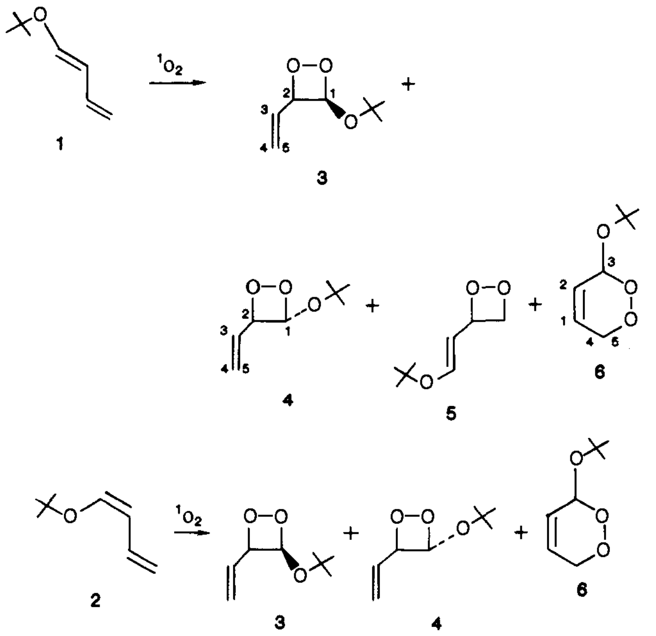


Table III. The Proton NMR Data for Dioxetanes **3** and **4** and Endoperoxide **6** as a Function of Solvent Composition

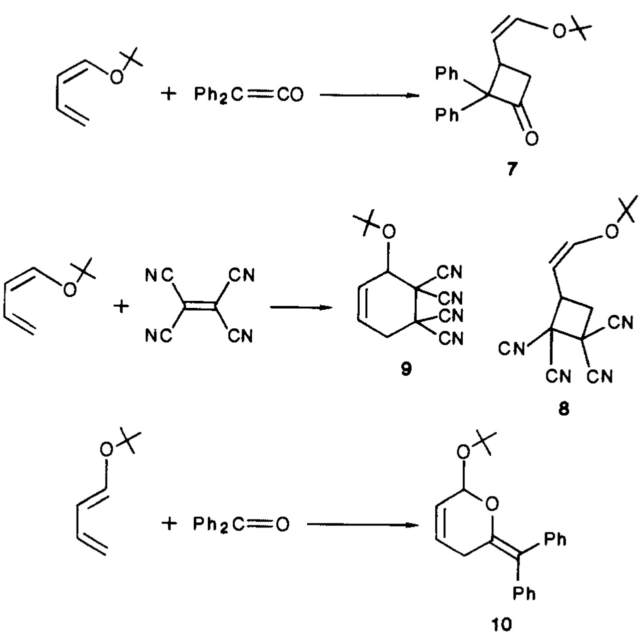
		chemical shift[a] mole fraction of acetone =						
compd	proton	1	0.778	0.466	0.178	0	slope	*r*
3	H_1	6.56	6.50	6.38	6.30	6.25	0.317	0.9989
	H_2	5.64	5.61	5.54	5.58	5.57		
	H_3	6.34	6.33	6.31	6.30	6.29		
	H_4	5.51	5.49	*b*	5.49	5.46		
	H_5	5.63	5.59	5.55	5.54	5.54		
4	H_1	6.57	6.52	6.46	6.39	6.35	0.219	0.9982
	H_2	5.94	5.92	5.91	5.89	*b*		
	H_3	6.47	6.54	b	6.48	6.47		
	H_4	5.48	5.47	5.46	*b*	*b*		
	H_5	*b*	*b*	*b*	*b*	*b*		
6	H_1	6.24	6.24	6.24	6.24	6.23		
	H_2	5.88	5.85	5.86	5.86	5.85		
	H_3	5.57	5.54	5.47	5.42	5.38	0.192	0.9980
	H_4	4.66	4.68	4.72	4.75	4.75		
	H_5	4.34	4.34	4.34	4.34	4.34		

[a] All chemical shifts are reported relative to Me_4Si at −78 °C. [b] Not observed buried under another peak.

acetone-d_6 solvent mixtures (Table II). As previously reported[6] for the dioxetanes formed in the singlet oxidations of 1,4-di-*tert*-butoxy-1,3-butadienes, the chemical shift of the proton adjacent to the *tert*-butoxy group is a sensitive function of solvent composition. The linear relationships (Table III) between the mole fraction of acetone-d_6 and these chemical shifts facilitated spectral assignments for the dioxetanes in these solvent mixtures. At −78 °C in the acetone-d_6 rich solvent mixtures, but to a lesser degree in the CD_2Cl_2 rich solvent mixtures, and not at all in pure CD_2Cl_2, acrolein and a small amount of an unidentified material were also formed. (See Table II.) The acrolein formed at low temperatures appears to be a primary product of photooxidation and not a dioxetane decomposition product. In support of this suggestion, control reactions demonstrated that the dioxetanes are thermally and photochemically stable under the reaction conditions.

The ability of Dabco (2.7×10^{-3} M) to quench the formation of all the products including acrolein demands that singlet oxygen be an essential intermediate in these reactions. The product ratios were also independent of the sensitizer utilized in the reaction (rose bengal, methylene blue, or TPP). Control reactions in argon atmospheres but under otherwise identical reaction conditions also demonstrated that dye or photochemically induced isomerizations of the dienes do not occur under the reaction conditions. Singlet oxygen induced isomerizations,[7] however, do appear to be occurring to some extent. Isomerized diene was observed after partial photooxidation in the reaction of the *Z* but not *E* diene in acetone-d_6.

Scheme II



The regiochemistry of addition of singlet oxygen to these dienes appears to be unique. The structures of the 2 + 2 cycloadducts formed in the reactions of diphenylketene (DPK) **7** and tetracyanoethylene **8** with the *Z* isomer **2** and the structure of the 4 + 2 cycloadduct formed in the reaction of DPK with the *E* isomer **1** (Scheme II) are consistent with cycloaddition proceeding by electrophilic addition to the terminus of the diene with the largest P_z coefficient and most favorable electrostatic potential.

Discussion

The nonstereospecific formation of the dioxetanes in the reactions of both **1** and **2** is reminiscent of the behavior of 1,4-di-*tert*-butoxy-1,3-butadienes.[6] This observation is consistent with zwitterionic[8] or biradical[9] intermediates which can rotate in competition with closure to the dioxetanes. The preference in both reactions for the cis-3,4-disubstituted dioxetanes can be rationalized by invoking an attractive interaction between the alkoxy group and allylic moiety in the open intermediate. A thermodynamic study of alkyl 1-propenyl ethers[10] has demonstrated that this electronic preference actually increases with the bulk of the alkoxy group. Similar counter steric effects have been observed in halopropenes[11] and trifluoromethyl-substituted enol ethers.[12]

The unique regiochemistry for the $^1O_2$ reactions can be rationalized by suggesting that these reactions proceed through symmetrical transition states (TS) in which the location of the largest adjacent coefficients rather than the largest coefficient controls the reaction. The additions of TCNE[13] and DPK[14] to 1,3-butadienes have both been shown to proceed via unsymmetrical TSs and their reactions at the diene terminus with the largest electron density is therefore not unexpected. We would argue, however, that $^1O_2$ also reacts unsymmetrically and that it should react with the same regiochemistry as TCNE or DPK. In support of this suggestion, Mehrshiekh-Mohammadi[15] has demonstrated

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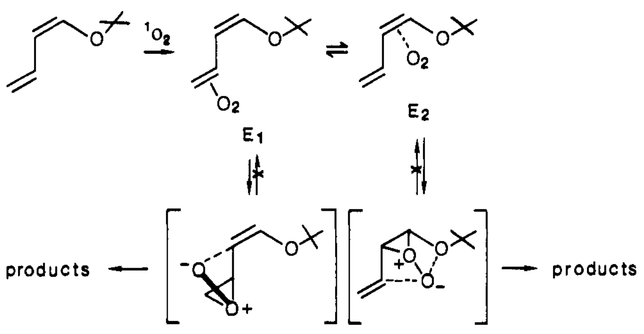
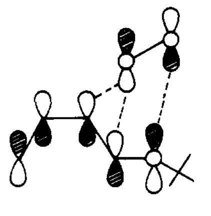
Scheme III



Scheme IV



that in $^1O_2$ additions to furans the symmetry of the TS is a function of the electron density distribution in the furan.

Rationalizations invoking differential steric effects[16] are also untenable because the steric demands for cycloadditions of $^1O_2$ to these dienes and the additions of DPK to *Z* double bonds are both expected to be minimal.[17]

We prefer the suggestion that secondary orbital interactions perhaps in a perepoxide like TS favors reaction at the more highly substituted double bond. Or perhaps more reasonably, reaction occurs through the thermodynamically less stable exciplex[18] (E_2) because of stabilizing perepoxide interactions[19] in its TS for collapse to produce (Scheme III). Both of these mechanisms invoke irreversible formation of perepoxides consistent with the elegant isotope effect studies of Stephenson.[19] Only one of the two possible perepoxides which could form at each double bond is depicted in Scheme III. The stabilizing interactions in these perepoxides can be most easily visualized by examination of the dominant HOMO LUMO interaction in these complexes[20] (Scheme IV). When the high lying lone pair on the *tert*-butoxy group is mixed with the p-orbitals of the diene, and the HOMO is depicted as pentadienyl anion like, satisfactory frontier orbital overlap is achieved. No information on whether the interconversions of the η^2 exciplexes (E_1 and E_2) are associative or dissassociative is available, but both mechanistic types have been suggested for ring whizzing in η^4 organometallic systems.[21]

The direct formation of acrolein in the reactions run in acetone-d_6 rich solvent mixtures is symptomatic of radical cation involvement. Similar direct formations of olefinic cleavage products have previously been observed in the photooxidations of tetraphenylethylene,[22] 1,1-diphenylethylene,[23] 1,1-dianisylethylene,[24] and *cis*- and *trans*-stilbene.[25] A considerable amount of evidence[26] has been collected that suggests that these reactions proceed via the electron-transfer mechanism shown in Scheme V. This mechanism, however, does not explain the formation of acrolein in the reactions of **1** and **2**. The dye cannot be acting as an electron acceptor since the amount of acrolein formed is independent of dye. The DABCO quenching experiments, implicating singlet oxygen as a necessary precursor to direct acrolein formation, however, suggest the mechanism depicted in Scheme VI.

Scheme V

$$\text{acceptor} + h\nu \rightarrow \text{acceptor}^* \qquad (1)$$

$$\text{acceptor}^* + \text{olefin} \rightarrow \text{acceptor}^{\bullet-} + \text{olefin}^{\bullet+} \qquad (2)$$

$$\text{acceptor}^{\bullet-} + O_2 \rightarrow \text{acceptor} + O_2^{\bullet-} \qquad (3)$$

$$\text{olefin}^{\bullet+} + O_2^{\bullet-} \rightarrow \text{olefin}O_2 \qquad (4)$$

$$\text{olefin}O_2 \rightarrow \text{cleavage products} \qquad (5)$$

Scheme VI

$$\text{dye} + h\nu \rightarrow \text{dye}^* \qquad (1)$$

$$\text{dye}^* + O_2 \rightarrow \text{dye} + {}^1O_2 \qquad (2)$$

$${}^1O_2 + \mathbf{1} \rightarrow [O_2^{\bullet-}\mathbf{1}^{\bullet+}] \qquad (3)$$

$$[O_2^{\bullet-}\mathbf{1}^{\bullet+}] + \mathbf{1} \rightarrow [O_2^{\bullet-}\mathbf{1}^{+}\text{–}\mathbf{1}^{\bullet}] \qquad (4)$$

$$[O_2^{\bullet-}\mathbf{1}^{+}\text{–}\mathbf{1}^{\bullet}] + O_2 \rightarrow \text{acrolein} \qquad (5)$$

$$[O_2^{\bullet-}\mathbf{1}^{+}\text{–}\mathbf{1}^{\bullet}] \rightarrow \text{acrolein} \qquad (6)$$

Electron transfer to singlet oxygen has previously been invoked to explain the photooxidation of an enamine.[27] The steric demands in the dimerization, step 4 (Scheme VI), provide an explanation for the lack of direct cleavage products in the reactions of the more sterically hindered, but certainly more easily oxidized, 1,4-di-*tert*-butoxy-1,3-butadienes.[6] The reaction of oxygen with the monomer radical cation is expected to be much slower than this dimerization step. Nelsen[28] in a cyclic voltammetry study reports rate constants for oxygen addition to radical cations on the order of 10^2 to 10^3 M^{-1} s^{-1}. Farid,[29] on the other hand, quotes a rate of 6×10^9 M^{-1} s^{-1} for the reaction of 1,1-diphenylethylene radical cation with its neutral precursor. The radical and cation centers are farther removed from each other and the reaction with oxygen is anticipated to be more rapid in the nonconjugated dimer. In support of this suggestion, we note that Haynes[30] has recently reported that photolysis of 1-*tert*-butyl-1,3-cyclohexadiene, in the presence of trityl tetrafluoroborate and oxygen, resulted in its dimerization followed by its reaction with oxygen. The observation that the direct formation of acrolein is shut-off by addition of a less polar solvent is also supportive of this mechanism. The extended lifetime of the superoxide–$\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ ion pair necessary to allow dimerization to compete with internal collapse is undoubtedly due to the delocalized nature of the diene radical cations.

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Conclusion

The reactions of (*E*)- and (*Z*)-1-*tert*-butoxy-1,3-butadiene with singlet oxygen have been reported. The regiochemistry of these reactions has been explained in terms of a favorable frontier orbital interaction. The reactions have been suggested to proceed through reversibly formed singlet oxygen diene complexes which precede the irreversible formations of the perepoxides. In polar solvents where the charge-transfer character of the singlet oxygen diene complex is large, addition of a second molecule of diene at the sterically unencumbered end of the complex competes with simple addition of singlet oxygen. The reaction of the resultant dimer with either superoxide or oxygen is expected to be rapid and leads to acrolein though a yet unidentified mechanism. Additional studies to clarify the charge-transfer character of these reactions and the mechanism of acrolein formation are currently in progress.

Experimental Section

Preparative gas chromatographic separations were carried out on a Gow Mac Series 550 utilizing a 0.25 in. by 20 ft column packed with 20% Carbowax 20M on Chromosorb W NAW. The retention times for the *E* and *Z* dienes were 15 and 11.4 min, respectively, when the oven was set to 100 °C, the detector to 200 °C, the injector to 160 °C, the collector to 220 °C, and the flow rate of helium to 86 mL/min. Proton and carbon NMR spectra were obtained on a JEOL FX270 at 270 and 67.83 MHz, respectively, and the chemical shifts are referenced to Me_4Si. Mass spectral data were obtained on a VG-ZAB-1F by electron impact.

Acetone-d_6 (Aldrich) was distilled from either $CaSO_4$ or $NaSO_4$ and stored over 4A molecular sieves. Methylene-d_2 chloride (Aldrich) was filtered through activity grade 1 basic alumina prior to use. Tetracyanoethylene (Eastman Kodak) was purified by recrystallization from methylene chloride followed by sublimation. Bulk benzene was stirred over sulfuric acid, shaken with bicarbonate, washed with water, distilled, and stored over 4A molecular sieves. Benzene-d_6 (Aldrich), isobutylene (Pfaltz and Bauer), benzil (Aldrich), mercury(II) oxide (Aldrich), hydrazine hydrate (Aldrich), Rose Bengal (Aldrich), TPP (Aldrich), mesoporphyrin-IX-dimethyl ester (Sigma), and Methylene Blue (Baker) were used without further purification.

1,4-Di-*tert*-butoxy-2-butyne was synthesized by the method of Hiranuma and Miller[31] in 74% yield.

***cis*- and *trans*-1,4-di-*tert*-butoxy-2-butene** were prepared by a modified procedure according to Brandsma.[4] A flame-dried, 100 mL, 3-necked, round-bottomed flask was fitted with a dry ice condensor, septum, and stopper, and 8 g (0.04 mol) of 1,4-di-*tert*-butoxy-2-butyne, 12 g (0.16 mol) of *tert*-butyl alcohol, and 13 mL of THF were added. Liquid Ammonia (39 mL) was condensed into the reaction flask and 6.3 g (0.09 mol) of methanol etched lithium was added over a period of 7 to 8 min. After the addition was complete, the reaction was stirred for an additional 30 min and then poured over ice, extracted with ether (2 × 50 mL), dried over $MgSO_4$, and rotary evaporated. It was finally distilled at reduced pressure (bp 118 °C (19 mmHg)) to give 4.54 g of a 88% cis/12% trans mixture of 1,4-di-*tert*-butoxy-2-butene. This mixture which was contaminated with 9.6% of the starting material was used directly in the next step.

(*E*)- (1) and (*Z*)-1-*tert*-butoxy-1,3-butadiene (2) were synthesized by a modified procedure of Brandsma.[4] To a flask cooled in an ice bath, containing 0.87 g (0.0085 mol) of diisopropylamine and 50 mL of THF in a nitrogen atmosphere, 5.3 mL of 1.6 m *n*-BuLi in hexane was added. After 20 min of stirring this mixture (1.54 g, 0.0077 mol) of *cis*-/*trans*-1,4-di-*tert*-butoxy-2-butene was added and the reaction mixture was allowed to warm and stir at room temperature for 2 h. The reaction mixture was worked up by pouring it into 35 mL of pentane, washing this solution with 26 mL of 5% $NaHCO_3$ and 26 mL of brine, and finally drying the mixture with $MgSO_4$. The dienes were obtained by removal of the solvent and distillation at reduced pressure (bp 52 °C at 20 (mmHg), yield 43% of which 59% was the *Z* and 41% the *E* diene). The two isomers were separated by preparative gas chromatography. (*Z*)-1-*tert*-Butoxy-1,3-butadiene: ^{1}H NMR (acetone-d_6) δ 6.67 (dddd, J = 17.4, 10.9, 10.4, 0.9 Hz, 1 H), 6.35 (dddd, J = 6.2, 1.5, 0.9, 0.7 Hz, 1 H), 5.09 (dddd, J = 10.9, 6.2, 0.7, 0.7 Hz, 1 H), 4.97 (dddd, J = 17.4, 2.4, 0.7, 0.7 Hz, 1 H), 4.79 (dddd, J = 10.4, 2.4, 1.5, 0.7 Hz, 1 H), 1.29 (s, 9 H); ^{13}C NMR (acetone-d_6) δ 27.98 (q, J = 125 Hz), 76.99 (s), 108.14 (d, J = 153 Hz), 112.03 (t, J = 153 Hz), 131.25 (d, J = 153 Hz), 141.71 (d, J = 175 Hz). (*E*)-1-*tert*-Butoxy-1,3-butadiene: ^{1}H NMR (acetone-d_6) δ 6.81 (d, J = 11.9 Hz, 1 H), 6.27 (ddd, J = 17.2, 11.0, 11.0 Hz, 1 H), 5.58 (dd, J = 11.9, 11 Hz, 1 H), 4.87 (dd, J = 17.2, 2.0 Hz, 1 H), 4.69 (dd, J = 11.0, 2.0 Hz, 1 H), 1.26 (s, 9 H); ^{13}C NMR (acetone-d_6) δ 28.13 (q, J = 122 Hz), 77.23 (s), 110.48 (t, J = 157 Hz), 110.91 (t, J = 151 Hz), 135.08 (d, J = 149 Hz), 147.01 (d, J = 173 Hz).

3,6-Dihydro-3-*tert*-butoxy-1,2-dioxin (6) was synthesized on a preparative scale by placing 56.5 mg of *Z* diene **2** in a photolysis flask containing 10 mL of acetone and Rose Bengal. Irradiation was conducted with a 750W-120V tungsten lamp through a 75% w/v sodium nitrite filter while oxygen bubbled through the solution at −78 °C. The reaction was monitored by TLC and was complete in less than 7 h. After the dioxetane products were allowed to decompose the solvent was removed by rotary evaporation and the dioxin was isolated by flash column chromatography: ^{1}H NMR (acetone-d_6) δ 6.14 (dddd, J = 10.1, 4.4, 1.5, 1.5 Hz, 1 H), 5.79 (dddd, J = 10.1, 4.0, 2.2, 1.5 Hz, 1 H), 5.41 (bddd, J = 2.2, 1.8, 1.5 Hz, 1 H), 4.61 (bdddd, J = 17.0, 4.0, 1.8, 1.5 Hz, 1 H), 4.27 (bddd, J = 17.0, 4.4, 1.5 Hz, 1 H), 1.27 (s, 9 H); ^{13}C NMR (acetone-d_6) δ 28.88 (q, J = 127 Hz), 69.16 (t, J = 146 Hz), 75.30 (s), 92.89 (d, J = 159 Hz), 125.35 (d, J = 169 Hz), 127.90 (d, J = 169 Hz).

Diphenylketene was prepared by the method of Smith[32] in 53% yield (lit. 58%).

3-(*cis*-1-*tert*-Butoxyethenyl)-2,2-diphenylcyclobutanone (7) was prepared by gently heating a mixture of 84.9 mg of *Z*-diene **2** (0.67 mmol) and 185.9 mg (0.96 mmol) of diphenylketene in 3 mL of benzene for 48 h. The benzene was removed on the rotary evaporator, hexane was added, a residue was removed by filtration, and the cyclobutanone was isolated as a yellow oil by removal of the hexane. ^{1}H NMR ($CDCl_3$) δ 7.1–7.35 (m, 10 H), 6.28 (dd, J = 6.2, 1.1 Hz, 1 H), 4.04 (dd, J = 9.5, 6.2 Hz, 1 H), 4.35 (ddd, J = 9.5, 9.2, 8.8 Hz, 1 H), 3.27 (dd, J = 17.6, 9.2 Hz, 1 H), 2.97 (dd, J = 17.6, 8.8 Hz, 1 H), 1.37 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 28.13 (q, J = 121 Hz), 31.13 (d, J = 136 Hz), 50.43 (t, J = 138 Hz), 80.06 (s), 107.29 (d, J = 166 Hz), 126.57, 126.51, 127.3, 127.76, 128.09, 128.25, 130.00, 140.62 (d, J = 166 Hz), 140.63 (s), 142.22 (s), 209.39 (s); mass spectrum, found 320.1749, calcd 320.1777.

2-*tert*-Butoxy-5,6-dihydro-6-diphenylmethylidene-1,2-pyran (10) was prepared by gently heating, in a nitrogen atmosphere, 78 mg (0.68 mmol) of *E*-diene **1** and 140 mg (0.72 mmol) of diphenylketene in 3 mL of benzene for 24 h. After removal of the benzene 53 mg of the product was obtained by preparative thin layer chromatography. ^{1}H NMR ($CDCl_3$) δ 7.37–7.11 (m, 10 H), 5.91 (dddd, J = 10.1, 3.7, 3.7, 1.3 Hz, 1 H), 5.68 (dddd, J = 10.1, 2.6, 2.2, 2.2 Hz, 1 H), 5.54 (br s, 1 H), 2.99 (dddd, J = 20.2, 3.7, 2.2, 2.2 Hz, 1 H), 2.89 (dddd, J = 20.2, 3.7, 2.2, 2.2 Hz, 1 H), 1.14 (s, 9 H).

1,1,2,2-Tetracyano-3-(*cis*-1-*tert*-butoxyethylenyl)cyclobutane (8) was prepared by dissolving 55.5 mg (0.43 mmol) of TCNE in 5 mL of benzene and adding 54 mg (0.43 mmol) of *Z*-diene **2**. The reaction mixture turned immediately green but faded after 80 s. A few minutes later, the 2 + 2 adduct precipitated from solution. The solid was isolated by suction filtration and recrystallized from benzene/hexane. ^{1}H NMR ($CDCl_3$) δ 6.61 (dd, J = 5.9, 1.1 Hz, 1 H), 4.47 (dd, J = 5.9, 6.2 Hz, 1 H), 4.37 (dddd, J = 11.4, 8.8, 6.2, 1.1 Hz, 1 H), 3.15 (dd, J = 12.5, 8.8 Hz, 1 H), 2.95 (dd, J = 12.5, 11.4 Hz, 1 H), 1.63 (s, 9 H); ^{13}C NMR δ 25.58 (q, J = 125 Hz), 33.62 (s), 36.07 (t, J = 150 Hz), 40.01 (d, J = 142 Hz) 43.49 (s), 78.91 (s), 98.15 (d, J = 166 Hz), 109.71 (s), 110.52 (s), 111.26 (s), 126.70 (s), 145.70 (d, J = 182 Hz); mass spectrum, found 254.1158, calcd 254.1169; mp 100–102 °C. Monitoring this reaction in benzene-d_6 demonstrated that this reaction proceeds to give both the 2 + 2 (69%) and 4 + 2 (31%) cycloaddition products. The 2 + 2 adduct slowly rearranged[13b] to the 4 + 2 adduct. After 48 h 2 + 2 and 4 + 2 adducts were observed.

3-*tert*-Butoxy-4,4,5,5-tetracyanocyclohexene was prepared by dissolving 35 mg (0.27 mmol) of TCNE in 5 mL of benzene and adding 34 mg (0.27 mmol) of the *E*-diene **1**. A flash of green color was observed during the addition. After removal of the solvent almost pure 4 + 2 adduct was isolated in 60% yield. Purification by recrystallization from benzene/hexane gave beige crystals: mp 75–76.5 °C; ^{1}H NMR (C_6D_6) δ 5.18 (ddd, J = 10.6, 4.4, 2.2 Hz, 1 H), 4.69 (dddd, J = 10.6, 2.9, 2.2, 1.8 Hz, 1 H), 4.49 (bddd, J = 2.6, 2.2, 1.8 Hz, 1 H), 2.10 (ddd, J = 19.0, 2.6, 2.2 Hz, 1 H), 1.69 (dddd, J = 19.0, 4.4, 1.8, 1.8 Hz, 1 H), 0.90 (s, 9 H); ^{13}C NMR (C_6D_6) δ 27.53 (q, J = 127 Hz), 31.22 (t, J = 133 Hz), 38.22 (s), 44.99 (s), 68.77 (d, J = 148 Hz), 78.06 (s), 109.38 (s), 110.96 (s), 111.36 (s), 111.91 (s), 121.86 (d, J = 168 Hz).

Photolysis Conditions. An acetone-d_6 solution that was 0.042–0.054 M in diene and 1×10^{-5} M in Rose Bengal was placed in a 5-mm NMR tube. This solution was saturated with oxygen for 30 min at −78 °C while being protected from the light and then irradiated for 70 min at −78 °C through a 0.5% $K_2Cr_2O_7$ filter solution. The irradiation was conducted with a WIKO CWA 120V-750W projector lamp. The reactions were monitored at either −80 or −65 °C by low-temperature NMR.

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