chemically generated hydrogen atoms on Titan may also account for the presence of HCN and absence of acetonitrile in its atmosphere.

Chromophore Formation. The hydrogen atom initiated oligomerization of acetylene appears to be a more plausible route to organic chromophores on Jupiter than the direct photolysis of acetylene. The latter process cannot proceed in the presence of ammonia because ammonia is a strong absorber of solar UV than acetylene. The hydrogen atom initiated reaction proceeds at low temperatures and is only partially inhibited by molecular hydrogen. The oligomer formed in the presence of ammonia incorporates hydrogen atoms and NH groupings. The incorporation of other radicals present in the Jovian atmosphere ($^{\bullet}PH_2$, $^{\bullet}CN$, and possibly $^{\bullet}OH$) may result in the generation of oligomers with different visible spectral properties than the one formed in our laboratory studies. For example, the chlorine atom initiated oligomerization of acetylene results in the formation of yellow to orange products instead of brown polymers.[70] These colors may reflect the incorporation of chromophoric chlorine groups into the oligomers.

Acknowledgment. This research was supported by Grant PR 10-38765 from NASA. The Model 1800 FT-IR was a gift to the Chemistry Department from Perkin-Elmer. Preliminary studies were performed by Dr. H. Khwaja, and we thank him for the design of the CaF_2 cell. We thank Dr. F. Raulin for bringing the abstract of Masanet et al. (1982) to our attention.

Registry No. 1, 151-56-4; **6**, 592-56-3; HCN, 74-90-8; NH_3, 7664-41-7; CH_3CN, 75-05-8; HC≡CH, 74-86-2; acetylene (homopolymer), 25067-58-7.

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Additions of Singlet Oxygen to Alkoxy-Substituted Dienes. The Mechanism of the Singlet Oxygen 1,2-Cycloaddition Reaction

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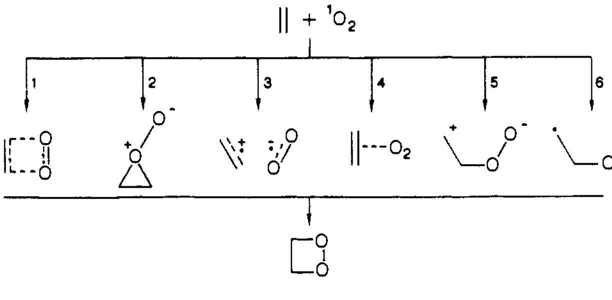
Abstract: The reactions of singlet oxygen with (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-1,4-dimethoxy-1,3-butadienes are reported. These compounds react to give dioxetanes as the major oxidized products. All three compounds are suggested to react via zwitterions, which collapse to dioxetanes before rotational equilibrium is reached. The zwitterions are stabilized in the more polar solvents, and as a result their rotation competes more effectively than in less polar solvents with closure to the dioxetanes.

In 1969 Kopecky and Mumford[2] reported that the base cyclization of a bromo hydroperoxide allowed the first successful isolation of a 1,2-dioxetane. In 1970 Bartlett and Schaap[3] and Mazur and Foote[4] simultaneously reported the successful isolation of these strained peroxides from addition of singlet oxygen to an olefin. It soon became apparent[5] that this formal 2 + 2 cycloaddition of singlet oxygen was to take its place along with the ene[6] and 4 + 2 cycloaddition[7] as ubiquitous modes of singlet oxygen reactivity.

The mechanism of the singlet oxygen 1,2-cycloaddition reaction has been extensively debated in the literature.[8] The mechanisms that have most often been considered are shown in Scheme I. Mechanism 1 is a concerted 2s + 2a cycloaddition and should be promoted by the small size of singlet oxygen.[5] Analysis of frontier orbital interactions in the favorable olefin-HOMO singlet oxygen-LUMO orbital arrangements, however, suggest that the olefin should act as the antarafacial component rather than as a suprafacial component as is experimentally observed.[8]

Scheme I



Mechanism 2 proceeds through a perepoxide intermediate. Perepoxides have received considerable support as intermediates in the singlet oxygen ene reaction.[9] Particularly persuasive

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[1] Jagiellonian University, Krakow, Poland.

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evidence for these perepoxide intermediates include the elegant isotope effect work of Stephenson,[10] the cis effect,[11] and the recent observation of diastereoselective ene reactions in the photooxidation of silyl cyanohydrins.[12] Unfortunately, these experimental tests are not amenable to the study of the 1,2-cycloadditions of singlet oxygen, and much less evidence for a perepoxide intermediate in these reactions is available. Nevertheless, the substituent effect data[13] and trapping experiments[14] of Schaap and the recently reported regiochemistry of singlet oxygen addition to dienes[15] all implicate the perepoxide as an intermediate in the 1,2-cycloaddition of singlet oxygen.

Mechanism 3 involves an electron transfer from the olefin to singlet oxygen and should be most important for electron-rich olefins, the same olefins that have a propensity to undergo the 1,2-cycloaddition reaction. Enamines,[16] phenols,[17] and enol ethers,[13] all appear to form complexes or transition states with significant electron transfer to oxygen (14% for enol ethers[13] and 44% for phenols[17]).

Mechanism 4 proceeds through an exciplex intermediate. Exciplexes have become popular intermediates in singlet oxygen chemistry.[18] Koch[19a] and Stevens[19b] discussed exciplex (oxciplex) intermediates in the late 1960s and early 1970s. It is not entirely clear that these exciplexes and the charge transfer intermediate (mechanism 3) are distinct species.

Mechanism 5 invokes a zwitterion intermediate. This mechanism has received a considerable amount of support because in systems in which the ene and 2 + 2 cycloaddition compete, increasing solvent polarity favors formation of the 2 + 2 product.[20] In addition, elegant trapping experiments[21] and the observation of rearrangement products[22] provide compelling evidence for ionic intermediates. The 2 + 2 cycloaddition, however, in most cases[23] is a stereospecific reaction,[24] and zwitterions, if formed, have lifetimes too short to rotate in competition with closure to give the 1,2-dioxetanes.

Mechanism 6 proceeds through a biradical intermediate. The generalized valence-bond calculation of Harding and Goddard[25] places the biradical intermediate 7 kcal/mol below the perepoxide.

We present here the results of additions of singlet oxygen to (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-1,4-dimethoxy-1,3-butadienes (**1–3**, respectively) and compare their reactivities to the previously reported[23] 1,4-di-*tert*-butoxy-1,3-butadienes. These studies were undertaken with the expectation that, if zwitterions are genuine intermediates in 2 + 2 reactions of singlet oxygen, the allylic stabilization and concomitant increased lifetimes afforded these species, formed in the reactions of **1–3**, might allow rotation to compete with closure to the dioxetanes. Indeed these studies have provided the only well-documented examples of nonstereospecific dioxetane formations. This result and other key observations will be utilized to construct a comprehensive mechanism for the singlet oxygen 2 + 2 cycloaddition.

Table I. Extinction Coefficients and Wavelength Maxima for (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-1,4-Dimethoxy-1,3-butadienes (R = Me) and Di-*tert*-butoxy-1,3-butadienes (R = *t*-Bu)

compd	run	λ_{max}, nm	ϵ, L mol^{-1} cm^{-1}	*r*
E,*E* (R = Me)	1	235	11 540	0.9999
	2		11 566	0.9997
	3		11 464	0.9998
	average		11 524	
E,*Z* (R = Me)	1	244	14 272	0.9999
	2		14 086	0.9999
	3		14 301	0.9999
	average		14 219	
Z,*Z* (R = Me)	1	252	21 502	0.9998
	2		21 585	0.9997
	3		21 585	0.9998
	average		21 557	
E,*E* (R = *t*-Bu)	1	245	28 776	0.9999
	2		31 662	0.9995
	average		30 219	
E,*Z* (R = *t*-Bu)	1	251	24 250	0.9999
	2		24 521	0.9993
	3		24 944	0.9998
	average		24 572	
Z,*Z* (R = *t*-Bu)	1	254	31 339	0.9999
	2		30 559	0.9993
	3		31 376	0.9997
	average		31 092	

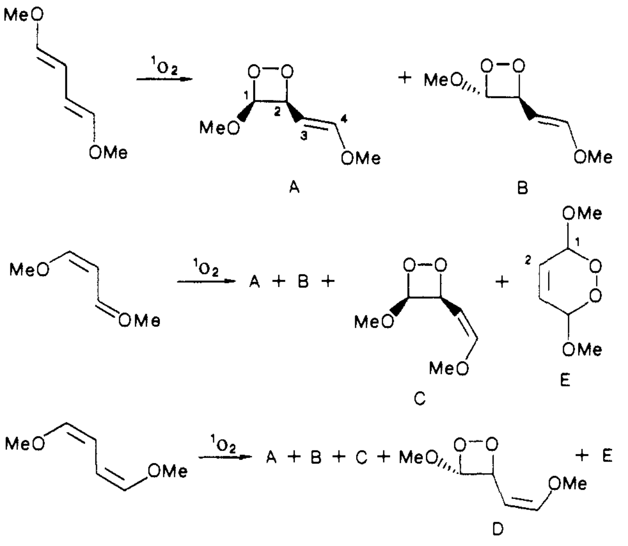
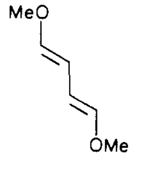


Figure 1.



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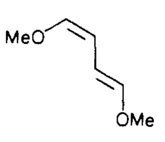

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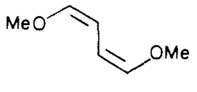

3

Results

Dienes **1–3** were synthesized by the method of Miller[26] and were separated by preparative gas chromatography. We observed a 6:62:32 *E*,*E*:*E*,*Z*:*Z*,*Z* ratio in our synthesis rather than the previously reported 8:30:62 isomer ratio. This ratio, however, may not reflect the thermodynamic preference. Viehe and Franchimont[27] reported a 9.1:40:50.9 *E*,*E*:*E*,*Z*:*Z*,*Z* ratio for the 1,4-di-

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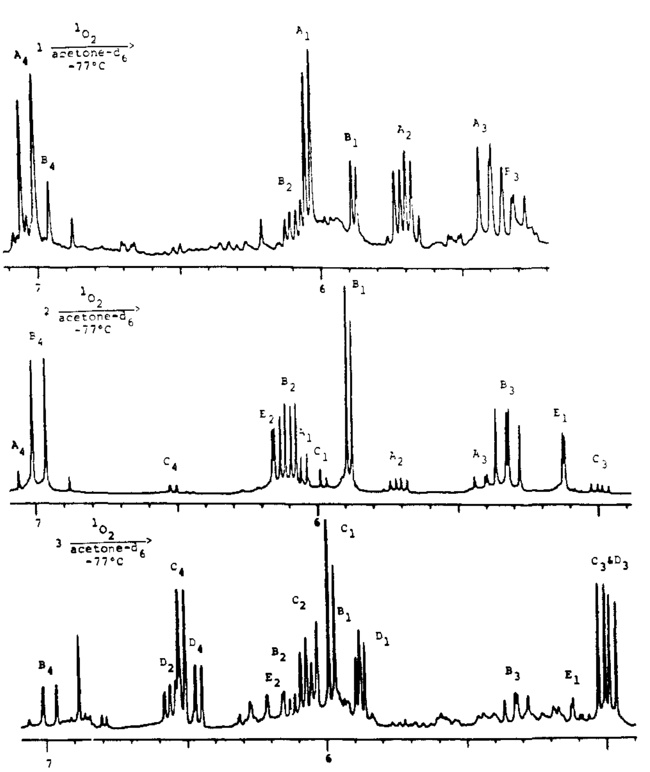
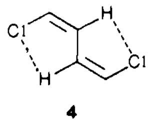


Figure 2. Proton NMR spectra of photooxidation mixtures from reaction of dienes **1**-**3** at -77 °C in acetone-d_6. See Figure 1 for numbering scheme.

chloro-1,3-butadienes and attributed it to a nonbonded interaction **4**. The proton and carbon NMR data for all three isomers are



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reported in the Experimental Section. The extinction coefficients and λ_{max} for these compounds are given in Table I along with those for the 1,4-di-*tert*-butoxy-1,3-butadienes for comparison.

The photooxidations of these pure dienes were conducted in dilute deuteriated solvents in order to increase the lifetime of singlet oxygen and consequently the rate of reaction and at low temperatures through appropriate filter solutions to prevent light absorption by either the starting materials or the products.

Dilute solutions were utilized to prevent dye-induced isomerizations of the dienes. At 0.13 M and below, less than 3% isomerization was observed in the absence of oxygen. At higher temperatures (vida infra), however, dye-induced isomerization was more extensive especially for diene **3** (as much as 7% isomerization) even at the lowest concentrations conveniently used for NMR studies. These methoxy-substituted dienes in comparison to the previously studied *tert*-butoxy-substituted compounds[23] have a greater tendency to lose their configurational integrities by dye-induced, singlet oxygen induced,[28] and acid-catalyzed pathways. Halogenated solvents in particular had to be treated with basic alumina to prevent acid-catalyzed isomerizations.

Low temperatures were used to prevent detrimental side reactions that have substantial activation barriers. Singlet-oxygen reactions have activation enthalpies near zero[29] and are not appreciably slower at the lower temperatures used in this study.

The products formed in the reactions of **1**-**3**, conducted at -80 °C in acetone-d_6 with Rose Bengal as a sensitizer, under these carefully controlled conditions are shown in Figure 1. Singlet oxygen was implicated as the reactive intermediate in these reactions because the product ratios were independent of the sensitizer utilized in the photooxidations.

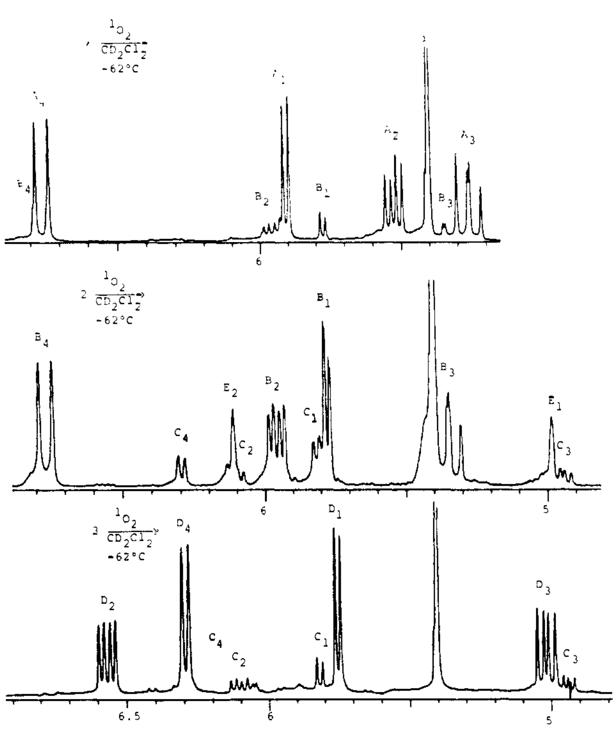

Figure 3. Proton NMR spectra of photooxidation mixtures from reactions of dienes **1**-**3** at -62 °C in CD_2Cl_2. See Figure 1 for numbering scheme.

Table II. ^1H NMR Data for Oxidation Products in the Reactions of Dimethoxy (R = CH_3) and Di-*tert*-butoxy (R = *t*-Bu) Dienes

	A	B	C	D	E
		R = CH_3			
$\delta(H_1)$, ppm	6.01	5.86	5.93	5.85	5.08
$\delta(H_2)$	5.67	6.06	6.05	6.52	6.12
$\delta(H_3)$	5.37	5.32	4.97	4.99	
$\delta(H_4)$	6.99	6.94	6.48	6.42	
$\delta(CH_3)$	3.55	3.45	3.48	3.48	3.47
	3.67	3.65	3.70	3.70	
J_{12}, Hz	5.5	4.8	5.5	4.9	2.2
J_{23}	10.4	10.6	10.6	10.6	
J_{34}	12.6	12.8	6.2	6.2	
		R = *t*-Bu			
$\delta(H_1)$, ppm	6.41	6.33	6.38	6.35	5.38
$\delta(H_2)$	5.49	5.90	5.99	6.41	5.89
$\delta(H_3)$	5.20	5.32	4.82	4.97	
$\delta(H_4)$	7.16	7.06	6.85	6.80	
$\delta(CH_3)$	1.23	1.22	1.24	1.22	1.12
	1.11	1.19	1.12	1.12	
J_{12}, Hz	6.2	5.5	6.2	5.1	1.5
J_{23}	10.3	10.6	10.6	10.6	
J_{34}	11.7	12.1	6.2	6.2	

The sensitivities of these products precluded their isolations. The structures of the products, however, were unambiguously assigned with the aid of exhaustive single frequency decoupling. Proton NMR spectra of the reaction mixtures at -77 °C in acetone-d_6 and at -62 °C in methylene chloride-d_2 are given in Figures 2 and 3, respectively. The accuracy of these assignments can be readily verified by comparison to the chemical shifts of the products formed in the photooxidation of the 1,4-di-*tert*-butoxy-1,3-butadienes as shown in Table II. In addition, as anticipated, upon warming to room temperature, the NMR peaks assigned to the sensitive dioxetanes, but not the peaks assigned to the endoperoxide, disappeared concomitant with the appearance of the NMR peaks of *cis*- and *trans*-3-methoxyacrolein.

The reactions of all three isomeric dienes were examined as a function of solvent composition. The proton chemical shifts of the products were not as sensitive to solvent changes as was

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Table III. Product Composition as a Function of Solvent

diene	solvent	% A	% B	% C	% D	% E
1	acetone-d_6	71	29			
	CD_2Cl_2	83	17			
2	acetone-d_6	9	74	2		15
	acetone-d_6/CD_2Cl_2 (0.749)[a]		78	8		14
	acetone-d_6/CD_2Cl_2 (0.501)		74	10		16
	acetone-d_6/CD_2Cl_2 (0.246)		73	11		16
	CD_2Cl_2		77	13		10
	CD_3CN		63	9		27
3	acetone-d_6	2	19	46	29	3
	acetone-d_6/CD_2Cl_2 (0.749)			62	38	
	acetone-d_6/CD_2Cl_2 (0.501)			38	62	
	acetone-d_6/CD_2Cl_2 (0.246)			24	76	
	CD_2Cl_2			16	84	
	CD_3CN			50	50	

[a] Mole fraction of acetone-d_6.

Table IV. Product Composition as a Function of Reaction Temperature[a]

diene	T, °C	% A	% B	% C	% D	% E
1	-80	71	29			
	-60	73	27			
	-40	63	37			
	-20	56	42			2
2	-80	9	74	2		15
	-60	14	57	5		24
	-40	16	36	4		43
	-20	15	35	4		46
3	-80	2	19	46	29	3
	-60	4	17	44	29	6
	-40	10	24	24	25	17
	-20	13	22	13	23	29

[a] In acetone-d_6.

observed previously for the di-*tert*-butoxy dienes. H_1 and H_4 in the dioxetanes are linearly related to the mole fraction of acetone-d_6, but the slopes of these plots are only about one-half that observed for the di-*tert*-butoxy compounds. The product compositions in the different solvents are shown in Table III. The ratios of the products were determined by integration and by cutting and weighing of appropriate NMR peaks. These ratios are only accurate to ±5%.

The effect of temperature on the product composition was also investigated. Extensive changes in the product ratios occurred as the temperature was increased from -80 to -20 °C as shown in Table IV. Isomerizations of the dienes are more facile in argon atmospheres at the higher temperatures, but control experiments demonstrated that these oxygen-independent isomerizations cannot totally account for the dramatic shift in product makeup.

Discussion

The salient discoveries that must be explained by any acceptable mechanism include the following.

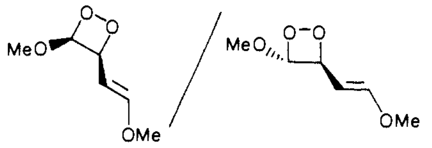
(1) The preponderance of the cis-substituted dioxetane in the reaction of the *E*,*E* diene **1**.

Table V. Experimental and MM2 Calculated Thermodynamic Parameters $\Delta H°$, $\Delta S°$ for the $E \rightleftharpoons Z$ Isomerization of Alkyl 1-Propenyl Ethers

	experimental[a]		MM2[b]	
alkyl	$\Delta H°$, kcal/mol	$\Delta S°$, cal/mol deg	H_f	$\Delta H°$
cis-CH_3			-32.74	
	0.10	0.68		-0.19
trans-CH_3			-32.55	
cis-CH_2CH_3			-41.00	
	-0.47	-0.17		-0.38
trans-CH_2CH_3			-40.62	
cis-$CH(CH_3)_2$			-50.82	
	-0.68	-0.43		-1.13
trans-$CH(CH_3)_2$			-49.69	
cis-$C(CH_3)_3$			-60.11	
	-0.70	-1.26		-1.23
trans-$C(CH_3)_3$			-58.88	

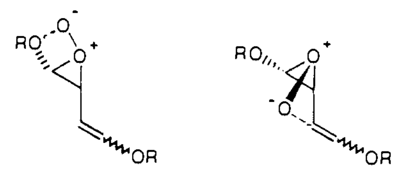
[a] Reference 29. [b] This work.

Scheme II

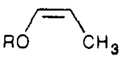


EE: 71 / 29 = 2.45
EZ: 9 / 74 = 0.12

Scheme III



The preference for the apparently more sterically hindered products in the reactions of alkoxy-substituted substrates has been observed previously. Cis-substituted dioxetanes are the major products in the reaction of all three isomeric di-*tert*-butoxy 1,3-dienes with singlet oxygen.[23] Taskinen and Liukas[30] examined the mercuric acetate catalyzed isomerizations of several alkyl 1-propenyl ethers **5** and also observed that the more hindered *Z* enol ethers were preferred and attributed it to an attractive interaction between the ether oxygen atom and the methyl group. We were able to verify this thermodynamic preference for the *Z* enol ether with MM2[31] calculations, which also remarkably mimicked the observed trend of increasing *Z* population with increasing size of the alkyl group[32] (Table V).



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(2) The different ratio of cis- to trans-substituted dioxetanes formed in the reaction of the *E*,*E* diene **1** and the *E*,*Z* diene **2**. (Scheme II) This result rules out the possibility that any common intermediate or any thermodynamically equilibrated set of intermediates are formed in the reactions of singlet oxygen with these two dienes.

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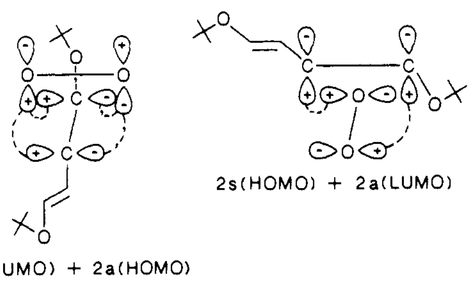
Scheme IV



(3) A dramatic difference in the response of the reactions of dienes **1** and **3** to changes in solvent composition. The *E,E* diene is insensitive to solvent polarity changes (Table III) but the *Z,Z* diene product ratio is dramatically altered over the same solvent polarity range.

These results suggest two possible explanations for the reactions of alkoxy dienes with singlet oxygen.

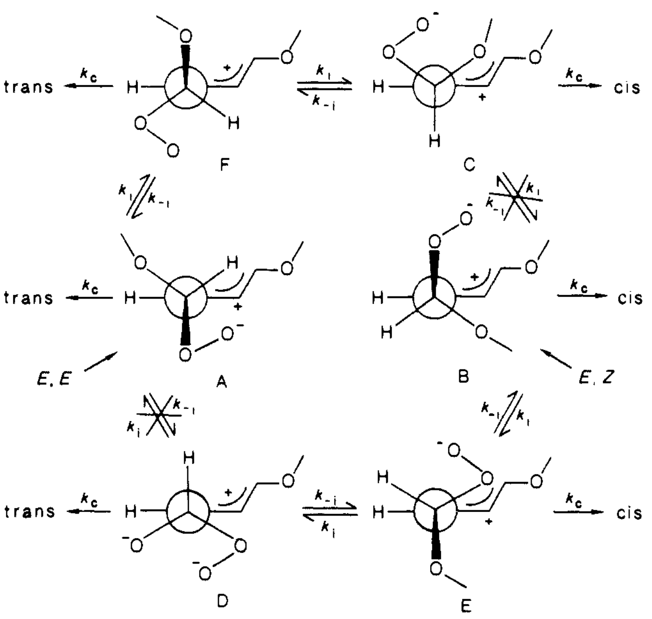
The first explanation was offered earlier to interpret the reactivity of the isomeric 1,4-di-*tert*-butoxy-1,3-butadienes.[23] This explanation suggested that *E* and *Z* olefinic linkages reacted by different mechanisms. The effect of solvent on the reaction of the *Z,Z* diene induced us to suggest that the addition of singlet oxygen to *Z* linkages leads to zwitterionic intermediates. The absence of a similar solvent effect in the reaction of the EE diene, however, is reminiscent of the cycloadditions of ketene and its derivatives[33] and induced us to suggest a concerted addition of singlet oxygen to *E* olefinic linkages.

The duality of mechanisms is understandable in energetic terms if the precursor to the zwitterion is a perepoxide. The perepoxide is expected to be stabilized by virtue of its interaction with both the vinyl and methoxy groups in the *Z* diene.[34] Only one such stabilizing interaction in the *E,E* perepoxide (Scheme III) energetically allows competition and access to the 2s + 2a energy surface.

The predominant formation of the cis dioxetane in the reaction of **1** is that anticipated from the most favorable frontier orbital interaction in the 2s + 2a transition state. (Scheme IV) The 2s(LUMO) + 2a(HOMO) interaction is more stabilizing than the 2s(HOMO) + 2a(LUMO) interaction.[35] The predominate formation of the cis dioxetane in the reaction of **3**, on the other hand, reflects the thermodynamic stability of the cis alkoxy configuration and/or the zwitterion rotomer preceding its formation.

An alternative explanation, which circumvents the necessity to suggest a sterically demanding 2s + 2a cycloaddition, invokes the formation of zwitterions in the reactions of all three dienes. A single zwitterionic mechanism in the reactions of these dienes is only compatible with the results if incomplete rotomer equilibration occurs prior to dioxetane formation. A sixfold rotational interconversion diagram for the zwitterions formed in the reactions of **1** and **2** is shown in Scheme V. Radiating outward from the diagram are arrows indicating the stereochemistry of the dioxetanes formed by least motion collapse of the zwitterion rotomer. Rotomers A and B are formed directly by attack of singlet oxygen on **1** and **2**, respectively.

Scheme V

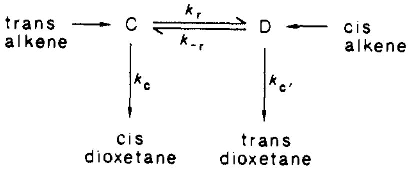


The ratios of dioxetane products formed in the reactions of **1** and **2** are sensitive functions of the magnitudes of the conformational interconversion (k_i's) and collapse (k_c's) rate constants. If $k_c >>> k_i$, then retention of stereochemistry in the reactions of both **1** and **2** would be observed. If $k_i >>> k_c$, complete thermodynamic rotomer equilibration would occur, producing the same product ratio in both reactions. If, however $k_i \sim k_c$, different product ratios in the two reactions would be obtained, consistent with the observed results. The near equivalence of k_i, the rate of rotation about a single bond, and k_c, the rate of closure to form a four-membered ring, undoubtably reflects an attractive interaction between the nucleophilic oxygen atom and the allylic cation, which enhances the rate of four-membered ring formation.

C and D are more stable than the other four rotomers depicted in Scheme V. A, B, E, and F are hyperconjugatively destabilized by the electron withdrawing groups perpendicular to the allylic cation. In addition, coplanarity of the allylic moiety and both CO bonds in C and D allow mixing of the allylic cation and π lone pair on oxygen resulting in a stabilized homoallylic cation. Similar arguments have been utilized to explain the conformational preference for allylic alcohols in electron-rich and electron-poor systems.[36] Allylic oxygen prefers to be gauche to electron-rich double bonds but eclipsed to electron-poor olefinic linkages.[37]

The predominant formation of a cis-substituted dioxetane in the reaction of the *E,E* diene and a trans-substituted dioxetane in the reaction of the *E,Z* diene would occur if C is most accessible in the reaction of **1** and D most accessible in the reaction of **2**. This situation would be encountered if the barriers involving *tert*-butoxy or methoxy eclipsing (those processes marked with the X in Scheme V) divided the six rotomers into two nonequilibrating or slowly equilibrating sets. The smaller cis/trans ratio (71/29 = 2.45) observed in the addition of $^1O_2$ to diene **1** in comparison to the trans/cis ratio (74/9 = 8.22) observed in the reaction of diene **2** reflects the lower barrier (A → D) for methoxy hydrogen than methoxy allylic cation (B → C) crossing and is indicative of leakage from A to D.

If the cis dioxetane is derived only by collapse of rotomer C and the trans dioxetane only by collapse of rotomer D, we can write the following simplified kinetic scheme for the formations of the dioxetanes by addition of singlet oxygen to the trans and cis diene linkages:



In this scheme k_r and k_{-r} are phenomenological rate constants

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Table VI. Relative Rate Constants for the Reaction of Di-*tert*-butoxy Dienes with Singlet Oxygen[a]

diene	solvent	p	q	$(k_c/k_r)^c$
E,E	$(CD_3)_2CO$	5.25		
	$(CD_3)_2CO/CD_2Cl_2$ (4)[b]	7.33		
	CD_2Cl_2	10.11		
	$(CD_3)_2CO/CD_3CN$ (1)[b]	7.33		
	THF-d_8	4.56		
	average	6.92		
Z,Z	$(CD_3)_2CO$		0.36	1.10
	$(CD_3)_2CO/CD_2Cl_2$ (4)[b]		0.41	2.01
	$(CD_3)_2CO/CD_2Cl_2$ (1)[b]		1.56	4.21
	$(CD_3)_2CO/CD_2Cl_2$ (0.25)[b]		7.33	6.09
	CD_2Cl_2		9.00	6.23

[a] Taken from ref 39. [b] The volume: volume ratio of solvents. [c] Calculated by using the average value of p.

describing the rates of rotational interconversions of rotomers C and D, and k_c and $k_{c'}$ are the rates of collapse of C and D, respectively, to the dioxetanes.

The rate constants k_r and k_{-r} are smaller than k_c and $k_{c'}$ allowing D in addition of singlet oxygen to trans double bonds and C in addition to cis double bonds to be treated with the steady-state approximation. Considering first addition of singlet oxygen to a trans double bond, the steady-state concentration of D is given by:

$$(\mathrm{d}D/\mathrm{d}t)_{\mathrm{trans}} = k_r\mathrm{C} - (k_{-r} + k_{c'})\mathrm{D} = 0$$

$$(\mathrm{C}/\mathrm{D})_{\mathrm{trans}} = (k_{-r} + k_{c'})/\mathrm{k}_r$$

and

$$(\mathrm{d[cis]}/\mathrm{d[trans]})_{\mathrm{trans}} = (k_c/k_{c'})(\mathrm{C}/\mathrm{D})$$

Since the concentrations of the cis and trans dioxetanes are zero at the beginning of the reaction,

$$([\mathrm{cis}]/[\mathrm{trans}])_{\mathrm{trans}} = p = k_c(k_{-r} + k_{c'})/k_{c'}k_r \qquad (1)$$

A similar equation (eq 2) can be derived for addition of singlet oxygen to a cis double bond. Both eq 1 and 2 can be expressed

$$([\mathrm{trans}]/[\mathrm{cis}])_{\mathrm{cis}} = q = k_{c'}(k_r + k_c)/k_ck_{-r} \qquad (2)$$

in terms of ratios of rate constants $a = k_{-r}/k_r$; $b = k_c/k_r$; $c = k_{c'}/k_c$, giving

$$p = (a/c) + b$$

$$q = (c/a)(1 + b)$$

By use of these two equations, b, the ratio of rate of closure to rotation, can be expressed in terms of the experimentally derivable quantities p and q:[38]

$$b = k_c/k_r = (pq - 1)/(q + 1)$$

A tabulation of p, q, and k_c/k_r for the more extensively studied reactions of (*E,E*)- and (*Z,Z*)-1,4-di-*tert*-butoxy-1,3-butadienes,[39] which are not plagued with even a minor loss of configurational integrity, is shown in Table VI. Despite the sensitivity of p and q to errors associated with integration of NMR spectra, it is clear that in the reaction of the *Z,Z* diene, rotation competes more effectively with closure in the more polar solvents. This is the anticipated result, since a more effectively solvated zwitterion should have more time to rotate.

The dramatic solvent effect observed in the reaction of the *Z,Z* isomers but not the *E,E* isomers in the reactions of both the dimethoxy and di-*tert*-butoxy dienes can be rationalized by examination of the perepoxides formed upon reaction of singlet oxygen with a trans and cis double bond (Scheme VI). Perepoxides I–III are stabilized by virtue of interactions with syn groups[11] and do not either sterically allow or electronically demand additional solvent stabilization. These perepoxides either rapidly close to dioxetanes or open to tight zwitterions that rotate and then close to the dioxetanes. Perepoxide IV, which is only formed in the reactions of the *Z,Z* dienes, however, requires solvent stabilization and opens to a solvated zwitterion with an increased lifetime, which allows rotation to compete with closure.

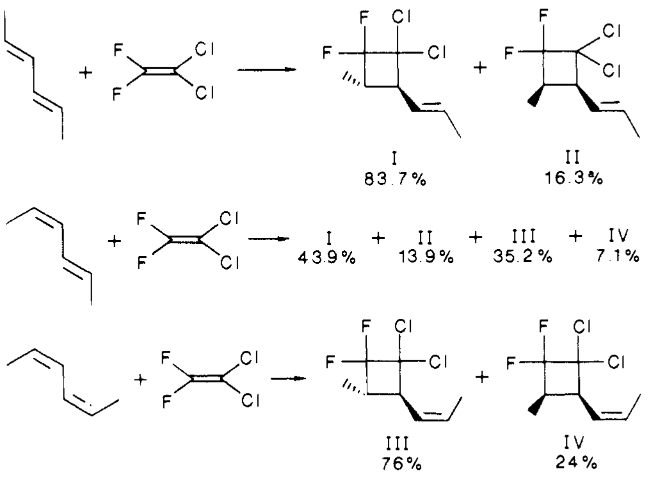
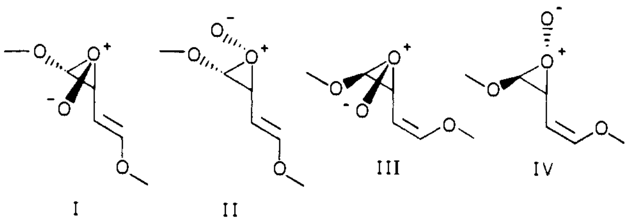


Figure 4.

Scheme VI



It is instructive to compare these results to those obtained in the now classical study of Bartlett[40] in which he examined the additions of 1,1-dichloro-2,2-difluoroethylene (1122) to isomeric 2,4-hexadienes (Figure 4). In a series of elegant papers Bartlett demonstrated that these reactions proceed through biradical intermediates. The ratio of (I/II) formed in the reaction of the *E,E* diene (5.13) and in the reaction of the *E,Z* diene (3.15) are more similar in magnitude than the analogous ratios (Scheme II) determined in this study. This suggests that either (1) in these hydrocarbon analogues the methyl crossings C $\rightleftharpoons$ B, and A $\rightleftharpoons$ D, (Scheme V) compete effectively with the ring closure reactions or, more likely, (2) the hydrocarbon structures analogous to A, F, E, and B (Scheme V) are not hyperconjugatively destabilized and that both cis and trans isomers are available from both the *E,E* and *E,Z* isomers without the necessity to pass over the methyl crossing barriers.

Conclusion

Data for the singlet oxygen 2 + 2 cycloadditions to the isomeric 1,4-dimethoxy-1,3-butadienes have been presented. It has been argued that these results are consistent with the formations of zwitterions, which collapse to dioxetanes before rotational equilibrium is attained. The zwitterions are stabilized in the more polar solvents and as a result their rotation competes more effectively than in less polar solvents with closure to the dioxetanes.

An alternative mechanism, which suggested competing concerted and zwitterion pathways, is inconsistent with the previously reported formations of methanol addition products in the reactions of both (*E,E*)- and (*Z,Z*)-1,4-di-*tert*-butoxy-1,3-butadienes.[8] The stereochemical requirements of the concerted pathway are energetically demanding and unlikely to be achieved with even a molecule as small as singlet oxygen.

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Table VII

diene	T, °C	irradiation time, min	% product 1	2	3
2	-80	150	0	100	0
	-40	30	2.2	96.8	1.0
	-40	60	4.9	93.2	1.9
3	-80	150	0	97.0	3.0
	-40	30	2.1	88.2	9.7
	-40	60	6.5	74.7	18.8

Experimental Section

Preparative gas chromatographic separations were accomplished on a Gow-Mac gas chromatograph utilizing a 0.25 in. × 30 ft column packed with 20% Carbowax 20M on NAW 80/100 Chromosorb W. The retention times for the *E,E* isomer **1** was 141 min; the *E,Z* isomer **2**, 153 min; and the *Z,Z* isomer **3**, 159 min when the temperature of the column was set to 115 °C, the injector to 200 °C, the detector to 200 °C, and the He flow rate to 120 mL/min.

The UV spectra for dienes **1**–**3** were obtained in HPLC grade *n*-heptane on a Hitachi UV-visible spectrophotometer.

^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX270 spectrometer at 270 and 63.8 MHz, respectively, and all the chemical shifts were referenced to Me_4Si. Product ratios were determined by cutting and weighing peaks from expanded proton NMR spectra.

Acetone-d_6 and methylene chloride-d_2 (Aldrich) were filtered through basic alumina prior to use. Rose Bengal and *meso*-tetraphenylporphyrin (Aldrich) were used directly without any further purification.

The temperatures of the photooxidations were controlled by submersion in a methanol bath cooled with a FTS-systems Flexicool refrigerator.

(*E,E*)-1,4-Dimethoxy-1,3-butadiene (1) was synthesized according to the procedure of Hiranuma and Miller:[26] ^{1}H NMR (acetone-d_6) δ 6.46 (dd, J = 9.1, 2.7 Hz, 2 H), 5.44 (dd, J = 9.1, 2.7 Hz, 2 H), 3.50 (s, 6 H); ^{13}C NMR δ 147.8 (d, J = 181 Hz), 102.5 (d, J = 151 Hz), 56.3 (q, J = 142 Hz).

(*E,Z*)-1,4-Dimethoxy-1,3-butadiene (2) was synthesized according to the procedure of Hiranuma and Miller:[26] ^{1}H NMR (acetone-d_6) δ 6.55 (d, J = 13.2 Hz, 1 H), 5.80 (d, J = 5.9 Hz, 1 H), 5.69 (dd, J = 13.2, 11.0 Hz, 1 H), 4.92 (dd, J = 11.0, 5.9 Hz, 1 H), 3.59 (s, 3 H), 3.53 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 149.1 (d, J = 181 Hz), 144.6 (d, J = 179 Hz), 103.4 (d, J = 157 Hz), 99.5 (d, J = 153 Hz), 59.6 (q, J = 144 Hz), 56.2 (q, J = 144 Hz).

(*Z,Z*)-1,4-Dimethoxy-1,3-butadiene (3) was synthesized according to the procedure of Hiranuma and Miller:[26] ^{1}H NMR (acetone-d_6) δ 5.85 (dd, J = 3.7, 1.5 Hz, 2 H), 5.26 (dd, J = 3.7, 1.5 Hz, 2 H), 3.59 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 145.7 (d, J = 181 Hz), 108.4 (d, J = 159 Hz), 59.8 (q, J = 149 Hz).

Methyl formate: ^{1}H NMR (acetone-d_6) δ 8.13 (q, J = 0.7 Hz, 1 H), 3.69 (d, J = 0.7 Hz, 3 H).

***trans*-2-Methoxyacrolein:** ^{1}H NMR (acetone-d_6) δ 9.39 (d, J = 7.7 Hz, 1 H), 7.64 (d, J = 12.4 Hz, 1 H), 5.59 (dd, J = 7.7, 12.4 Hz, 1 H), 3.83 (s, 3 H).

***cis*-2-Methoxyacrolein:** ^{1}H NMR (acetone-d_6) δ 9.98 (d, J = 8.4 Hz, 1 H), 7.19 (d, J = 6.2 Hz, 1 H), 5.00 (dd, J = 8.4, 6.2 Hz, 1 H), 3.93 (s, 3 H).

3,6-Dihydro-3,6-dimethoxy-1,2-dioxine (endoperoxide E, Figure 1): ^{1}H NMR (acetone-d_6) δ 6.04 (dd, J = 1.8, 0.7 Hz, 2 H), 4.97 (dd, J = 1.8, 0.7 Hz, 2 H), 3.44 (s, 6 H).

Photolysis Conditions. A solution of 5–15 mg of the diene and 10 μL of a 10^{-3} M stock solution of Rose Bengal in acetone-d_6 was placed in a 5-mm NMR tube, and cooled to -80 °C. The sample was then saturated with oxygen by continuous bubbling for 25–30 min. The continually agitated solution was then irradiated with a WKO 120-V 750-W lamp through a 0.5% $K_2Cr_2O_7$ filter solution. The progress of the reactions was monitored by low-temperature NMR at -62 to -77 °C.

Isomerization Studies. Acetone-d_6 solutions (1 mL) containing 5–15 mg of the diene and 10 μL of a 10^{-3} M stock solution of Rose Bengal were saturated with argon for 25–30 min. These reaction mixtures were then irradiated with a Sylvania WKO 120-V 750-W lamp through a 0.5% $K_2Cr_2O_7$ filter solution to give the results in Table VII.

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Relative Yields of Excited Ketones from Self-Reactions of Alkoxyl and Alkylperoxyl Radical Pairs

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Abstract: We have measured the ratios of excited ketones that arise from the self-reactions of alkoxyl ($2R_1R_2CHO^\bullet$) and peroxyl ($2R_1R_2CHO^\bullet$) radicals. This was accomplished by measuring the chemiluminescence emission from solutions of $R_1R_2CHO_2H$, or $R_1R_2CH_2$ and O_2, in the presence of a free-radical initiator *trans*-RON=NOR, in which R = *t*-Bu or R_1R_2CH in paired experiments. The excited states were trapped with 2-*tert*-butyl-9,10-dibromoanthracene or another fluorescent derivative of anthracene. The peroxyls were less efficient sources by 17%, 48%, 36%, and 42% than the alkoxyls for the cases in which $R_1R_2C{=}O$ was acetophenone in ethylbenzene, cyclohexanone in cyclohexane, and 1-tetralone in *t*-BuPh and in *t*-BuOH, respectively. The activation energy for formation of excited 1-tetralone (T_0 and/or S_1) from two 1-tetralylperoxyl radicals was 6 ± 3 kcal/mol higher than for production of the excited state from the corresponding pair of alkoxyl radicals. The results are consistent with but do not demand the hypothesis that excited carbonyl states arise in peroxyl terminations by way of alkoxyl pairs.

Chemiluminescence (CL) produced from the termination of alkylperoxyl radicals is a nearly ubiquitious property of oxidizing organic materials. The characteristic has been exploited for measurement of oxidation rates,[1,2] antioxidant efficacy,[3] and other properties,[4] although some details of the excitation process are not well established.

In a previous publication[5] we suggested that excited-state production from caged $R_1R_2CHO^\bullet$ radicals might be a feature common to the decompositions of nontertiary alkyl hyponitrites,

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