Compound **11**: ^{1}H NMR δ 6.22 (t, 1 H), 4.58 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.25 (dt, 2 H), 1.8–1.2 (unresolved m, 18 H), 0.14 (s, 9 H); ^{13}C NMR δ 142.1, 131.3, 98.9, 67.7, 62.3, 32.5, 30.9, 29.8, 29.4, 29.4, 29.2, 28.1, 26.2, 25.6, 19.7, -1.9.

10-Bromo-1-(2-tetrahydropyranyloxy)-(*Z*)-9-decene (10) was prepared in the same way as the *E* isomer **9** from 1-(2-tetrahydropyranyloxy)-10-(trimethylsilyl)-(*E*)-9-decene (**8**) in a 60% yield. No *E* isomer could be detected: ^{1}H NMR δ 6.15 (d, J_{AB} = 7.0 Hz, $CH_{2C}CH_B{=}CH_A$, 1 H), 6.10 (dt, J_{AB} = 7.0 Hz, J_{BC} = 6.8 Hz, 1 H), 4.58 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.19 (dt, 2 H), 1.8–1.2 (unresolved m, 18 H); ^{13}C NMR δ 134.7, 107.4, 98.6, 67.4, 62.0, 30.7, 29.6, 29.5, 29.2 (2 C), 28.9, 28.0, 26.1, 25.4, 19.5.

(*E*)-Butenyl-1,3,2-benzodioxaborole (12) was prepared from 1-butyne and catecholborane according to literature procedure[16] and was distilled before use.

(*Z*)-1-Butenyldisiamylborane (13) was prepared from 1-bromobutyne[17] and disiamylborane according to literature procedure.[18]

1-(2-Tetrahydropyranyloxy)-(9*E*,11*E*)-9,11-tetradecadiene (14). A mixture of (*E*)-1-butenyl-1,3,2-benzodioxaborole (**12**) (0.5 mL, 1 M in toluene), sodium ethoxide (0.5 mL, 2 M in ethanol), and 3-*tert*-butyl-4-hydroxyanisol (BHA) (5 mol %) was added to 10-bromo-1-(2-tetrahydropyranyloxy)-(*E*)-9-decene (**9**) (112 mg, 0.35 mmol) and $Pd(PPh_3)_4$ (3 mol %) in 1 mL of toluene at 25 °C.[12] The mixture was then warmed to 65 °C, and after about 45 min, the reaction was found to be complete by GC. Aqueous H_2O_2 (1 mL, 30% aqueous) and NaOH (1 mL, 2 M aqueous) were then added at 25 °C to destroy excess borane. The product was then taken up in Et_2O, which was washed (brine, H_2O) and dried ($MgSO_4$). Chromatography gave an 87% yield of **14** with no detectable isomers: ^{1}H NMR δ 6.05–5.90 (m, 2 H), 5.64–5.47 (m, 2 H), 4.58 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.02 (m, 4 H), 1.8–1.2 (unresolved m, 18 H), 0.96 (t, 3 H).

1-(2-Tetrahydropyranyloxy)-(9*Z*,11*E*)-9,11-tetradecadiene (15) was prepared as described above from the corresponding 10-bromo-1-(2-tetrahydropyranyloxy)-(*Z*)-9-decene (**10**) and (*E*)-1-butenyl-1,3,2-benzodioxaborole (**12**) in an 85% yield: ^{1}H NMR δ 6.30 (m, 1 H), 5.91 (dd, J_{AB} = 10.5 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.66 (dt, J_{CD} = 15.1 Hz, $J_{D,CH2}$ = 6.5 Hz, 1 H), 5.26 (dt, J_{AB} = 10.5 Hz, $J_{A,CH2}$ = 7.1 Hz, 1 H), 4.55 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.1 (m, 4 H), 1.8–1.2 (unresolved m, 18 H), 1.01 (t, 3 H).

1-(2-Tetrahydropyranyloxy)-(9*E*,11*Z*)-9,11-tetradecadiene (16) was similarly prepared from 10-bromo-1-(2-tetrahydropyranyloxy)-(*E*)-9-decene (**9**) and (*Z*)-1-butenyldisiamylborane in 73% yield (63% of pure diene contaminated with 10% of the terminal ene **22**) and was used as such in the next step. Compound **22**: ^{1}H NMR δ 5.89–5.69 (m, 1 H), 5.02–4.86 (dd, 2 H), 4.56 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.0 (m, 2 H), 1.8–1.2 (unresolved m, 12 H).

1-(2-Tetrahydropyranyloxy)-(9*Z*,11*Z*)-9,11-tetradecadiene (17) was similarly prepared from 10-bromo-1-(2-tetrahydropyranyloxy)-(*Z*)-9-decene (**10**) and (*Z*)-1-butenyldisiamylborane in a 73% yield (63% of pure diene contaminated with 10% of the terminal ene **22**) and was used as such in the next step.

Deprotection of the 1-(2-Tetrahydropyranyloxy)-9,11-tetradecadienes (14–17). A typical procedure was as follows. 1-(2-Tetrahydropyranyloxy)-(9*E*,11*Z*)-9,11-tetradecadiene (**16**) (100 mg, 0.34 mmol) was added to pyridinium tosylate (8.5 mg, 0.1 equiv) in ethanol (3 mL). 3-*tert*-Butyl-4-hydroxyanisol (BHA, 0.1 mol %) was then added to the mixture, which was warmed to 45 °C for 3 h. Sodium bicarbonate (100 mg) was added and the solvent evaporated. Chromatography yielded 85% of the isomerically pure product. The elution order of the alcohols on capillary GC on Carbowax 20 M, 25 m, at 160 °C was *Z,E*, *E,Z*, *Z,Z*, and *E,E*.

(9*E*,11*E*)-9,11-Tetradecadienol (18): ^{1}H NMR δ 6.05–5.98 (m, 2 H), 5.7–5.5 (m, 2 H), 3.65 (m, 2 H), 2.08 (m, 4 H), 1.37–1.27 (unresolved m, 12 H), 1.0 (t, 3 H); ^{13}C NMR δ 133.8, 132.3, 130.4, 129.5, 63.1, 32.9, 32.6, 29.4, 29.4, 29.1, 29.1, 25.7, 25.6, 13.7.

(9*Z*,11*E*)-9,11-Tetradecadienol (19): ^{1}H NMR δ 6.28 (dd, 1 H), 5.93 (dd, 1 H), 5.67 (dt, J_{CD} = 15.5 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{AB} = 10.2 Hz, 1 H), 3.62 (m, 2 H), 2.1 (m, 4 H), 1.35–1.25 (unresolved m, 12 H), 1.0 (t, 3 H); ^{13}C NMR δ 136.1, 130.0, 128.7, 124.8, 63.1, 32.8, 29.7, 29.4, 29.4, 29.2, 27.6, 25.8, 25.7, 13.6.

(9*E*,11*Z*)-9,11-Tetradecadienol (20): ^{1}H NMR δ 6.28 (dd, 1 H), 5.89 (dd, 1 H), 5.63 (dt, J_{AB} = 15.1 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{CD} = 10.4 Hz, 1 H), 3.62 (m, 2 H), 2.1 (m, 4 H), 1.35–1.25 (unresolved m, 12 H), 0.97 (t, 3 H); ^{13}C NMR δ 134.3, 131.3, 127.8, 125.3, 63.2, 33.1, 33.1, 29.8, 29.7, 29.7, 29.5, 26.1, 21.4, 14.7.

(9*Z*,11*Z*)-9,11-Tetradecadienol (21): ^{1}H NMR δ 6.27–6.12 (m, 2 H), 5.50–5.33 (m, 2 H), 3.65 (q, 2 H), 2.18 (m, 4 H), 1.36–1.24 (unresolved m, 12 H), 1.0 (t, 3 H); ^{13}C NMR δ 133.6, 132.0, 123.6, 123.1, 63.1, 32.9, 29.6, 29.5, 29.4, 29.2, 27.5, 25.8, 20.8, 14.2.

Acetylation of the 9,11-Tetradecadienols (18–21). A typical procedure was as follows. (9*E*,11*E*)-9,11-Tetradecadienol (**18**) (35 mg, 0.17 mmol) was added to acetic anhydride (0.8 mL) and pyridine (4 mL) at -10 °C and left in the refrigerator overnight. The mixture was then poured into ice–water, extracted (Et_2O), and chromatographed to give an almost quantitative yield of >99% pure product. No loss in isomeric purity was observed. The elution order of the acetates on capillary GC on Carbowax 20 M, 25m was *Z,E*, *E,Z*, *Z,Z*, and *E,E*.

(9*E*,11*E*)-9,11-Tetradecadienyl acetate (1): ^{1}H NMR δ 6.05–5.90 (m, 2 H), 5.65–5.5 (m, 2 H), 4.03 (t, 2 H), 2.05 (m, 4 H), 2.02 (s, 3 H), 1.37–1.22 (unresolved m, 12 H), 0.97 (t, 3 H).

(9*Z*,11*E*)-9,11-Tetradecadienyl acetate (2): ^{1}H NMR δ 6.28 (dd, 1 H), 5.93 (dd, 1 H), 5.69 (dt, J_{CD} = 15.5 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{AB} = 10.2 Hz, 1 H), 4.03 (t, 2 H), 2.1 (m, 4 H), 2.02 (s, 3 H), 1.33–1.23 (unresolved m, 12 H), 1.0 (t, 3 H).

(9*E*,11*Z*)-9,11-Tetradecadienyl acetate (3): ^{1}H NMR δ 6.2 (dd, 1 H), 5.9 (dd, 1 H), 5.6 (dt, J_{AB} = 15.1 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{CD} = 10.4 Hz, 1 H), 4.03 (t, 2 H), 2.17 (m, 4 H), 2.02 (s, 3 H), 1.37–1.21 (unresolved m, 12 H), 0.98 (t, 3 H).

(9*Z*,11*Z*)-9,11-Tetradecadienyl acetate (4): ^{1}H NMR δ 6.30–6.12 (m, 2 H), 5.48–5.36 (m, 2 H), 4.03 (t, 2 H), 2.15 (m, 4 H), 2.02 (s, 3 H), 1.35–1.23 (unresolved m, 12 H), 0.97 (t, 3 H).

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Reactions of Singlet Oxygen with Alkoxy-Substituted Dienes. Formation of Dioxetanes in the Singlet Oxygenations of *s*-Cis Fixed Dienes (*Z,Z*)- and (*E,Z*)-4,5-Diethylidene-2,2-dimethyl-1,3-dioxolanes

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Extensive investigations over the past several years have established that singlet oxygen has a proclivity to undergo 2 + 2^2 4 + 2,[3] and ene[4] reactions with organic substrates. In addition, physical quenching of singlet oxygen by substrates with low ionization potentials[5] or low triplet energies[6] also occurs.

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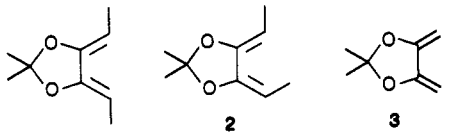
Recent studies with 1,3-butadienes have demonstrated that these substrates are excellent templates to explore the mechanistic details of all of these reactions.[7] In particular, the isomeric 1,4-di-*tert*-butoxy-1,3-butadienes[8] have already demonstrated their ability to act as sensitive probes of the singlet oxygen 2 + 2 energy surface. An intriguing loss of stereochemistry in those reactions provided evidence for freely rotating intermediates.[9]

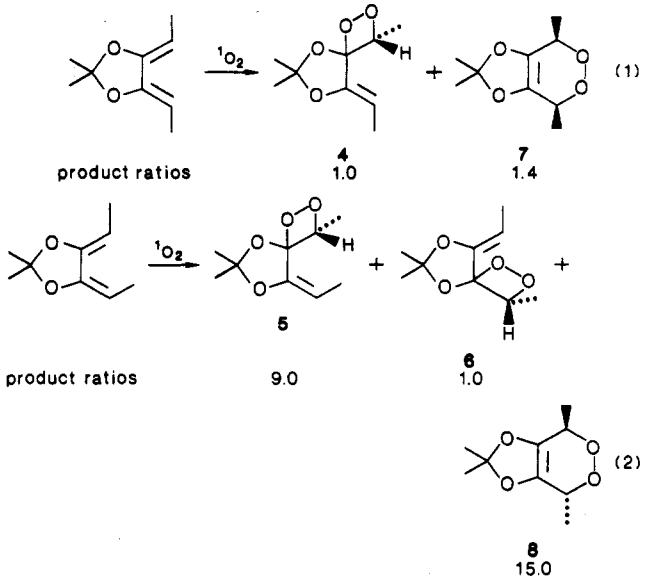
As part of our continuing program to design and demonstrate the utility of 1,3-butadiene mechanistic probes for the reactions of singlet oxygen and other electrophiles, such as triazolinediones,[10] we report here the reactions of singlet oxygen with 2,3-dialkoxy-1,3-butadienes **1**, **2**, and **3**.



1 **2** **3**

Compounds **1** and **2** were synthesized by the method of Scharf.[11] Compound **2** had not been previously reported but was a minor component (10%) formed in the synthesis of **1**. These two compounds were successfully separated and purified by preparative gas chromatography.

In the reactions of both these compounds 2 + 2 cycloaddition occurred in competition with 4 + 2 cycloaddition despite the fact that both compounds are tied *s*-cis. (eq 1 and 2) The singlet oxygen reactions were conducted by



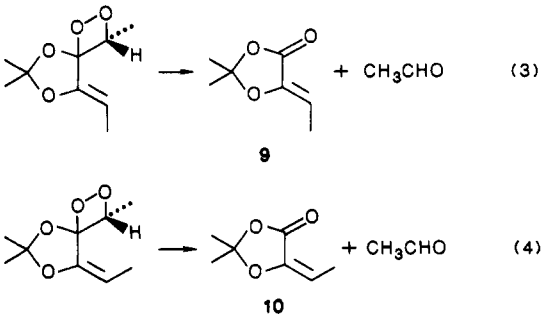
irradiation of oxygen-saturated acetone-d_6 solutions of the dienes and Rose Bengal at −78 °C through a 0.5% $K_2Cr_2O_7$ filter solution. The extent of reaction was monitored by low-temperature ^1H and ^{13}C NMR. Irradiation in the presence of DABCO or using *meso*-tetraphenylporphine and eosin as dyes verified that singlet oxygen was the reactive intermediate in these reactions. Control experiments in argon-saturated solutions demonstrated that both dienes maintained their stereochemical integrities under the influence of light and the sensitizing dyes. The absence of stereochemically scrambled dienes after partial photooxidations also demonstrated the inability of singlet oxygen to induced isomerizations[7a] of **1** or **2**.

Table I. Rates of Reaction of Singlet Oxygen with 1 and 2[a]

compd	$10^{-7}k$ (M^{-1} s^{-1})
1	3.2
2	2.3
E,E	8.5
E,Z	5.3
Z,Z	2.0

[a] Measured in methylene chloride using the Young kinetic method.

The proton NMR spectra of all five products were assigned with the aid of single frequency decoupling experiments and are consistent with the structures as shown in eq 1 and 2. The dioxetanes **4**, **5**, and **6** were not stable at room temperature but slowly decomposed (eq 3 and 4)



to form the corresponding lactones and acetaldehyde. Endoperoxide **7** but not **8** exhibited a temperature-dependent proton NMR spectrum. The doublet for the *cis*-methyl groups in **7** coalesced and were observed as two doublets at −80 °C consistent with a slow half-chair/half-chair interconversion.[12] The spectral data for all the compounds are given in the Experimental Section.

In contrast to the reactions of the isomeric 1,4-di-*tert*-butoxy-1,3-butadienes, compounds **1** and **2** were susceptible to overphotooxidation. Dioxetane **4** and both endoperoxides disappeared upon extended irradiation in an oxygen but not an argon atmosphere. Consequently the ratios of products shown in eq 1 and 2 were determined early in the reaction. These product ratios were invariant with a change in solvent from acetone-d_6 to CD_2Cl_2. The endoperoxides appeared to be more susceptible to photooxidative destruction than the dioxetanes perhaps due to the presence of a bis-activated double bond. The products of the overphotooxidation were not isolated or characterized.

The rates of reaction were measured by using the Young kinetic method[13] and are reported in Table I. These rates were determined at low concentrations of substrate in order to avoid quenching of diphenylisobenzofuran.[7b] The rates of reaction of (*E,E*), (*E,Z*),- and (*Z,Z*)-1,4-di-*tert*-butoxy-1,3-butadiene are included in Table I for comparison. The bis methylidene diene **3** was remarkably unreactive and no products were observed even after 4.5 h of irradiation. The increased ability of 1,4-bis-alkoxy

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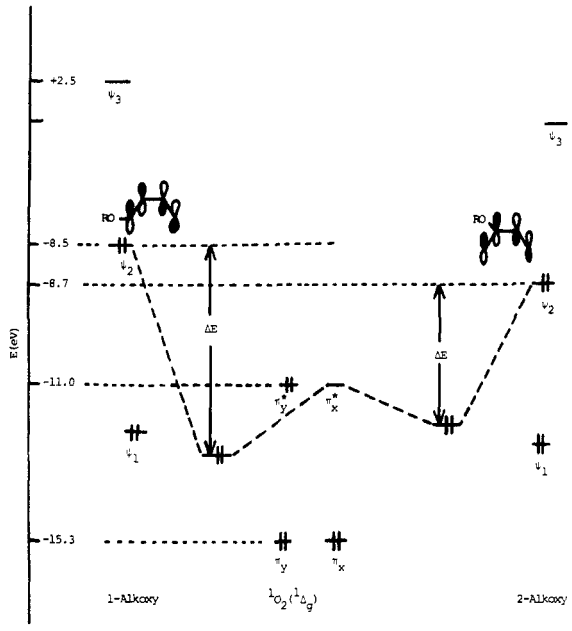

Figure 1. Molecular orbital diagram for the interaction of singlet oxygen with 1- and 2-alkoxy-substituted 1,3-butadienes.

substituents to enhance the singlet oxygen reactivity of 1,3-butadienes in comparison to 2,3-bis-alkoxy substituents is explicable in frontier molecular orbital terms as depicted in Figure 1.[14] The 1-substituent is more effective at raising the HOMO of the diene than is the 2-substituent,[15] leading to a larger stabilization energy and consequently a smaller activation barrier.

The poor Diels–Alder reactivity of diene 1 has been attributed[11] to a large separation between the terminal carbons in the 1,3-diene moiety (1,4-distance) and may be the underlying reason for the ability of the 2 + 2 cycloaddition to compete with the 4 + 2 cycloaddition of singlet oxygen.

Experimental Section

Preparation gas chromatographic separations were carried out on a Hewlett Packard 5710A gas chromatograph on a 20% Carbowax 20M/Chromsorb W NAW $^1/_4$ in. by 20 ft column. Proton and carbon NMR spectra were obtained on a JOEL FX 270 at 270 and 67.83 MHz, respectively. The proton and carbon spectra are referenced to tetramethylsilane. Mass spectra were obtained by electron impact on a VG-ZAB-1F. Infared spectra were obtained on a Beckman Microlab 600 spectrometer. Kinetic studies were completed on a Perkin-Elmer MPF-2A spectrofluorometer.

Photolysis Conditions. A mixture of 13–17 mg of 1 or 2 and 10 μL of a 10^{-3} M Rose Bengal stock solution was placed in 1 mL of acetone-d_6. Half of this solution was then placed in a 5-mm NMR tube and saturated with oxygen for 30 min. The irradiation was conducted with a WKO 750-W 120-V lamp through 1 cm of a 0.5% $K_2Cr_2O_7$ filter solution. The reaction was monitored by low-temperature NMR (−65 °C to −80 °C) after removing the oxygen by bubbling with argon for a half-hour.

(*Z*,*Z*)- and (*E*,*Z*)-4,5-Diethylidene-2,2-dimethyl-1,3-dioxolane (2). These compounds were synthesized by the method of Scharf[11] and were separated by preparative gas chromatography. The retention times were 19 min for 1 and 22 min for 2 when the helium flow rate was 120 mL/min, the injector temperature 200 °C, the detector temperature 200 °C, and the column temperature program set to 120 °C for 22 min and then ramped at 16 °C/min to 190 °C. (*Z*,*Z*)-1: ^{1}H NMR (acetone-d_6) δ 4.76 (q, *J* = 6.6 Hz, 2 H), 1.62 (d, *J* = 6.6 Hz, 6 H), 1.46 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 147.17 (s), 111.65 (s), 89.41 (d, *J* = 159 Hz), 26.19 (q, *J* = 127 Hz), 10.25 (q, *J* = 127 Hz); IR (film) 2925 (s), 1690 (s); high resolution mass spectrum for $C_9H_{14}O_2$ calcd 154.09938, found 154.1035. (*E*,*Z*)-2: ^{1}H NMR (acetone-d_6) δ 4.94 (q, *J* = 7.3 Hz, 1 H), 4.89 (q, *J* = 6.9 Hz, 1 H), 1.69 (d, *J* = 7.3 Hz, 3 H), 1.68 (d, *J* = 6.9 Hz, 3 H), 1.43 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 147.14 (s), 146.95 (s), 110.50 (s), 97.64 (d, *J* = 160 Hz), 93.86 (d, *J* = 156 Hz), 26.01 (q, *J* = 127 Hz), 11.23 (q, *J* = 127 Hz), 11.06 (q, *J* = 127 Hz); IR (film) 2915 (s), 1672 (s); high resolution mass spectrum for $C_9H_{14}O_2$ calcd 154.09938, found 154.0994.

(3*Z*,8*Z*)-8-Ethylidene-3,6,6-trimethyl-1,2,5,7-tetraoxaspiro[3.4]octane (4): ^{1}H NMR (acetone-d_6; −80 °C) δ 5.99 (q, *J* = 6.6 Hz, 1 H), 5.39 (q, *J* = 7.0 Hz, 1 H), 1.97 (s, 3 H), 1.69 (d, *J* = 7.0 Hz, 3 H), 1.67 (s, 3 H), 1.42 (d, *J* = 6.6 Hz, 3 H).

(3*Z*,8*E*)-8-Ethylidene-3,6,6-trimethyl-1,2,5,7-tetraoxaspiro[3.4]octane (5): ^{1}H NMR (acetone-d_6; −65 °C) δ 5.01 (q, *J* = 6.6 Hz, 1 H), 4.30 (q, *J* = 7.0 Hz, 1 H), 1.97 (s, 3 H), 1.66 (s, 3 H), 1.171 (d, *J* = 7.0 Hz, 3 H), 1.166 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (acetone-d_6; −65 °C) δ 120.37, 112.19, 110.85, 83.26, 80.49, 28.03, 27.56, 11.93, 9.40.

(3*E*,8*Z*)-8-Ethylidene-3,6,6-trimethyl-1,2,5,7-tetraoxaspiro[3.4]octane (6): ^{1}H NMR (acetone-d_6; −65 °C) δ 6.03 (q, *J* = 6.6 Hz, 1 H), 5.33 (q, *J* = 7.7 Hz, 1 H), 2.07 (d, *J* = 7.7 Hz, 3 H), 1.51 (s, 3 H), 1.49 (d, *J* = 6.6 Hz, 3 H), 1.35 (s, 3 H).

***cis*-4,7-Dihydro-2,2,4,7-tetramethyl-1,3-dioxolo[4,5-*d*]-*o*-dioxin (7):** ^{1}H NMR (acetone-d_6; −80 °C) δ 5.05 (dq, *J* = 1.4, 6.6 Hz, 1 H), 4.80 (dq, *J* = 1.4, 6.2 Hz, 1 H), 1.58 (s, 3 H), 1.55 (s, 3 H), 1.22 (d, *J* = 6.2 Hz, 3 H), 1.17 (d, *J* = 6.6 Hz, 3 H); (acetone-d_6; room temperature) δ 4.81 (q, *J* = 6.6 Hz, 2 H), 1.56 (s, 3 H), 1.52 (s, 3 H), 1.29 (d, *J* = 6.6 Hz, 6 H).

***trans*-4,7-Dihydro-2,2,4,7-tetramethyl-1,3-dioxolo[4,5-*d*]-*o*-dioxin (8):** ^{1}H NMR (acetone-d_6; −65 °C) δ 5.10 (q, *J* = 5.9 Hz, 2 H), 1.59 (s, 6 H), 1.18 (d, *J* = 5.9 Hz, 6 H).

(*Z*)-5-Ethylidene-2,2-dimethyl-1,3-dioxolan-4-one (9). This compound was isolated by preparative gas chromatography from the decomposition of 1,2-dioxetane 4: ^{1}H NMR (acetone-d_6) δ 5.55 (q, *J* = 7.3 Hz, 1 H), 1.73 (d, *J* = 7.3 Hz, 3 H), 1.62 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 162.90 (s), 140.32 (s), 111.59 (s), 105.17 (d, *J* = 162 Hz), 26.75 (q, *J* = 125 Hz), 10.71 (q, *J* = 127 Hz); IR (film) 3000 (m), 1790 (s).

(*E*)-5-Ethylidene-2,2-dimethyl-1,3-dioxolan-4-one (10). This compound was purified by recrystallization from acetone: ^{1}H NMR (acetone-d_6) δ 4.59 (q, *J* = 7.0 Hz, 1 H), 1.95 (s, 6 H), 1.25 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (acetone-d_6) δ 172.78 (s), 111.13 (s), 82.18 (d, *J* = 153 Hz), 81.15 (s), 28.33 (q, *J* = 129 Hz), 13.70 (q, *J* = 131 Hz); IR (CCl_4) 3000 (w), 1770 (s); high resolution mass spectrum for $C_7H_{10}O_3$ calcd 142.0630, found 142.0627.

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Supplementary Material Available: ^{1}H NMR spectra from which the data in eq 1 and 2 were derived (4 pages). Ordering information is given on any current masthead page.

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Metabolites of the Antarctic Sponge *Dendrilla membranosa*

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Studies by Dayton et al.[1] of the benthic community at McMurdo Sound, Antarctica, revealed that the sponge *Dendrilla membranosa* was extremely slow growing and was never observed to be eaten. Dayton concluded that

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