Sensitized Photooxygenation of 6-Heteroatom-Substituted Fulvenes: Primary Products and Their Chemical Transformations†

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Sensitized photooxygenation of 6,6-diethoxyfulvene (**1**) and 6,6-(ethylenedithio)fulvene (**9**) at −78 °C afforded diethoxyfulvene endoperoxide **2** and (ethylenedithio)fulvene endoperoxide **10**, respectively, as primary products. Further irradiation resulted in formation of the novel bisperoxides **3** and **11** from [2 + 2] cycloaddition of $^1O_2$ to the exocyclic double bond of the corresponding endoperoxides. The initial endoperoxides were characterized by NMR at low temperature and underwent a variety of chemical transformations to give highly oxygenated cyclopentane derivatives. In contrast, photooxygenation of 6,6-dipiperidinofulvene (**16**) and 6-(dimethylamino)fulvene (**17**) did not lead to chemical reaction; these compounds physically quench $^1O_2$ with rate constants on the order of 10^8 M^{-1} s^{-1}.

Introduction

Sensitized photooxygenation of 6-alkyl-substituted fulvenes has led to a number of interesting oxygenated derivatives.[1-6] Basselier carried out the first photooxidation of 1,2,3,4-tetraphenylfulvene and 1,2,3,4,6-pentaphenylfulvene.[7] Diepoxides of type **A** were isolated and suggested to derive from the corresponding endoperoxides. In studies of dimethylfulvene, Ohloff reported isolation of oxepinone **B**, keto aldehyde **C**, and hydroxy ketone **D** in 70% total yield.[1,8] The products were postulated to derive from dimethylfulvene endoperoxide **E**, which was subsequently observed by Uda at −55 °C by ^1H NMR.[4,9-11] In a separate study on the diimide reduction, Adam isolated the saturated endoperoxide derived from **E**,[12] thus providing strong evidence for the intermediate in the photooxygenation.

Recent studies by Erden et al. have provided more insight into the rearrangement of dimethylfulvene endoperoxide to the final oxygenated products.[13,14] Allene oxide **F** (or the tautomeric cyclopropanone **F'**) which was postulated earlier but eluded detection, was trapped by dienes and acetic acid on thermolysis of the saturated endoperoxide derived from **E**. This sequence provides a simple route to highly oxygenated 1,5-dicarbonyl compounds and tetrahydrofurans.[5,6] More surprisingly, a stable allene oxide **G** has been isolated and characterized from the thermolysis of the saturated endoperoxide derived from photooxygenation of 6-*tert*-butylfulvene.[15]

Photooxygenation of 6-heteroatom-substituted fulvenes was of particular interest, because the exocyclic double bond of the fulvene should be activated, and [2 + 2] cycloaddition of $^1O_2$ might be expected to compete with [2 + 4] addition. In addition, the presence of heteroatoms provides useful functional groups for further chemical transformations. We now report studies on the photooxygenation of 6-heteroatom substituted fulvenes which define the reaction pathway and primary products. All of the reactions were carried out at −78 °C, and the primary products were identified by low temperature NMR techniques. Chemical transformations of these primary products provided further support for the structure assignments.

Results

Photooxygenation of 6,6-Diethoxyfulvene (1). Rose Bengal-sensitized photooxygenation of **1** in acetone-d_6

† Part of this work was taken from F. Lin, Dissertation, University of California, Los Angeles, 1989.

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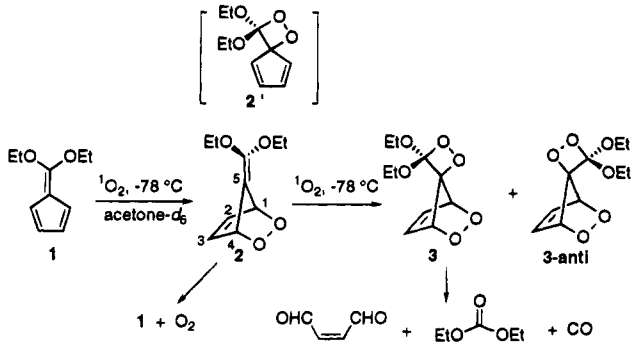
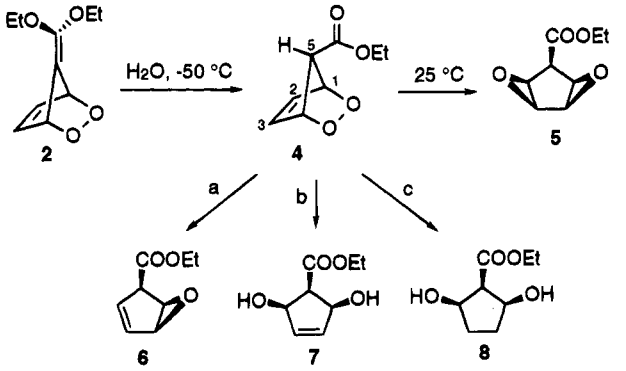
Scheme 1



Scheme 2



a: $(PhO)_3P$, $CHCl_3$, 0 °C; b: Ph_3P or $(CH_3)_2S$, $CHCl_3$, 0 °C; c: Pd-C/H_2, ethanol, 0 °C.

proceeded smoothly at −78 °C. A single product was obtained, as shown by ^1H NMR at −50 °C. The AA′ system of **1** at 6.67 and 6.17 ppm was replaced by two triplets at 6.59 and 5.65 ppm (J = *ca.* 1.8 Hz), which are characteristic chemical shifts and coupling constants of bicyclo[2.2.1] endoperoxides.[4] The ^{13}C signal at 119.8 ppm for C1 and C4 of **1** is replaced by a new peak at 77.94 ppm, indicating a change from sp^2 to sp^3 hybridized carbon attached to oxygen. Complete assignment of each proton and carbon was made possible by a ^1H–^{13}C HETCOR experiment. Based on the spectral data (Table 1) and subsequent chemical transformations described below (Scheme 1 and 2), the primary product is endoperoxide **2**, rather than dioxetane **2′**.

What is unique in endoperoxide **2** is the presence of an additional reactive double bond. Upon further irradiation, endoperoxide **2** took up another mole of $^1O_2$ to afford a novel bisperoxide **3** in 90% yield, as seen in the ^1H NMR by the disappearance of the triplet at 5.65 ppm (H1 and H4 of **2**) and the appearance of a new triplet at 5.37 ppm (J = 1.30 Hz) and also by the increased complexity (ABX_3 system) in the CH_2 region due to the prochirality. The syn configuration of **3** was established through a NOESY experiment, in which a cross peak was observed between the olefinic protons and the methyl of the ethoxy groups. The other product, formed in 10% yield, was tentatively assigned as the anti isomer of **3** based on the similarity of its proton chemical shifts with those of **3**.

Both endoperoxide **2** and bisperoxide **3** are unstable above −30 °C. Endoperoxide **2** began to release oxygen at −25 °C, reverting to **1** as the only identifiable product in 50% yield. However, bisperoxide **3** decomposed cleanly to diethyl carbonate and *cis*-2-butenedial, which were identified by comparison with the ^1H NMR data and GC retention time of authentic samples. Carbon monoxide was also identified by a positive Tollen's test on the gas evolved.

Chemical Transformations of 6,6-Diethoxyfulvene Endoperoxide 2. Water added readily to the exocyclic double bond to give a surprisingly stable endoperoxide ester **4** (Scheme 2), which could be isolated at 0 °C by flash column chromatography. The structure of **4** was characterized by ^1H and ^{13}C NMR (Table 1) and FT-IR. The syn configuration between the ester and peroxide group in **4** was established by NOE experiments. Saturation of the bridge proton (H5) produced a positive NOE for the olefinic protons (H2 and H3) and vice versa. Saturation of the methyl or methylene of the ethyl group did not produce a positive NOE for the olefinic protons, consistent with the syn configuration. At room temperature, endoperoxide **4** rearranged cleanly to the ethyl ester diepoxide **5** in about 24 h. The ^1H NMR spectrum

Table 1. Chemical Shift Values for Compounds 2–5 (δ, ppm, relative to TMS)[a]

	2[b]		3[b]		4[c]		5	
position	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1, 4	5.65	79.94	5.37	79.7	5.47	82.49	3.90	63.68
2, 3	6.59	137.13	6.60	135.0	6.52	134.93	3.57	51.73
5	–	113.03	–	106.0	3.20	61.18	3.00	45.43
6	–	140.46	–	116.0	–	166.74	–	168.32
OCH_2	3.83	65.04	3.86/3.79	59.6	4.19	66.08	4.26	61.48
CH_3	1.15	14.64	1.30	15.2	1.28	14.03	1.31	14.15

[a] Coupling constants in experimental section. [b] At −50 °C. [c] At 0 °C.

of **5** is very similar to that of cyclopentadiene diepoxide, which is formed from the rearrangement of cyclopentadiene endoperoxide.[16] Diepoxide **5** could not be further purified by column chromatography due to its sensitivity to acid and base. Complete assignment of the structure was made through a ^1H–^{13}C HETCOR experiment.

Ethyl ester endoperoxide **4** was reduced to epoxide **6** by triphenyl phosphite, but gave cyclopentenediol **7** with triphenylphosphine or dimethyl sulfide at 0 °C. Exhaustive hydrogenation of **4** in ethanol at 0 °C afforded cyclopentanediol **8**. Compounds **5**–**8** are all isomerically pure, and the relative stereochemistry of precursor **4** is retained.

Photooxygenation of 6,6-(Ethylenedithio)fulvene (9). Fulvene **9** reacted with $^1O_2$ much faster than 6,6-diethoxyfulvene, and a similar endoperoxide **10** formed cleanly at −78 °C (Scheme 3). The ^1H NMR spectrum of **10** resembled that of endoperoxide **2**, with two triplets at 6.71 (J = 2.02 Hz, H2 and H3) and 5.44 ppm (J = 2.20 Hz, H1 and H4) for the ring protons, and a singlet at 3.47 ppm for the ethylene bridge. The ^1H and ^{13}C NMR spectra indicate a plane of symmetry. ^{13}C NMR showed peaks for C2 and C1 at 136.38 and 81.31 ppm, and for C5 and C6 at 118.07 and 133.22 ppm, respectively (Table 2). No dioxetane (**10′**) was formed. Further irradiation of the sample resulted in the formation of ethylene dithiocarbonate[17] and *cis*-2-butenedial, presumably from the decomposition of the unstable bisperoxide **11**, which was characterized only by ^1H NMR at −70 °C (Table 2).

Chemical Transformations of (Ethylenedithio)fulvene Endoperoxide 10. Endoperoxide **10** reacted with triethylamine to give hydroxy ketone **12** (Kornblum

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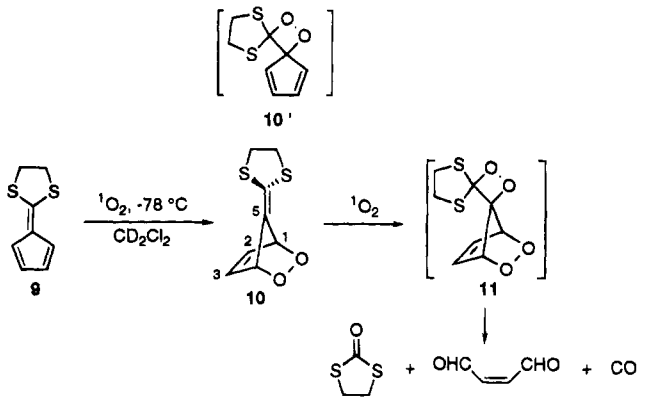
Table 2. Chemical Shift Values for Compounds 9–15 (δ, ppm, Relative to TMS)

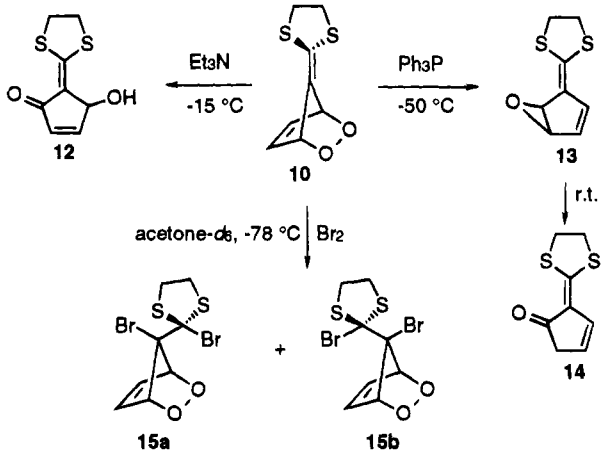
	9		10[a]		11:[a]	13:[b]	15a/15b:[b]
position	^{1}H	^{13}C	^{1}H	^{13}H	^{1}H	^{1}H	^{1}H
1, 4	6.32	128.89	5.44	81.31	5.28	6.16 (H1), 4.31 (H4)	6.28/6.25
2, 3	6.27	120.22	6.71	136.38	6.64	6.34 (H2), 4.14 (H3)	6.98/6.91
5	–	–	–	118.07	–	–	–
6	–	159.78	–	133.22	–	–	–
SCH_2	3.68	35.85	3.47	38.36	3.64/3.45	3.50	4.96/4.82

[a] At −70 °C. [b] At −50 °C.

Scheme 3



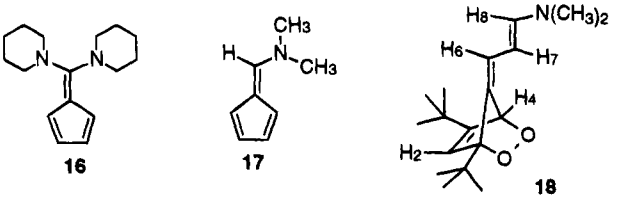
Scheme 4



De la Mare rearrangement[18]). Compound **12** was isolated and showed 3 signals for the ring protons at 7.27 (H3), 6.30 (H2), and 5.14 (H4) and a finely split ABCD system at 3.62, 3.48, 3.41, and 3.30 ppm for the ethylene protons. The ^{13}C NMR spectrum of **12** showed a total of 8 signals and a carbonyl at 191.20 ppm. Unlike endoperoxide **4**, **10** reacted readily and quantitatively with triphenylphosphine even at −50 °C to give a mixture of epoxide **13** and enone **14** (Scheme 4). At room temperature, epoxide **13** rearranged completely to the enone **14** through a hydride shift.

Bromine added cleanly to the exocyclic double bond at −78 °C to give two isomeric adducts **15a** and **15b** in about equal amounts, based on a COSY experiment. Unfortunately, the adducts are too labile to be isolated and assignment of the two isomers cannot be made based on the available information. The NMR data of compounds **9**, **10**, **11**, **13**, and **15a,b** are summarized in Table 2.

Photooxygenation of 6-*N* Substituted Fulvenes. Two 6-*N*-substituted fulvenes, 6,6-dipiperidinofulvene (**16**) and 6-(dimethylamino)fulvene (**17**) were prepared to invesigate their reactivity toward $^1O_2$. Surprisingly, neither **16** nor **17** reacted with $^1O_2$ under normal conditions. Both fulvenes were completely recovered even after 8 h irradiation either in acetone or chloroform, at normal or low temperature. Irradiation of a very dilute solution produced a black insoluble polymer. However, fulvene **16** physically quenched $^1O_2$ with a rate constant of 5×10^8 M^{-1} s^{-1}, as measured by time-resolved infrared singlet oxygen luminescence decay.[19]



In contrast, 1,3-di-*tert*-butyl-6-[(dimethylamino)vinyl]-fulvene, in which the amino group is isolated from the fulvene by an additional double bond, reacted readily with $^1O_2$ to give a complex mixture, in which the only identifiable product was DMF. Careful monitoring of the reaction progress by NMR at −76 °C indicated that at 50% conversion, a single oxygenated product was obtained, and the structure was assigned as the corresponding endoperoxide **18**. The enamine moiety is intact in this compound, as shown by the fact that the *trans* coupling (J = 13.04 Hz) between H7 (5.06 ppm) and H8 (6.34 ppm) remained unchanged. H6 appeared as a doublet (J = 10.71 Hz) at 5.57 ppm. ^{13}C and DEPT spectra of **18** showed six sp^2 carbon signals between 95.89 and 161.07 ppm. C1 and C3 were located at 94.69 and 80.54 ppm, respectively. The spectroscopic data is in good agreement with the proposed structure. Decomposition of **18** also led to a complicated mixture of products, which made isolation and purification impractical.

Discussion

The singlet oxygen chemistry of ketene ketals,[20–25] thioketene ketals,[26–30] and cyclopentadienes,[31] which together make up fulvene **1** and **9**, are well established.

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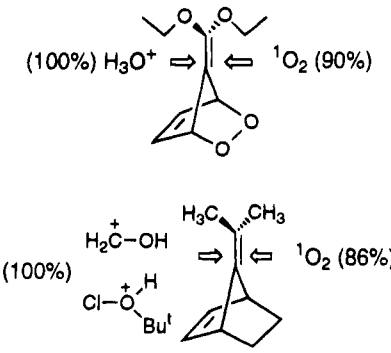
All react readily with $^1O_2$. Ketene ketals and cyclopentadiene react with $^1O_2$ at comparable rates: thioketene ketals react with $^1O_2$ even faster than ketene ketals. Cyclopentadiene reacts with $^1O_2$ to give endoperoxide exclusively; the ketals give dioxetanes which then cleave.

In diethoxyfulvene (**1**) and (ethylenedithio)fulvene (**9**), the diene moiety is expected to be more electron rich than ordinary dienes and the ketene ketal or thioketene ketal less so because the resonance characteristic of fulvenes shifts charge from the double bond into the ring. However, the exocyclic double bond should still be more electron rich and hence more reactive to $^1O_2$ than in dialkylfulvenes, especially in the case of (ethylenedithio)-fulvene (**9**), which should have less charge transfer than diethoxyfulvene (**1**), as shown by the lower dipole moments.[32]

Exclusive formation of endoperoxides **2** and **10** at the first stage of the photooxygenation clearly indicates that the diene moiety in these fulvenes is much more reactive than the exocyclic double bond, even in 6,6-diheteroatom substituted fulvenes. However, once the cyclopentadiene moiety is consumed, the exocyclic double bond behaves as a normal ketene ketal or thioketene ketal double bond, reacting with $^1O_2$ by a [2 + 2] pathway; the resulting dioxetanes cleave, as expected. Interestingly, the second mole of the electrophile $^1O_2$ attacks with high facial selectively, predominantly (>90%) from the peroxide side to give bisperoxide **3**. The nucleophile water, on the other hand, attacks the exocyclic double bond from the ring double bond side (100%) to afford endoperoxide **4**. A similar result was observed by Paquette et al. in the case of 7-isopropylidenenorbornene.[33-36] In this compound, $^1O_2$ approached the bridged double bond *anti* to the ring double bond, but protonated formaldehyde or *tert*-butyl hypochlorite approached *syn* to the ring double bond. This π-facial selectivity was explained by electrostatic repulsion between the lone pair electrons of $^1O_2$ and the electrostatic attraction between a positive electrophile (H^+) and the cyclopentene double bond, respectively. Quantitative calculations have recently been performed with 7-methylenenorbornene as a model by Houk et al.[37]

There is a marked difference in thermal stabilities between endoperoxides **2** and **4**, although they differ only at the 5-position. While endoperoxide **2** was unstable at −25 °C and decomposed to the starting fulvene **1** in 50% yield, endoperoxide **4** was reasonably stable at room temperature and rearranged quantitatively to diepoxide **8**, reminiscent of the rearrangement of 2,3-dioxabicyclo-[2.2.1]heptane.[38] The unique decomposition of endoperoxide **2** is probably a result of the exocyclic ketene ketal double bond, which may overlap with the σ^*_{C-O} bond and thus activate it.

Thermally, (ethylenedithio)fulvene endoperoxide **10** is



much more stable than diethoxyfulvene endoperoxide **2** and did not regenerate the starting fulvene. In contrast, bisperoxide **11** from **10** is much less stable than bisperoxide **3** from diethoxyfulvene endoperoxide **2**, consistent with the general instability of sulfide-substituted dioxetanes.[30]

It was surprising to find that 6-*N*-substituted fulvenes do not react with $^1O_2$ chemically, even though enamines are one of the most reactive substrates toward $^1O_2$.[39-43] The dipole moments of **17** and **16** are larger than those of **1** and **9**,[32] indicating more significant charge transfer and might have been expected to give an even more reactive diene moiety. However, a variety of dienophiles react with 6-(dimethylamino)fulvene in a [2 + 6] or [4 + 6] manner instead of via a [2 + 4] pathway.[44,45] However, [2 + 6] cycloaddition of singlet oxygen has never been reported. The fast physical quenching of $^1O_2$ by dipiperidinofulvene **16** strongly implies an electron or charge transfer interaction between the extremely electron-rich 6-*N*-substituted fulvenes and $^1O_2$.

Conclusions

6-*O*- and 6-*S*-substituted fulvenes react readily with $^1O_2$ to afford endoperoxides as primary products, as in the case of 6-alkyl-substituted fulvenes. The exocyclic double bond reacts with $^1O_2$ smoothly and with high facial selectivity in the second stage of photooxygenation to give bisperoxides. These highly oxygenated products are labile and decompose readily or undergo a variety of chemical transformations. On the contrary, 6-*N*-substituted fulvenes do not react with $^1O_2$ chemically but physically quench it.

Experimental Section

General. 6,6-Diethoxyfulvene (**1**),[32,46] 6,6-(ethylenedithio)-fulvene (**9**),[47] 6,6-dipiperidinofulvene (**16**),[48] and 6-(dimethylamino)fulvene (**17**)[49] were synthesized by literature procedures. 1,3-Di-*tert*-butyl-6-[(dimethylamino)vinyl]fulvene was a gift from Prof. K. Hafner. All ^1H and ^{13}C NMR data were

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taken on Bruker AM-360 or AM-500 machines equipped with a variable temperature probe. Low temperature NMR experiments were done in the following manner. The probe was cooled to the desired temperature, and then the sample, precooled in dry ice–acetone, was immediately placed in it. Usually 10 min or longer was needed before the probe temperature stabilized and good shimming could be achieved. The probe temperature fluctuation could be as small as 0.1–0.2 °C. Chemical shift values are in δ (ppm) relative to TMS. Carbon multiplicities were obtained by DEPT experiments.

Diethoxyfulvene Endoperoxide 2 and Bisperoxide 3. Fulvene **1** (68.1 mg, 0.41 mmol) was mixed with a tiny amount of Rose Bengal in 0.5 mL of acetone-d_6 in a 5 mm NMR tube. A slow stream of oxygen was introduced through a Teflon tube and photooxygenation was carried out at −78 °C with a 300 W xenon lamp and a $K_2Cr_2O_7$ filter (0.085 M, 3.5 cm). The progress of the reaction was monitored by ^{1}H NMR at −55 °C. After 5 h, all **1** had been converted into diethoxyfulvene endoperoxide **2**: ^{1}H NMR (360 MHz, acetone-d_6, −55 °C) δ 6.59 (t, 2 H, J = 1.90 Hz), 5.65 (t, 2 H, J = 1.74 Hz), 3.83 (q, 4 H, J = 6.97 Hz), 1.15 (t, 6 H, J = 6.98 Hz); ^{13}C NMR (90 MHz, acetone-d_6, −55 °C) δ 140.46 (s), 137.13 (d), 113.03 (s), 79.94 (d), 65.04 (t), 14.64 (q).

Further irradiation of endoperoxide **2** for 2.5 h afforded bisperoxide **3** in 90% yield: ^{1}H NMR (360 MHz, acetone-d_6, −55 °C) δ 6.60 (t, 2 H, J = 1.85 Hz), 5.37 (t, 2 H, J = 1.30 Hz), 3.86 (m, 2 H), 3.77 (m, 2 H), 1.30 (t, 6 H, J = 7.14 Hz); ^{13}C NMR (90 MHz, acetone-d_6, −55 °C) δ 135.0 (d), 116.0 (s), 106.0 (s), 79.7 (d), 59.6 (t), 15.2 (q); *anti*-**3** was also formed in 10% yield, ^{1}H NMR (360 MHz, acetone-d_6, −55 °C) 6.65 (t, 2 H, J = 1.80 Hz), 5.30 (t, 2 H, J = 1.35 Hz), 4.17 (m, 4 H), 1.25 (t, 6 H, J = 7.06 Hz).

Thermolysis of Bisperoxide 3. 6,6-Diethoxyfulvene (**1**) (150 mg, 0.91 mmol) was photooxygenated in acetone in a 10 mm NMR tube for 8 h at −70 °C. A test tube containing a solution of Tollen's reagent was connected with the NMR tube via a Teflon tubing. As the NMR tube warmed to room temperature, a stream of bubbles was observed coming out of the end of the tubing inside the test tube. At the same time, light blue to green luminescence was observed in the dark, which could be stopped by putting the NMR tube back into dry ice/acetone bath. After the evolution of bubbles stopped, a thin mirror formed inside the wall of the test tube above the solution. The decomposed reaction mixture contained diethyl carbonate, which was characterized by GC and NMR in comparision with an authentic sample, and *cis*-2-butenedial:[12] ^{1}H NMR (360 MHz, $CDCl_3$) δ 10.61 (dd, 2 H, J = 5.30, 2.70 Hz), 6.68 (dd, 2 H, J = 5.30, 2.70 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 192.90, 142.00.

Endoperoxide 4 and Diepoxide 5. To an acetone-d_6 solution of **2** prepared from 100 mg (0.60 mmol) of **1** was added 12 μL (0.66 mmol) of H_2O at −78 °C, and the reaction was returned to room temperature. ^{1}H NMR of the reaction mixture showed the formation of endoperoxide **4** in almost quantitative yield. **4** could be further purified by flash column chromatography at 0 °C: ^{1}H NMR (360 MHz, $CDCl_3$, 0 °C) δ 6.52 (t, 2 H, J = 2.20 Hz), 5.47 (dt, 2 H, J = 2.20, 1.10 Hz), 4.19 (q, 2 H, J = 7.12 Hz), 3.20 (s, 1 H), 1.28 (t, 3 H, J = 7.12 Hz); ^{13}C NMR (90 MHz, $CDCl_3$, 0 °C) δ 166.74 (s), 134.93 (d), 82.49 (d), 66.08 (t), 61.18 (d), 14.03 (q); FT-IR cm^{-1} 2982.8 (w), 1738.3 (s), 1377.2 (w), 1231.8 (s), 1036.4 (m), 933.3 (w), 841.6 (m). Endoperoxide **4** could also be directly prepared by photooxygenation of **1** at 0 °C using wet CH_2Cl_2 as solvent.

A solution of **4** gradually rearranged to diepoxide **5** on standing at room temperature, and rearrangement was complete in 24 h. After evaporation of solvent, **5** was obtained in almost quantitative yield. Purification of **5** by flash column chromatography failed even at −40 °C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.26 (q, 2 H, J = 7.17 Hz), 3.90 (m, 2 H), 3.57 (m, 2 H), 3.00 (t, 1 H, J = 3.23 Hz), 1.31 (t, 3 H, J = 7.17 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 168.32 (s), 63.68 (d), 61.48 (t), 51.73 (d), 45.43 (d), 14.15 (q); FT-IR cm^{-1} 2981.2 (m), 1732.5 (s), 1369.6 (w), 1203.6 (m), 1031.3 (m), 945.2 (m), 865.3 (m), 717.6 (m); HRMS calcd for $C_8H_{10}O_4$ 170.0576, obsd 170.0577.

Cyclopentene Epoxide 6. Compound **4** (120 mg, 0.71 mmol) was reduced with triphenyl phosphite (217 mg, 0.7 mmol) at room temperature in 1.0 mL of $CHCl_3$ for 30 h. After evaporation of solvent, pure epoxide **6** was obtained in 38% yield by flash column chromatography using CH_2Cl_2:petroleum ether (3:2) and pure CH_2Cl_2 as eluent: ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.22 (m, 1 H, part of AB), 6.01 (m, 1 H, part of AB), 4.22 (q, 2 H, J = 7.28 Hz), 4.05 (m, 1 H), 3.82 (m, 1 H), 3.68 (m, 1 H), 1.29 (t, 3 H, J = 7.28 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 169.57 (s), 135.66 (d), 132.64 (d), 61.24 (t), 58.58 (d), 55.65 (d), 52.14 (d), 14.16 (q); FT-IR cm^{-1} 2984.2 (m), 1736.9 (s), 1372.5 (m), 1292.3 (m), 1026.7 (m), 958.8 (m), 835.3 (m), 810.6 (w); HRMS calcd for $C_8H_{10}O_3$ 154.0627, obsd 154.0627.

Cyclopentenediol 7. Compound **4** (96 mg, 0.57 mmol) was mixed with dimethyl sulfide in 1.0 mL of CH_2Cl_2, and the reaction was left at 0 °C for 2 days. After evaporation of solvent, diol **7** (43 mg, 47%) was obtained by flash column chromatography using CH_2Cl_2 and then CH_2Cl_2:methanol (10:1) as eluent. Similarly, diol **7** was obtained in 30% yield using triphenylphosphine as reducing agent: ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.20 (d, 2 H, J = 1.22 Hz), 4.80 (t, 2 H, J = 6.15 Hz), 4.27 (q, 2 H, J = 7.10 Hz), 3.14 (d, 2 H, J = 7.25 Hz), 3.11 (t, 1 H, J = 6.01 Hz), 1.32 (t, 3 H, J = 7.10 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.09 (s), 136.54 (d), 74.77 (d), 61.15 (t), 52.06 (d), 14.17 (t); FT-IR cm^{-1} 3451.2 (br, s), 3056.9 (w), 2985.6 (w), 1722.4 (s), 1363.3 (m), 1190.5 (m), 1064.1 (m), HRMS calcd for $C_8H_{12}O_4$ 172.0732, obsd 172.0739.

Cyclopentane Diol 8. Compound **4** (60 mg, 0.36 mmol) was mixed with 2.0 mL of ethanol, and the solution was deoxygenated by freeze-pump-thaw cycles. Pd–C (10%, 2 mg) was added, and hydrogenation was carried out at 0 °C with a hydrogen balloon for 20 h. The reaction mixture was filtered, and the filtrate was condensed. ^{1}H NMR of the crude product showed the major product to be diol **8** (>85%) with ca 7% diol **7**. Diol **8** was purified by flash column chromatography using CH_2Cl_2 and then CH_2Cl_2:methanol (10:1) as eluent: ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.53 (m, 2 H), 4.26 (q, 2 H, J = 7.24 Hz), 3.56 (d, 2 H, J = 6.11 Hz), 2.57 (t, 1 H, J = 4.60 Hz), 2.03–1.96 (m, 4 H), 1.32 (t, 3 H, J = 7.24 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.90 (s), 74.38 (d), 61.02 (t), 54.78 (d), 32.45 (t), 14.13 (q); FT-IR cm^{-1} 3479.6 (br, m), 2975.1 (m), 1714.0 (s), 1258.8 (m), 1203.4 (m), 1049.6 (m), 797.4 (m); HRMS calcd for $C_8H_{15}O_4$ (M + 1) 175.0966, obsd 175.0970.

(Ethylenedithio)fulvene Endoperoxide 10. Compound **9** (17 mg, 0.1 mmol) was dissolved in 0.4 mL of 10^{-5} M TPP/CD_2Cl_2 solution in a 5 mm NMR tube. Photooxygenation was carried out at −78 °C with a 1% $BiCl_3$/HCl filter (≥360 nm, 3.5 cm). The reaction was monitored by ^{1}H NMR at −70 °C. After 5 min, **9** was completely converted to endoperoxide **10**. ^{1}H NMR (500 MHz, CD_2Cl_2, −70 °C) δ 6.71 (t, 2 H, J = 2.03 Hz), 5.43 (t, 2 H, J = 2.03 Hz), 3.47 (s, 4 H); ^{13}C NMR (125 MHz, CD_2Cl_2, −70 °C) δ 136.38 (d), 133.22 (s), 118.07 (s), 81.31 (d), 38.36 (t).

Further irradiation of the sample under the same conditions resulted in formation of ethylene dithiocarbonate[17] and *cis*-2-butenedial. Bisperoxide **11**: ^{1}H NMR (500 MHz, CD_2Cl_2, −70 °C) δ 6.64 (t, 2 H, J = 2.25 Hz), 6.28 (t, 2 H, J = 2.25 Hz), 3.64 (m, 2 H), 3.45 (m, 2 H). Ethylene dithiocarbonate: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.77 (s), identical to the lit. value.[17]

Cyclopentenone 12. Triethylamine (50 μL, 0.35 mmol) was added at −78 °C to a CH_2Cl_2 solution of 0.3 mmol of **10**. The mixture was allowed to warm to −20 °C over a period of 24 h. ^{1}H NMR of the crude product showed that the formation of **12** is almost quantitative. It was isolated as a light yellow solid by column chromatography using CH_2Cl_2 as eluent: mp 118–119 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, 1 H, J = 5.90, 2.35 Hz), 6.30 (dd, 1 H, J = 5.90, 1.03 Hz), 5.14 (dd, 1 H, J = 2.35, 1.03 Hz), 3.62 (m, 1 H), 3.48 (m, 1 H), 3.41 (m, 1 H), 3.30 (m, 1 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 191.20 (s), 157.30 (s), 154.60 (d), 136.82 (d), 123.54 (s), 73.92 (d), 38.79 (t), 37.18 (t); UV (CH_2Cl_2, nm) 336, 275; HRMS calcd for $C_8H_8S_2O_2$ 199.9966, obsd 199.9999.

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Cyclopentene Epoxide 13 and Enone 14. A slight excess of triphenylphosphine dissolved in a small amount of CD_2Cl_2 was added to a CD_2Cl_2 solution of **10** at −78 °C, and the reactants were mixed by bubbling argon. ^1H NMR spectrum was taken immediately at −50 °C and epoxide **13** and enone **14** were present. ^1H NMR data of **13** is in Table 2. At room temperature, **13** completely isomerized to **14**. The solvent was evaporated and **14** was purified as a light yellow solid by column chromatography with CH_2Cl_2 as eluent: ^1H NMR (500 MHz, CD_2Cl_2) δ 6.86 (dt, 1 H, J = 6.86, 2.14 Hz), 6.06 (dt, 1 H, J = 6.86, 2.29 Hz), 3.48 (m, 2 H), 3.46 (m, 2 H), 2.98 (dd, 2 H, J = 2.29, 2.14 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 200.48 (s), 149.88 (s), 133.28 (d), 125.76 (s), 125.63 (d), 42.91 (t), 39.49 (t), 36.79 (t); UV (CH_2Cl_2, nm) 357, 345, 274; HRMS calcd for $C_8H_8S_2O$ 184.0017, obsd 184.0016.

Endoperoxide 15a/15b. Br_2 (5 μL, 0.10 mmol) was added to an equimolar amount of **10** in 0.5 mL of acetone-d_6 at −78 °C. The deep red color of bromine disappeared immediately and ^1H NMR at −50 °C showed **10** was completely converted. A COSY spectrum showed the reaction gave two products which were assigned as isomeric bromine adducts **15a** and **15b**, which could not be further distinguished. The ^1H NMR data of the two isomers are in Table 2.

Endoperoxide 18. The fulvene (17 mg) was dissolved in 0.5 mL of 2.0×10^{-5} M Rose Bengal−acetone-d_6 solution. Photooxygenation was carried out at −78 °C. ^1H NMR monitoring indicated that at 50% conversion, a single product, the corresponding endoperoxide **18**, was formed in 46% yield (the other 4% corresponded to DMF): ^1H NMR (500 MHz, acetone-d_6, −76 °C) δ 6.35 (s, 1 H), 6.34 (d, 1 H, J = 13.04 Hz), 5.98 (s, 1 H), 5.57 (d, 1 H, J = 10.71 Hz), 5.06 (dd, 1 H, J = 13.04, 10.71 Hz), 2.60 (br, s, 6 H), 1.10 (s, 9 H), 1.04 (s, 9 H); ^{13}C NMR (90 MHz, acetone-d_6, −56 °C) δ 161.07 (s), 144.46 (d), 140.75 (s), 128.76 (d), 108.46 (d), 95.89 (d), 94.69 (s), 80.54 (d), 33.10 (s), 32.92 (s), 31.79 (q), 29.95 (q), 27.97 (q). Further irradiation or decomposition of **17** gave complicated mixtures of products, which could not be purified.

Determination of Singlet Oxygen Quenching Rate Constant by 6,6-Dipiperidinofulvene (16). Measurements of (k_r + k_q) were made by monitoring the effect of added substrate on the observed decay rate (k_{obsd}) of $^1O_2$ as measured by its luminescence at 1270 nm;[19] $k_{obsd} = (k_r + k_q)[S] + k_d$, where ($k_r$ + k_q) is the total removal of $^1O_2$ by substrate, [S] is the concentration of substrate, and k_d is the rate constant for radiationless decay of $^1O_2$. Plots of k_{obsd} vs [S] are linear (r = 0.994) with slope (k_r + k_q) of 5.95×10^8 M^{-1} s^{-1}. Since there is no chemical reaction between $^1O_2$ and **16**, the physical quenching rate constant of $^1O_2$ by **16**, k_q, is equal to the total deactivation.

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Supplementary Material Available: ^1H NMR spectra for compounds **3**, **10**, **12**, **14**, and **15** and ^{13}C NMR spectra for compounds **2**, **4**–**8**, and **18** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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