mL of pure petroleum ether, 100 mL of 1% EtOAc/petroleum ether, and 200 mL of 3% EtOAc/petroleum ether. The first 50 mL was discarded. The next 350 mL was concentrated in vacuo to give a total of 8.44 g (95%) of the α-diazo β-keto ester as an oil: R_f (20% EtOAc/hexane) 0.80; ^{13}C NMR 191.9, 161.6, 128.5, 125.0, 51.9, 39.8, 21.7, 12.5; ^1H NMR (250 MHz, $CDCl_3$) 3.83 (s, 3 H), 2.90 (t, J = 7.3, 2 H), 2.73 (q, J = 6.6, 2 H), 1.62 (d, J = 6.6, 3 H); IR ($CHCL_3$) 3090, 3020, 2980, 2150, 1720, 1655, 1440, 1410, 1370, 1350, 1320, 1230, 1140, 1105, 1060, 1010, 995, 935, 880; MS, 196 (6), 153 (24), 149 (33), 136 (32), 121 (27), 109 (26), 108 (51), 101 (24), 95 (77).

Preparation of 2. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 5 mg (0.01 mmol) of $PdCl_2(PhCN)_2$. Ester **1** (338 mg, 1.85 mmol, in 3.7 mL CH_3CN) was added via syringe. 2,2'-Azobis(2-methyl-propionitrile) (34 mg, 0.21 mmol, 10% by weight) was then added. The mixture was magnetically stirred at reflux for 3 h. The reaction mixture was allowed to cool and evaporated directly onto 0.5 g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 10-g column.[8] The column was then eluted with 50-mL portions of 3–10% acetone/petroleum ether, in 1% increments. The first 280 mL was discarded. The next 160 mL was concentrated in vacuo to give 158 mg (1.02 mmol, 55%) of **2** as a clear yellow oil: R_f (20% acetone/hexane) 0.22; ^{13}C NMR 19.4 (q), 32.8 (t), 35.0 (t), 51.8 (q), 132.3 (s), 163.7 (s), 185.6 (s), 203.5 (s); ^1H NMR 2.4 (s, 3 H), 2.5 (t, J = 5.0, 2 H), 2.7 (t, J = 5.0, 2 H), 3.85 (s, 3 H); IR 2983, 1754, 1721, 1638, 1553, 1442, 1341, 1293, 1254, 1232, 1145, 1062, 1012, 974; MS, 154.063 (31), 123 (100), 122 (43), 96 (46), 95 (40).

Preparation of 4. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and changed with 7 mg (0.02 mmol) of $PdCl_2(PhCN)_2$. Ester **4** (268 mg, 1.37 mmol) was added in 2.7 mL of toluene via syringe. The mixture was refluxed for 5 h, then allowed to cool, and evaporated directly onto 0.5 g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 20-g silica gel column. The column was eluted with 50-mL portions of 3–11% acetone/petroleum ether, in 1% increments. The first 100 mL was discarded. The next 150 mL was concentrated in vacuo to give 33.2 mg (0.19 mmol, 14%) of cyclopropane **4a** as an oil: R_f (20% acetone/hexane) 0.30; ^{13}C NMR 207.7 (s), 169.5 (s), 52.2 (q), 42.8 (s), 39.3 (t), 38.2 (d), 29.3 (d), 17.0 (t), 8.7 (q); ^1H NMR 3.75 (s, 3 H), 2.7–1.85 (m, 6 H), 1.2 (d, 3 H); IR 3060, 2980, 1750, 1725, 1460, 1415, 1320, 1250, 1110, 1040, 985; MS, 168 (30), 140 (30), 137 (92), 136 (57), 126 (44), 109 (35), 108 (39), 81 (64), 79 (49), 69 (32), 59 (100), 41 (57). The following 120 mL was concentrated in vacuo to give 78.0 mg (0.41 mmol, 34.0%) of enone **4** as a clear yellow oil, identical with **6** prepared below.

Preparation of 6. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 7 mg (0.02 mmol) of $PdCl_2(PhCN)_2$. Ester **5** (191.1 mg, 0.97 mmol) was added in 1.93 mL of toluene via syringe. The mixture was refluxed for 3 h, then allowed to cool, and evaporated directly onto 0.3-g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 10-g silica gel column. The column was eluted with 50-mL portions of 3–11% acetone/petroleum ether, in 1% increments. The first 250 mL was discarded. The next 120 mL was concentrated in vacuo to give 76 mg (0.45 mmol, 46%) of **6** as a clear yellow oil: R_f (20% acetone/hexane) 0.25; ^{13}C NMR 11.9 (q), 25.9 (t), 29.9 (t), 34.9 (t), 51.9 (q), 131.8 (s), 163.8 (s), 190.0 (s), 203.8 (s); ^1H NMR 1.21 (t, J = 7.6, 3 H), 2.50 (t, J = 4.9, 2 H), 2.72 (t, J = 4.9, 2 H), 2.82 (q, J = 7.6, 2 H), 3.85 (s, 3 H); IR 2982, 2362, 1752, 1722, 1627, 1550, 1462, 1437, 1344, 1292, 1224, 1202, 1150, 1020, 1000, 977; MS, 168.079 (30), 137 (72), 136 (100), 108 (32), 81 (38).

Preparation of 8 and 9. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 4.3 mg (0.01 mmol) of $PdCl_2(PhCN)_2$, 237 mg (2.5 mmol) of $LiBF_4$, and 1 mL of CH_3NO_2. The mixture was magnetically stirred at reflux for 1 h. Ester **7** (291 mg, 1.3 mmol) in 1.6 mL of CH_3NO_2 was added via syringe, followed by 3 mg of methylene blue. The reaction mixture was allowed to stir an additional hour at reflux. The mixture was allowed to cool to room temperature and then was quenched with distilled H_2O. Extracting solvent was added, and the two layers were separated. The aqueous layer was extracted four times with extracting solvent (25-mL portions). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was evaporated directly onto 2 g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 10-g silica gel column. The column was then eluted with 50-mL portions of 3–9% acetone/petroleum ether in 1% increments. The first 100 mL was discarded. The following 48 mL was concentrated in vacuo to give 55.4 mg (0.29 mmol, 22%) of **9** as a light yellow oil. The next 140 mL was discarded. The following 120 mL was concentrated in vacuo to give 130 mg (0.67 mmol, 51%) of **8** as a light yellow oil.

8: R_f (20% acetone/hexane) 0.29; ^{13}C NMR 25.1 (t), 27.0 (t), 30.1 (t), 35.2 (t), 41.0 (t), 42.0 (d), 51.8 (q), 129.3 (s), 163.7 (s), 190.6 (s), 202.6 (s); ^1H NMR 3.8 (s, 3 H), 3.5 (br d, J = 13.4, 1 H), 2.5–2.9 (m, 2 H), 1.1–2.4 (m, 8 H); IR 2962, 1752, 1722, 1634, 1554, 1450, 1438, 1360, 1322, 1299, 1274, 1240, 1230, 1160, 1020, 980; MS, 194.094 (40), 163 (67), 162 (100), 134 (80), 106 (39), 95 (69).

9: R_f (20% acetone/hexane) 0.52; ^{13}C NMR 23.5 (t), 25.0 (t), 32.1 (d), 39.6 (d), 44.4 (t), 52.5 (q), 59.8 (d), 127.1 (d), 128.6 (d), 169 (s), 211 (s); ^1H NMR 5.6–6.0 (m, 2 H), 3.8 (s, 3 H), 3.1 (m, 1 H), 1.1–2.7 (m, 8 H); IR 2952, 1759, 1732, 1552, 1253, 1220, 1003, 975; MS, 194.096 (18), 162 (35), 140 (35), 135 (100), 116 (34), 108 (33), 107 (30), 106 (34).

Preparation of 11. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 5.1 mg (0.01 mmol) of $PdCl_2(PhCN)_2$, 196 mg (2.1 mmol) of $LiBF_4$, and 1 mL of toluene. The mixture was magnetically stirred at reflux for 1.5 h. Ester **10** (218.8 mg, 1.04 mmol) in 1.1 mL of toluene was added via syringe. The reaction mixture was allowed to stir an additional 15 min at reflux. The mixture was allowed to cool to room temperature and evaporated directly onto 0.5 g of 60–100 mesh silica gel. The absorbed mixture was added to the top of a 10-g column. The column was eluted with 50-mL portions of 2–12% acetone/petroleum ether, in 1% increments. The first 320 mL was discarded. The next 140 mL was concentrated in vacuo to give 101 mg (0.56 mmol, 53%) of **11** as a light yellow oil: R_f (20% acetone/hexane) 0.30; ^{13}C NMR 204.1 (s), 192.5 (s), 164.0 (s), 131.4 (s), 51.9 (q), 34.6 (t), 30.4 (d), 25.7 (t), 20.6 (q); ^1H NMR 3.85 (s, 3 H), 3.5–3.7 (m, 1 H), 2.66 (t, J = 2.0, 8, 2 H), 2.48 (t, J = 2.0, 2 H), 1.20 (d, J = 6.9, 6 H); IR 2994, 1722, 1626, 1555, 1437, 1549, 1494, 1253, 1236, 1172, 1146, 1022; MS, 182.0943 (16), 151 (52), 150 (100), 135 (36), 122 (36).

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Registry No. **1**, 62344-19-8; **2**, 23260-43-7; **3**, 62344-21-2; **4**, 103191-92-0; **5**, 62344-22-3; **7**, 103191-93-1; **8**, 103191-94-2; **9**, 103191-95-3; **10**, 62344-23-4; **11**, 103191-96-4; $PdCl_2(PhCN)_2$, 14220-64-5; $H_2C{=}CH(CH_2)_2COCH_2CO_2CH_3$, 30414-57-4.

Synthesis of Labeled (±)-2-Amino-3-butenoic Acids

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L-2-Amino-3-butenoic acid (L-vinylglycine, **1**), a naturally occurring unsaturated amino acid isolated from mush-

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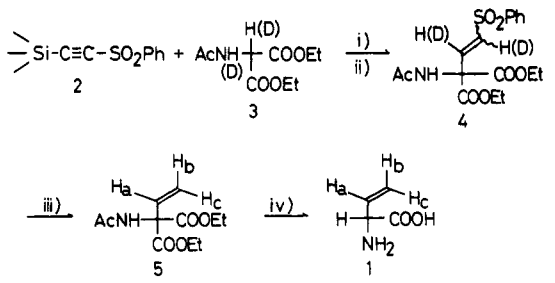
Scheme I[a]



[a] (i) Potassium *tert*-butoxide, THF, −10 to −15 °C; (ii) H_2O or D_2O; (iii) aluminum amalgam, dioxane, H_2O or D_2O; (iv) 6 N HCl, CH_3OH–H_2O (1:1), reflux.

rooms,[1] is an irreversible inhibitor of certain pyridoxal phosphate dependent enzymes,[2] while for others, notably cystathionine γ-synthase,[3] cystathionine γ-lyase,[4] and L-methionine γ-lyase,[5] it can serve as a good substrate. In these latter cases, as well as in the threonine synthetase[6] reaction, vinylglycine has been implicated or postulated as an intermediate. This biological stimulus has prompted a number of syntheses of **1** both as the racemate[3,7] and as a pure enantiomer.[8] Only one report has appeared of labeled forms of **1**: Chang and Walsh[3] prepared the *Z*-[4-$^2H_1$] (**1**, H_c = ^2H) and *E*-[3,4-$^2H_2$] (**1**, H_a and H_b = ^2H) compounds by reduction of acetylenic intermediates.

For a stereochemical study of these enzymatic processes we have developed a simple and practical new synthesis of (±)-**1**, based on the recently reported vinyl cation synthon, phenyl 2-(trimethylsilyl)ethynyl sulfone[9] (**2**), which allows introduction of a deuterium label at each of the three vinyl positions.

Reaction of diethyl acetamidomalonate (**3**) with **2** in the presence of potassium *tert*-butoxide gave diethyl acetamido[2-(phenylsulfonyl)vinyl]malonate (**4**). A reaction time of 1 h at −10 °C[10] afforded a kinetically controlled mixture of (*Z*)- and (*E*)-**4** (3:1), which could be separated easily by chromatography. On the other hand, overnight reaction at room temperature gave the pure *E* isomer of **4**.

The labeled forms of **4** in which both olefinic hydrogens were replaced by deuterium, (*Z*)- and (*E*)-[3,4-$^2H_2$]-**4**, were prepared by the same procedure beginning with deuterium-exchanged[11] **3** and working up the reaction with deuterium oxide. The extent of deuterium incorporation at each of the vinyl positions was shown by ^1H NMR to be greater than 95%.

Reductive desulfurization of **4** was accomplished with aluminum amalgam[9] to yield diethyl acetamidovinylmalonate (**5**, H_a, H_b, H_c = ^1H). Complete retention of configuration was observed when the same procedure was applied to (*Z*)- and (*E*)-[3,4-$^2H_2$]-**4**, affording (*E*)-[3,4-$^2H_2$]-**5** (H_a and H_b = ^2H, H_c = ^1H) and (*Z*)-[3,4-$^2H_2$]-**5** (H_a and H_c = ^2H, H_b = ^1H), respectively. The isomers of **5** monodeuterated at C-4, (*E*)-[4-$^2H_1$]-**5** and (*Z*)-[4-$^2H_1$]-**5**, were obtained by corresponding reduction of (*E*)- and (*Z*)-**4**, respectively, in dioxane moistened with deuterium oxide. The trideuterovinyl compound (**5**, H_a, H_b, H_c = ^2H) could similarly be prepared by reduction of either (*E*)- or (*Z*)-[3,4-$^2H_2$]-**4** with aluminum amalgam in dioxane containing D_2O.

Hydrolysis and decarboxylation of **5** gave **1** in 80% yield. No loss of isotope was observed when the deuterated forms of **5** were hydrolyzed.

Experimental Section

Proton NMR spectra, IR spectra, and GC–mass spectra were recorded on JEOL-JNM-MH-100, Shimazu IR-400, and Hitachi M-52 spectrometers, respectively. Melting and boiling points are uncorrected. Deuterium oxide and methanol-d_1 were purchased from MSD Isotopes. Representative procedures are described below.

(*Z*)- and (*E*)-Diethyl Acetamido[2-(phenylsulfonyl)-vinyl]malonate (4). A mixture of **3** (6.6 g, 30 mmol) and potassium *tert*-butoxide (0.50 g, 4.5 mmol) in dry THF (distilled from benzophenone ketyl) was stirred for 1 h at room temperature and then cooled to −10 to −15 °C, and a solution of **2** (5.0 g, 20 mmol) in dry THF (20 mL) was slowly added. After the mixture was stirred for 1 h at this temperature, water (5 mL) was added, and the solution was stirred overnight. The reaction mixture was extracted with ether, and the extracts were washed with dilute alkali to remove unreacted **3** and dried over 3A molecular sieves. Concentration at reduced pressure left a crystalline residue (5.5 g, 75% based on **2**). The geometrical isomers were separated by chromatography on silica gel (Merck Si-60), eluting with 3:1 CCl_4–$CHCl_3$. (*Z*)-**4**: mp 94–95 °C; ^1H NMR ($CDCl_3$) δ 1.28 (t, *J* = 6 Hz, 6 H), 1.93 (s, 3 H), 4.26 (q, *J* = 6 Hz, 4 H), 6.25 (d, *J* = 12 Hz, 1 H), 7.4–8.0 (m, 7 H). (*E*)-**4**: mp 108.5–109.0 °C; ^1H NMR ($CDCl_3$) δ 1.24 (t, *J* = 6 Hz, 6 H), 1.96 (s, 3 H), 4.23 (q, *J* = 6 Hz, 4 H), 6.41 (d, *J* = 16 Hz, 1 H), 7.12 (br s, 1 H), 7.35–8.00 (m, 6 H); IR (CH_2Cl_2) 3380, 2980, 1735, 1680 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_7S$: C, 53.26; H, 5.52; N, 3.65. Found: C, 53.52; H, 5.57; N, 3.67.

When the reaction mixture was allowed to stand overnight at room temperature before addition of water, the *E* isomer was the sole product.

The *Z* and *E* isomers of [3,4-$^2H_2$]-**4** were prepared by this procedure using deuterium-exchanged[11] **3** as the starting material and substituting deuterium oxide for water. The ^1H NMR spectra showed no more than 2–4% hydrogen present on the olefinic carbons.

Diethyl Acetamidovinylmalonate (5). Aluminum amalgam was prepared by dipping small pieces of aluminum foil (3 × 4 cm^2, 4.5 g) for a few minutes in a 0.5% aqueous solution of mercuric chloride. The amalgam was filtered and added immediately to a solution of (*E*)-**4** (2.0 g, 5.2 mmol) in dioxane, and the mixture was stirred 2 days at 5–10 °C under argon. The reaction mixture was filtered, and the residue was washed several times with ether. The combined filtrate and washings were concentrated under reduced pressure to afford **5** (1.2 g, 82%), which was purified by silica gel chromatography: bp 135–137 °C (1.0 torr); ^1H NMR (CCl_4) δ 1.24 (t, *J* = 7 Hz, 6 H), 1.97 (s, 3 H), 2.12 (q, *J* = 7 Hz, 4 H), 5.04 (d, *J* = 16 Hz, 1 H), 5.07 (d, *J* = 11 Hz, 1 H), 6.30 (dd, *J* = 16 and 11 Hz, 1 H), 6.75 (br s, 1 H); IR (CCl_4) 3410, 2950, 1735, 1690 cm^{-1}; mass spectrum; *m/z* 198, 170, 128, 100.

The *Z* and *E* isomers of [3,4-$^2H_2$]-**5** were prepared by the same procedure starting with the *E* and *Z* isomers of [3,4-$^2H_2$]-**4**: mass spectra; *m/z* 200, 172, 130, 102.

For preparation of (*E*)- and (*Z*)-[4-$^2H_1$]-**5**, the corresponding *E* and *Z* isomers of **4** were reduced by the above procedure, with deuterium oxide substituted for water in each stage and the

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(10) Lower temperatures than this decreased the yield.
(11) The two exchangeable hydrogens of **3** were replaced with deuterium by stirring **3** in a mixture of deuterium oxide, methanol-d_1, and a trace of dry pyridine followed by removal of the solvents under reduced pressure.

starting material being subjected to a preliminary exchange of the amide hydrogen with D_2O. In these experiments, the aluminum amalgam was prepared by using a 0.5% solution of mercuric chloride in D_2O, rinsed twice with THF moistened with D_2O, and finally with dry THF. The mass spectra of the isomers of 5-d_1 showed m/z 199, 171, 129, and 101.

(±)-2-Amino-3-butenoic Acid (1). A mixture of 5 (1.2 g, 50 mmol), 6 N HCl (10 mL), and methanol (10 mL) was heated under reflux for 4 h. The reaction mixture was concentrated to dryness in vacuo, and the residue was applied to an ion-exchange column (Dowex-50, H^+ form), which was eluted with 1% aqueous pyridine to provide 1 (0.4 g, 80%): ^1H NMR (D_2O, pD 5.0) δ 4.40 (d, J = 8 Hz, 1 H), 5.58 (dd, J = 17 and 10 Hz, 2 H), 5.9-6.4 (td, J = 17, 10, and 8 Hz, 1 H). For ^1H NMR spectra of 1, (*E*)- and (*Z*)-[4-$^2H_1$]-1, and (*Z*)-[3,4-$^2H_2$]-1, see supplementary material.

Registry No. 1, 52773-87-2; (*E*)-[4-$^2H_1$]-1, 103384-16-3; (*Z*)-[3,4-$^2H_2$]-1, 103384-17-4; 2, 32501-93-2; 3, 1068-90-2; 3 (deuterium exchanged), 14341-56-1; (*E*)-4, 103384-10-7; (*Z*)-4, 103384-11-8; (*E*)-[3,4-$^2H_2$]-4, 103384-12-9; (*Z*)-[3,4-$^2H_2$]-4, 103384-13-0; 5, 70562-47-9; (*E*)-[3,4-$^2H_2$]-5, 103384-14-1; (*Z*)-[3,4-$^2H_2$]-5, 103384-15-2.

Supplementary Material Available: NMR spectra of 1, (*E*)- and (*Z*)-[4-$^2H_1$]-1, and (*Z*)-[3,4-$^2H_2$]-1 (2 pages). Ordering information is given on any current masthead page.

Singlet Oxygen Production from the Reactions of Alkylperoxy Radicals. Evidence from 1268-nm Chemiluminescence

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Substantial evidence obtained over the last three decades demonstrates that alkylperoxy radicals react via a tetraoxide intermediate which decomposes to give radical or nonradical products.[1-10] For primary and secondary

$$2RR'R''COO^{\bullet} \rightleftharpoons RR'R''COOOOCRR'R'' \quad (1)$$

$$RR'R''COOOOCRR'R'' \rightarrow RR'R''COOCRR'R'' + O_2 \quad (2)$$

$$RR'R''COOOOCRR'R'' \rightarrow 2RR'R''CO^{\bullet} + O_2 \quad (3)$$

$$RR'HCOOOOCRR'H \rightarrow RR'CO + RR'CHOH + O_2 \quad (4)$$

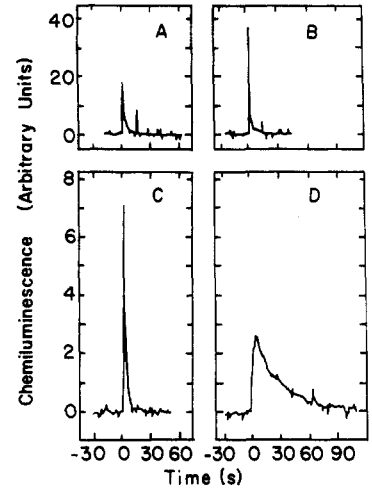

Figure 1. Chemiluminescence at 1268 nm in the reaction of ceric ion with hydroperoxides. Conditions, 1 mM ceric ammonium nitrate, 1 mM hydroperoxide, 20 mM hydrochloric acid, deuterium oxide solvent: (A) cumyl hydroperoxide; (B) 13-hydroperoxylinoleic acid; (C) ethyl hydroperoxide; (D) *tert*-butyl hydroperoxide.

alkylperoxy radicals, reaction 4 is the favored route of decomposition for the tetraoxide intermediate.[4] Reaction 4 may generate either an electronically excited oxygen molecule or an electronically excited ketone.[5] Spin restriction requires that excited singlet oxygen be produced if the ketone product is in its ground state.[5] Alternatively, an electronically excited triplet ketone and ground-state triplet oxygen may be the products.[5] Considerable experimental support for the production of singlet oxygen by reaction 4 comes from the chemical trapping study of Howard and Ingold,[5] the spectroscopically resolved chemiluminescence demonstrated by Bogan et al.,[6] and the data of Hawco et al. from chemiluminescence and chemical trapping experiments.[7] Nakano et al. and Inaba et al. have also reported visible chemiluminescence in the reaction of peroxy radicals, but the spectral analysis of the emission they observed had little correlation with dimolecular singlet oxygen chemiluminescence.[8] Reaction 4 does not occur with tertiary alkylperoxy radicals,[5,9] but Thomas has pointed out that reaction 2 should also produce singlet oxygen.[10] Howard and Ingold were unable to detect the characteristic endoperoxide product from 9,10-diphenylanthracene in the reaction of *tert*-butyperoxy radicals, but they felt this result may have been due to the destruction of the expected endoperoxide product by the *tert*-butylperoxy radicals.[5]

Studies in this laboratory have recently demonstrated characteristic singlet oxygen emission at 1268 nm in the reaction of 13-peroxylinoleic acid radicals.[11] In view of the high sensitivity and high specificity of 1268-nm emission for singlet oxygen in complex systems,[12] I undertook studies of singlet oxygen production from the bimolecular reactions of alkylperoxy radicals.

Results and Discussion

The reaction of ceric ion with hydroperoxides was used to produce peroxy radicals in aqueous solution.[5,7-8] As

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