velosil ODS-5, Nomura Chemical, 10 × 250 mm; flow rate, 2.5 mL/min; UV detection at 254 nm; eluant, 88% methanol) to afford amphidinolide C (**1**, t_R 10.9 min; 6 mg) in 0.0015% yield (wet weight).

Amphidinolide C (1): colorless amorphous solid; $[\alpha]^{26}_D$ −106° (*c* 1, $CHCl_3$); UV (MeOH) 240 nm (ε 26 000); IR (film) 3400, 2930, 1705, and 1035 cm^{-1}; ^1H NMR (Table II); ^{13}C NMR ($CDCl_3$) δ 12.52 (q), 13.81 (q), 14.45 (q), 15.33 (q), 15.45 (q), 16.09 (q), 22.35 (t), 28.15 (t), 30.02 (t), 31.42 (t), 31.89 (t), 36.81 (t), 38.74 (t), 39.79 (d), 42.54 (d), 45.47 (t), 46.00 (t), 48.34 (t), 49.16 (d), 70.70 (d), 74.91 (d), 76.26 (d), 76.79 (d), 77.20 (d), 78.77 (d), 79.65 (d), 79.77 (d), 81.29 (d), 110.20 (t), 115.71 (t), 124.54 (d), 124.95 (d), 127.29 (d), 130.75 (d), 139.88 (s), 140.11 (s), 144.56 (s), 149.13 (s), 171.02 (s), 207.66 (s), and 213.63 (s); FABMS (positive ion; glycerol as a matrix) *m/z* 715 $(M + H)^+$ and 697 $(M - H_2O + H)^+$; HREIMS *m/z* 696.4236 ($M - H_2O$; calcd for $C_{41}H_{60}O_9$, 696.4237).

Tetraacetate (2). Amphidinolide C (**1**, 4.7 mg) was treated with 0.3 mL of acetic anhydride and 0.3 mL of pyridine at room temperature for 17 h. After evaporation of the solvent, purification by silica gel column chromatography (Wako gel C-300, 7 × 70 mm) eluted with hexane/acetone (3:1) afforded the tetraacetate (**2**, 4.0 mg): ^1H and ^{13}C NMR (Table I); FABMS (positive ion; diethanolamine as a matrix) *m/z* 988 (M + diethanolamine + H)$^+$.

Compound 3. In the $CDCl_3$ solution of **2** (5 mg in 0.5 mL), **2** was slowly oxidized by air to give the peroxide **3**, which was separated by a silica gel column chromatography (Wako gel C-300, 7 × 70 mm) eluted with hexane/acetone (3:1). After 3-4 months, the ratio of **2** and **3** in the $CDCl_3$ solution was approximately 3:1. **3**: ^1H NMR ($CDCl_3$) δ 6.51 (dd, *J* = 15.3 and 10.9 Hz, H-26), 6.07 (d, *J* = 10.9 Hz, H-27), 5.91 (s, H-10), 5.64 (dd, *J* = 15.3 and 7.7 Hz, H-25), 5.55 (s, H-29), 5.48 (m, H-13), 5.37 (d, *J* = 4.1 Hz, H-7), 5.28 (dd, *J* = 7.7 and 6.8 Hz, H-24), 5.16 (dd, *J* = 6.1 and 4.1 Hz, H-7), 5.05 (s, H-41), 4.96 (s, H′-41), 4.82 (d, *J* = 15.8 Hz, H-36), 4.44 (d, *J* = 15.8 Hz, H′-36), 4.30 (m, H-20), 4.14 (m, H-23), 4.09 (m, H-6), 3.87 (m, H-3), 3.07 (m, H-16), 2.15, 2.10, 2.04, and 2.04 (each 3 H, s, Ac × 4), 1.69 (3 H, s, H_3-40), 1.30 (3 H, s, H_3-37), 1.06 (3 H, d, *J* = 7.1 Hz, H_3-39), 1.05 (3 H, d, *J* = 6.5 Hz, H_3-38), 0.97 (3 H, d, *J* = 7.3 Hz, H_3-35), and 0.90 (3 H, t, *J* = 7.3 Hz, H_3-34); FABMS (positive ion; diethanolamine as a matrix) *m/z* 1020 (M + diethanoamine + H)$^+$.

Acknowledgment. We thank Prof. T. Yamasu, University of the Ryukyus, for providing the dinoflagellate and M. Hamashima and S. Kaneko for technical assistance. This study was performed through Special Coordination Funds of the Science and Technology Agency of the Japanese Government.

Supplementary Material Available: Figures 1-4 consisting of the COSY, RCT2, ^1H-^{13}C COSY, and HMBC spectra of **2** (6 pages). Ordering information is given on any current masthead page.

Reaction of Singlet Oxygen with Thiirane: Peroxysulfenic Acid Intermediate as a New Oxidizing Species[1]

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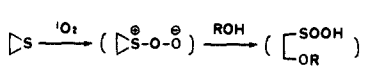
Contribution from the Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan. *Received February 17, 1987*

Abstract: The reaction of singlet oxygen with 7-thiabicyclo[4.1.0]heptane (cyclohexene sulfide) in methanol has been investigated. The first example for epoxidation of olefins by the active oxidizing species generated in photooxygenation of the thiirane is provided. It suggests that the active oxidizing species is probably the peroxysulfenic acid intermediate derived from ring opening of a thiirane peroxide intermediate by nucleophilic attack of methanol.

The oxidation of sulfur compounds with singlet oxygen ($^1O_2$) has been extensively studied, and much attention has been devoted to their structures and the reactivities of peroxidic intermediates.[2-7]

Scheme I



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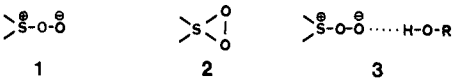
Recently, Foote et al.[4g] elegantly proposed that there are two intermediates in the singlet oxygenation reaction of sulfide in aprotic solvents, in which an initial nucleophilic persulfoxide intermediate **1** reacts with an electrophile such as diphenyl sulfoxide, loses singlet oxygen, or collapses to an electrophilic thiadioxirane intermediate **2** that reacts with a nucleophile such as sulfide. Meanwhile, in protic solvents the persulfoxide intermediate is stabilized by hydrogen bonding as **3**.[4e,7] The function of the alcohol was interpreted as decreasing the negative charge density on the persulfoxide, thus promoting nucleophilic attack by a second sulfide. Since no direct trapping of the intermediates has been achieved,[8] however, the structures of them are still controversial.[2-7] Accordingly, the molecule that may serve as a diagnostic test for a persulfoxide intermediate is clearly desirable for mechanistic studies of the oxidation reaction of sulfides. The candidate is thiirane.[5f,9] The particular advantage of thiirane



1 **2** **3**

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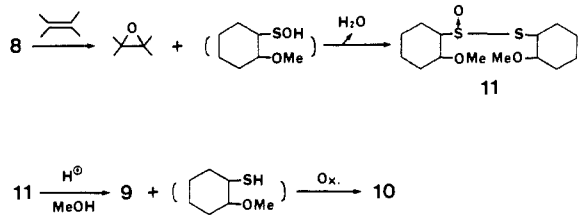
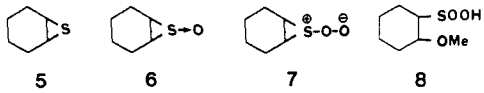
Scheme II



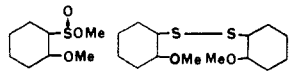
is that the persulfoxide intermediate might react easily with alcohol to give a new oxidizing species, peroxysulfenic acid **4**[2] (Scheme I), similar to the case of the acid-catalyzed ring opening of thiirane oxides.[10] We report here evidence for the first trapping of a persulfoxide intermediate by methanol to afford the peroxysulfenic acid intermediate that oxidizes olefins to epoxides and sulfides to sulfoxides.

Results and Discussion

7-Thiabicyclo[4.1.0]heptane (cyclohexene sulfide, **5**)[11] reacts with singlet oxygen in the presence of methylene blue as sensitizer and light. If the photooxygenation is carried out under nitrogen or in the absence of a sensitizer or light, no reaction occurs. The oxygenation is inhibited by 1-phenyl-3-[*p*-(diethylamino)-styryl]-5-[*p*-(diethylamino)phenyl]-2-pyrazoline,[12] a known singlet oxygen quencher. These control experiments make it probable that singlet oxygen is the primary oxygenating species. Photooxygenation of **5** in methylene chloride gave the polymeric products. Since photooxygenation of **5** in the presence of dimethyl



sulfoxide gave thiirane sulfoxide **6** (79% yield)[13] and dimethyl sulfone, however, the initial formation of peroxythiirane oxide **7** is evident.[4e,g,7] Photooxygenation of **5** in the presence of methanol to give peroxysulfenic acid **8**[14] is evidenced by the change in products as a function of added olefin. Photooxygenation in **5** in methanol gave sulfinate **9** (35%) and disulfide **10** (30%). Since

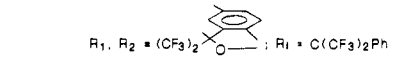


acid-catalyzed methanolysis of **6** afforded thiosulfinate **11** by dehydrogenation of the corresponding sulfenic acid,[15] **6** is an alternative source of products **9** and **10** for oxidation in methanol. It is known that thiirane oxides undergo nucleophilic ring opening in the presence of a strong acid.[10] In the case where the nucleophile is methanol, the product is a methoxy thiosulfinate.[10b,c] The products are generally believed to arise from dehydration of a sulfenic acid, which is assumed to be the primary product from the ring opening.[15] Similar to the case of thiirane oxides,[10] however, it seems to be reasonable that nucleophilic attack by methanol as solvent on **7** to give **8** would also preferentially take place compared with that on **7** by a sulfide nucleophile to afford

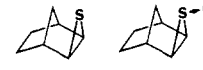
Table I. ρ Values for Various Electrophilic Oxygen Atom Transfer Reactions

system	oxygen acceptor[a]	ρ (vs σ)	ref
5/$^1O_2$/MeOH	A	−0.74	this work
HOOH	B	−0.98	24
PhC(O)OOH	A	−2.50	25
Et_2S/$^1O_2$/MeOH	B	−0.61	5b
$Ph_2S(OR_f)_2$/HOOH[b]	A	−0.43	6h
$R_1R_2S(OR_f)_2$/HOOH[b]	A	−0.86	6h

[a] A = $(p\text{-}XC_6H_4)_2S$; B = $p\text{-}XC_6H_4SPh$. [b]



6. When the intermediate was generated in the presence of excess norbornene or cyclohexene, **9** and **10** were produced in 37% and 29% yields, respectively, together with the epoxide. Possible reactions leading to the observed products are shown in Scheme II. **10** might be obtained by oxidation[16] of the corresponding thiol derived from methanolysis of **11**. Photoepoxidation of olefins did not take place at all in the absence of **5**. An oxenoid mechanism, which could resemble those in biological epoxidations,[17] is suggested for the epoxidation reactions. When the photooxygenation was carried out in the presence of norbornene at −40 °C in a solution of methanol–methylene chloride (9:1), *exo*-norbornene oxide[18] was obtained in 37% yield. Yields were determined by GLC, and the reaction conditions are not optimized. Addition of a radical trap (triphenylmethane)[19] in concentrations up to 5 × 10^{-3} M does not have any influence on epoxidation: norbornene oxide, 21% in the absence and 20% in the presence of a trap at 15 °C. Similarly, cyclohexene is converted into the corresponding epoxide in 47% yield at 15 °C in a methylene chloride solution containing methanol (0.5 M). Cyclohexene oxide was identified as the ring-opening product 2-methoxycyclohexanol.[20] 2-Cyclohexen-1-ol and 2-cyclohexen-1-one as radical–oxidation products[21] were not obtained at all. No epoxide was obtained in the photooxygenation of diethyl sulfide in methanol in the presence of norbornene. In contrast to the case of **5**, photooxygenation of 3-thiatricyclo[3.2.1.$0^{2,4}$]octane (norbornene sulfide, **12**)[22] in methanol gave the corresponding sulfoxide **13**[23] quantitatively, and no epoxidation took place in the presence of olefin. Since



only few reactivities of the active oxidizing intermediates **1–3**, generated in the photooxygenation of sulfides, have been known hitherto to oxidize sulfide,[4,5b] sulfoxide,[4c,7] and an active α-C–H bond[5f,6g] and to cause oxidative decarboxylation of α-keto carboxylic acids,[5d] it is worthwhile that **8** is effective for the epoxidation of olefins. In turn, the intermediate structure might surely be persulfoxide **7**.

Photooxygenation of **5** in methanol–methylene chloride in the presence of diphenyl sulfide, which is relatively stable toward $^1O_2$,[4b] gave diphenyl sulfoxide in 80% yield. Competitive kinetic studies of the oxidation of symmetrically disubstituted diphenyl sulfides showed the oxidant to be electrophilic, describing a ρ value vs σ of −0.74 (Table I). The negative ρ value is comparable with those for the oxidation with hydrogen peroxide[24] and perbenzoic acid[25]

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and also for the oxidation in photooxygenation of diethyl sulfide in methanol.[5b] Hydrogen trioxide (ROOOH), an oxygen analogue of peroxysulfenic acid, electrophilically oxidizes sulfide to sulfoxide. These results are similar to those of intermediates derived from hydrogen peroxide and Martin's sulfuranes[6h] capable of epoxidizing olefins.

In summary, the trapping of a persulfoxide intermediate of thiirane by methanol might afford the peroxysulfenic acid that is able to oxidize olefins to epoxides and sulfides to sulfoxides. The peroxysulfenic acid intermediate might be derived from ring opening of a thiirane peroxide intermediate by nucleophilic attack of methanol. It is noteworthy that this is a first example for efficient epoxidation of olefins by the active oxidizing species generated in the photooxygenation of sulfides.

Experimental Section

IR spectra were recorded with a Hitachi 260-50 spectrometer, ^{1}H NMR spectra with a Varian EM 360A spectrometer and a JEOL JNM PMX-60SI spectrometer, and ^{13}C NMR spectra with a JEOL JNM JX-100 spectrometer. Deuteriated chloroform was used as the solvent. Chemical shift values are reported (δ) relative to internal tetramethylsilane standard. Mass spectral data were obtained on a Hitachi RMU-6M Mass spectrometer and exact mass data on JEOL JMS-D300 mass spectrometer. Gas chromatography was done on a Hitachi 163 gas chromatograph equipped with a fid detector. Gel permeation chromatography was performed on a series of JAIGEL 1H and 2H columns with a flow of 3.5 mL min^{-1} of chloroform on a LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd.

Reagent-grade solvents were used for the experiments in methylene chloride and methanol. Methylene chloride was refluxed over calcium chloride and distilled before use. Methanol was refluxed over calcium oxide and distilled before use. Methylene blue (Kanto Chemical) and deuteriated chloroform for spectroscopy (Merck) were used as received. Norbornene (Tokyo Kasei) was used as received. Cyclohexene (Tokyo Kasei) was used after distillation. Their epoxides were prepared according to the literature method.[18] Cyclohexene sulfide[11] and norbornene sulfide[21] were synthesized by the reported method. These sulfides were oxidized with *m*-chloroperbenzoic acid to afford the corresponding sulfoxides.[13] Diphenyl sulfide (Tokyo Kasei) was used as received. Bis(*p*-chlorophenyl), bis(*p*-methylphenyl), and bis(*p*-methoxyphenyl) sulfides were prepared according to the literature method.[26]

The light source was two 500-W tungsten–halogen lamps. Irradiations were carried out in Pyrex tubes in a water bath while oxygen was passed through.

Photooxygenation. General Procedures. A 0.05 M solution of the thiirane containing methylene blue as sensitizer was photooxygenated at −40 °C. The solvent was removed under reduced pressure, and the residue was subjected to preparative HPLC and analytical GLC.

Photooxygenation of 5. The fraction from preparative HPLC was shown to consist of polymeric products. In the presence of dimethyl sulfoxide (2.5 M), the corresponding thiirane oxide (**6**)[13] was obtained in 79% yield as determined by NMR measurement, accompanied by dimethyl sulfone. In the case of photooxygenation of **5** in methanol, three fractions were isolated by preparative HPLC. The first product was bis(2-methoxycyclohexyl) disulfide (**10**): 29% yield; IR (NaCl) 1190, 1110, 1095 cm^{-1}; ^{1}H NMR δ 3.38 (s, 6 H), 3.02–3.24 (m, 2 H), 2.61–2.84 (m, 2 H), 1.06–2.38 (m, 16 H); ^{13}C NMR δ 81.14 (d), 56.36 (q), 54.37 (d), 30.94 (t), 29.94 (t), 24.95 (t), 23.48 (t); MS, *m/e* 290 (M$^+$). Anal. Calcd for $C_{14}H_{26}O_2S_2$: C, 57.78; H, 9.02. Found: C, 57.70; H, 9.08. The isomeric mixture was not separated. The second product was methyl *trans*-2-methoxycyclohexanesulfinate:[9] 30% yield; IR (NaCl) 1190, 1120, 1090, 990 cm^{-1}; ^{1}H NMR δ 3.82 (s, 3 H), 3.33 (s, 3 H), 3.22–3.46 (m, 1 H), 2.48–2.72 (m, 1 H), 1.04–2.40 (m, 8 H); ^{13}C NMR δ 78.49 (d), 68.81 (d), 56.13 (q), 55.72 (q), 30.53 (t), 24.66 (t), 23.54 (t), 19.0 (t); MS, *m/e* 192 (M$^+$). Anal. Calcd for $C_8H_{16}O_3S_1$: C, 49.97; H, 8.38. Found: C 49.90; H, 8.44. The third product was methyl *cis*-2-methoxycyclohexanesulfinate:[9] 7% yield; IR (NaCl) 1190, 1120, 1090, 990 cm^{-1}; ^{1}H NMR δ 3.80 (s, 3 H), 3.38 (s, 3 H), 3.32 (m, 1 H), 1.04–2.76 (m, 9 H); ^{13}C NMR δ 77.85 (d), 68.05 (d), 56.36 (q), 55.83 (q), 30.47 (t), 24.31 (t), 23.48 (t), 18.73 (t); MS, *m/e* 193 (M$^+$). Anal. Calcd for $C_8H_{16}O_3S_1$: C, 49.97; H, 8.38. Found: C, 50.47; H, 8.29.

Methanolysis of 6. To 10 mL of a methanol solution containing concentrated sulfuric acid was added 200 mg of **6** in 5 mL of methanol with stirring in an ice–water bath. After 2 h, **6** completely disappeared. *S*-2-methoxycyclohexyl 2-methoxycyclohexanethiosulfinate (**11**) was isolated in 52% yield by silica gel column chromatography using methylene chloride–ethyl acetate as eluent: IR (NaCl) 1190, 1120, 1090, 1070 cm^{-1}; ^{1}H NMR δ 3.40 (s, 3 H), 3.37 (s, 3 H), 2.73–3.80 (m, 4 H), 1.10–2.53 (m, 16 H); ^{13}C NMR δ 82.02 (d), 81.60 (d), 69.22 (d), 68.81 (d), 56.30 (q), 56.01 (q), 32.58, 31.35, 30.24, 29.94, 24.89, 24.66, 23.48, 22.08; MS, *m/e* 306 (M$^+$); exact mass calcd for $C_{14}H_{26}O_3S_2$ 306.1322, found 306.1295.

Photooxygenation of 5 in the Presence of Olefins. Photooxygenation of **5** in the presence of norbornene (2.5 M) at −40 °C in a solution of methanol–methylene chloride (9:1) afforded *exo*-norbornene oxide[18] in 37% yield. Yields was determined by GLC (4 mm × 3 m glass column packed with 5% PEG-20M-P on Uniport HP; column temperature, 130 °C). When the reaction was carried out at 15 °C, *exo*-norbornene oxide was identified as the corresponding ring-opening products such as *exo*-2-methoxybicyclo[2.2.1]heptan-*syn*-7-ol and the *-anti*-7-ol reported by Brettle et al.[27] by means of GLC analysis (4 mm × 3 m glass column packed with 5% PEG-20M-P on Uniport HP; column temperature, 130 °C). Similarly, in the presence of cyclohexene (2.5 M), 2-methoxycyclohexanol[20] as the acid-catalyzed ring-opening product of cyclohexene oxide derivatives was obtained in 47% yield (GLC conditions: 4 mm × 2 m glass column packed with 2% Silicon OV-1 on Uniport HP; column temperature, 80 °C).

Photooxygenation of 5 in the Presence of Diphenyl Sulfide. The formation of diphenyl sulfoxide in 80% yield in the photooxygenation of **5** in the presence of diphenyl sulfide (1 M) was analyzed by GLC (4 mm × 1 m glass column packed with 5% PEG-20M-P on Uniport HP; column temperature, 200 °C). Competitive kinetic studies of the photooxygenation of **5** in methanol in the presence of 4,4′-disubstituted diphenyl sulfide was carried out as follows. k_{rel} was determined by the following equation: $k_{rel} = [\log (A - X)/A]/[\log (B - Y)/B] = XB/YA$, where A and B are the amounts of sulfides used in the reaction and X and Y are the amounts of sulfoxides formed by the reaction. k_{rel} (R = 0.9957): *p*-Cl, 0.48; H, 1; *p*-Me, 2.1; *p*-MeO, 2.5. Products ratios were determined by GLC at an early stage (i.e., 10% conversion).

Photooxygenation of Sulfides in the Presence of Norbornene. Diethyl sulfide (0.05 M) (norbornene sulfide, 0.05 M) was photolyzed in a mixture of methanol and methylene chloride in the presence of norbornene (2.5 M). Only the corresponding sulfoxide was observed by NMR and GLC analysis, and none of the epoxide was obtained at all.

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Registry No. 5, 286-28-2; **6**, 21386-28-7; **8**, 111616-09-2; *trans*-**9**, 106471-44-7; *cis*-**9**, 106565-30-4; **10**, 111616-07-0; **11**, 111616-08-1; PhSPh, 139-66-2; PhS(O)Ph, 945-51-7; 4,4′-ClC$_6$H$_4$SC$_6$H$_4$Cl, 5181-10-2; 4,4′-MeC$_6$H$_4$SC$_6$H$_4$Me, 620-94-0; 4,4′-MeOC$_6$H$_4$SC$_6$H$_4$OMe, 3393-77-9; 4,4′-ClC$_6$H$_4$S(O)C$_6$H$_4$Cl, 80-07-9; 4,4′-MeC$_6$H$_4$S(O)C$_6$H$_4$Me, 1774-35-2; 4,4′-MeOC$_6$H$_4$S(O)C$_6$H$_4$OMe, 1774-36-3; norbornene, 498-66-8; *exo*-norbornene oxide, 3146-39-2; *exo*-2-methoxybicyclo[2.2.1]heptan-*syn*-7-ol, 55013-25-7; *exo*-2-methoxybicyclo[2.2.1]heptan-*anti*-7-ol, 55013-26-8; cyclohexene, 110-83-8; 2-methoxycyclohexanol, 2979-24-0.

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