structure by PE spectroscopy and the detailed photochemical behavior of **4**.

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Registry No. **4**, 101493-51-0; **5**, 37939-70-1; **6**, 101493-52-1; **7**, 101493-53-2; **8**, 101493-54-3; **9**, 101493-55-4; **10**, 101493-56-5; **11**, 101493-57-6; **12**, 101493-58-7; **13**, 101493-59-8; **14**, 101493-60-1; **15**, 101493-61-2; **16**, 101493-62-3; **17**, 87306-22-7; **18**, 101493-64-5; i, 101493-63-4; $PhSSO_2Ph$, 1212-08-4; *cis*-1-lithio-2-vinylcyclopropane, 60711-85-5; *trans*-1-lithio-2-vinylcyclopropane, 60711-84-4.

Thioozonide Decomposition: Sulfur and Oxygen Atom Transfer. Evidence for the Formation of a Carbonyl *O*-Sulfide Intermediate

M. G. Matturro,* R. P. Reynolds, R. V. Kastrup, and
C. F. Pictroski

Exxon Research and Engineering Company
Corporate Research Science Labs
Clinton Township, Annandale, New Jersey 08801

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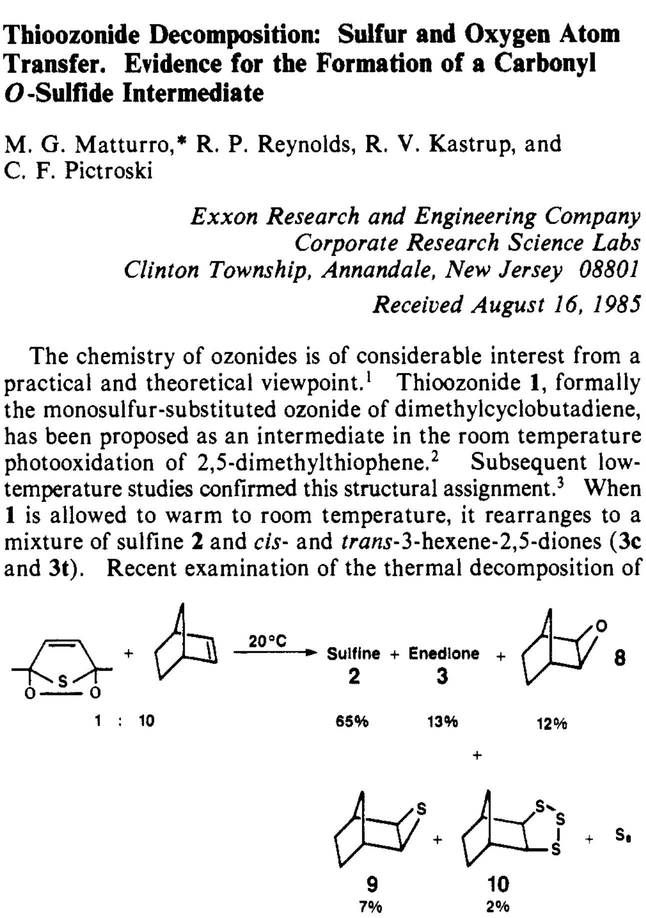
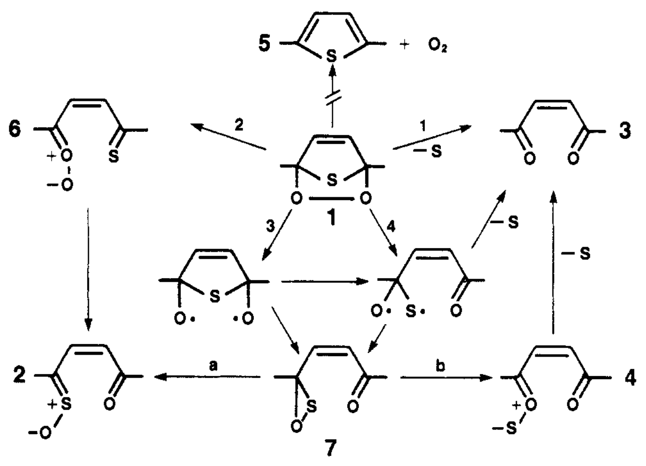
The chemistry of ozonides is of considerable interest from a practical and theoretical viewpoint.[1] Thioozonide **1**, formally the monosulfur-substituted ozonide of dimethylcyclobutadiene, has been proposed as an intermediate in the room temperature photooxidation of 2,5-dimethylthiophene.[2] Subsequent low-temperature studies confirmed this structural assignment.[3] When **1** is allowed to warm to room temperature, it rearranges to a mixture of sulfine **2** and *cis*- and *trans*-3-hexene-2,5-diones (**3c** and **3t**). Recent examination of the thermal decomposition of **1** has led to a proposed mechanism[4] involving a carbonyl sulfide **4** as an intermediate along the sulfur expulsion pathway to **3c**; however, no experimental support for this hypothesis was given. Carbonyl *O*-sulfides have also been implicated as intermediates from the photolysis of oxathiiranes.[5] We now wish to report evidence[6] for the formation of **4** during the decomposition of **1** and that elemental sulfur (S_8) is formed during the reaction by concatenation of sulfur atoms or fragments (S_2, S_3, etc.).



When a 0.25 M solution of 2,5-dimethylthiophene (**5**) was irradiated for 15 min at -50 °C in an aerated solution of $CDCl_3$ containing methylene blue, a quantitative conversion to thioozonide **1** was obtained as determined by ^1H NMR (-40 °C). The absorptions for dimethylthiophene **5** were replaced by new singlets at 2.12 (6 H) and 6.46 (2 H) ppm. Warming the solution to room temperature (20 °C) resulted in the formation of both sulfine **2** (67%) and *cis*-3-hexene-2,5-dione (**3c**) (33%). As the reaction proceeded, some rearrangement of **3c** to the trans isomer **3t** was also observed. The identity of the products was confirmed by spectroscopic analysis[7] and in the case of **3c** and **3t** by comparison with authentic materials.[8] A plot of -ln [**1**] vs. time for the 0.25 M case gave a straight line ($r^2 = 0.996$) indicating a first-order process with a half-life of 23 min ($T = 20 \pm 1$ °C); however, the mechanism of decomposition must be more complicated since preliminary measurements show a dependence on starting substrate concentration and traces of oxygen ($[\mathbf{1}]_0 = 0.09$ M, $t_{1/2} = 12$ min; $[\mathbf{1}]_0 = 0.43$ M, $t_{1/2} = 57$ min). Further studies are under way to define rigorous conditions that give reproducible rate constants.

Scheme I



In Scheme I several possible mechanistic routes for the formation of **2** and **3c** are given. Initial steps may include (1) cheletropic expulsion of sulfur, (2) retro-1,3-dipolar cycloaddition, (3) O-O bond homolysis, and (4) O-O bond cleavage with simultaneous β-scission. Retro-[4 + 2] cycloaddition to regenerate thiophene and singlet oxygen is not observed. Pathway 2 would involve the generation of a carbonyl oxide intermediate **6** which might transfer oxygen internally and lead to sulfine **2**. Polar solvents would be expected to favor the formation of a dipolar species and decomposition of **1** in methanol has been shown to increase the yield of sulfine **2** to 85%, at the expense of enedione formation.[4] Direct singlet sulfur expulsion (path 1) is energetically unlikely but cannot be rigorously excluded on the basis of available experimental observations. Such an expulsion pathway may involve the release of concatenated sulfur species (S_2, S_3, S_4, etc.).[8] Pathways 3 and 4 potentially lead to the same oxathiirane intermediate and are in principle distinguishable by kinetic analysis.[10] The formation of an oxathiirane from the biradicals produced in steps 3 and 4 is reasonable based on CASSCF calculations (double-ζ plus bond polarization functions).[11] The calculation reproduced the experimental geometry of the sulfine (thioformaldehyde *S*-oxide) and predicted its observed stability. All other

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(6) We believe that this is the first nonspectroscopic evidence for the formation of a carbonyl sulfide intermediate. Other attempts to trap such a species with dipolarophiles were unsuccessful. See ref 5.

(7) Sulfine **2**: ^1H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 2.47 (s, 3 H), 6.52 (2 H, A portion of AX quartet, $J = 9.8$ Hz), 7.74 (2 H, X portion of AX quartet, $J = 9.8$ Hz); ^{13}C NMR ($CDCl_3$, ^1H decoupled) δ 30.4 (degenerate), 122.4, 128.1, 193.0, 196.8; MS, *m/e* 144 (M^+, 6.5%), 102 (10.1), 101 (49.8), 87 (16.6), 59 (6.9), 43 (100), 42 (8.5). *cis*-3-Hexene-2,5-dione (**3c**): ^1H NMR ($CDCl_3$) δ 2.32 (s, 6 H), 6.31 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.1, 135.2, 200.0; MS, *m/e* 112 (M^+, 11.2%), 97 (18.9), 69 (15.8), 43 (100). *trans*-3-Hexene-2,5-dione (**3t**): ^1H NMR ($CDCl_3$) δ 2.39 (s, 6 H), 6.81 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.3, 137.2, 198.1.

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(9) Miller, K. J.; Moschner, K. F.; Potts, K. T. *J. Am. Chem. Soc.* **1983**, *105*, 1706-1712.

(10) Evidence for a β-scission concerted with O-O bond homolysis has been given for 2,3-dioxabicyclo[2.2.1]heptane. Coughlin, D. J.; Salomon, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2761-2763.

(11) Karlström, G.; Roos, B. O.; Carlsen, L. *J. Am. Chem. Soc.* **1984**, *106*, 1557-1561.

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isomers examined had energies above that of the sulfine: carbonyl *O*-sulfide, 9 kcal/mol; three-membered-ring oxathiirane, 20 kcal/mol; oxathiirane, open form, 33 kcal/mol (small singlet–triplet separation). On the basis of these predictions,[12] oxathiirane **7** can ring open in two ways to give (a) sulfine **2** or (b) carbonyl *O*-sulfide **4**.[13] Loss of sulfur from **4** either spontaneously or by pairwise coupling with another carbonyl *O*-sulfide to eliminate S_2 would lead to the observed enedione **3**.

To intercept the proposed intermediates, **1** was allowed to decompose in the presence of a 10-fold excess of norbornene at room temperature (20 °C) under nitrogen. When all of the thioozonide had reacted, as determined by ^{1}H NMR, analysis of the mixture revealed the formation of the expected products, sulfine (65%) and enediones **3c** and **3t** (13%) as well as norbornene epoxide **8** (12%), thiirane **9** (7%), trisulfide **10** (2%), and elemental sulfur (S_8). The structures of the trapping products were determined by ^{1}H NMR (400 MHz), mass spectral analysis, and comparison with authentic materials.[14] Thiirane and epoxide formation demonstrates the presence of active sulfur- and oxygen-transfer agents. The most likely candidates include a carbonyl *O*-sulfide and oxide, the ring-opened oxathiirane biradical, and for sulfur-transfer alone, sulfur atoms or allotropes. Several investigators have demonstrated the production of carbonyl oxides by the thermolysis of furan endoperoxides[15,16] and the reaction of singlet oxygen with diazo compounds.[17] In the latter case, olefin trapping experiments showed that *cis*- and *trans*-epoxides were generally formed from the corresponding olefins although in low yield.

When thioozonide **1** was allowed to decompose in the presence of an excess of *cis*-2,5-dimethyl-3-hexene, the *cis*-epoxide (cis/trans = 17.5) and *cis*-thiirane (cis/trans = 7.3) were formed with high stereoselectivity and low yield (≤4%). The trans olefin afforded only the *trans*-epoxide and thiirane.[18] The similarity (low yield and specificity) of oxygen and sulfur atom transfer during thioozonide decomposition strongly suggests that carbonyl oxides and sulfides are intermediates.[19] Sulfur radicals would be expected to give larger amounts of the trans isomer via bond rotation and closure.

Typically 1,3-dipoles react with olefins to form 1:1 cycloadducts. The corresponding adduct for carbonyl oxide trapping has been observed during the ozonolysis of methyl vinyl ether.[20] No analogous examples of carbon *O*-sulfide trapping have been reported; although the expected product, a simple 1,2-oxathiolan, has been shown to possess appreciable stability.[21] We have observed no products of this type during decomposition of **1**. This is not surprising in view of the low yield of epoxides and thiirane obtained and the expected thermal lability of the initial cycloadduct (**4** + olefin) due to extended conjugation. Alternatively, the formation of epoxide or thiirane may occur by direct attack of oxygen or sulfur in **6** or **4** on the olefin double bond.

Control experiments show that no thiirane is formed by heating a mixture of norbornene and sulfur in methylene chloride. The apparent trapping of the thermally generated S_3 fragment, perhaps the sulfur analogue of ozone, is unusual and suggests that a concatenation mechanism is involved during the formation of S_8. Other studies are under way to elucidate the nature of the actual sulfur expulsion step.

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Registry No. **1**, 67711-62-0; **2**, 28030-87-7; **3c**, 17559-81-8; **3t**, 820-69-9; **5**, 638-02-8; **8**, 3146-39-2; **9**, 39558-58-2; **10**, 23657-27-4; (*Z*)-*i*-PrCH=CHPr-*i*, 10557-44-5; (*E*)-*i*-PrCH=CHPr-*i*, 692-70-6; 2-norbornene, 498-66-8; *cis*-3,4-oxa-2,5-dimethylhexane, 59175-38-1; *cis*-3,4-epithio-2,5-dimethylhexane, 101630-80-2; *trans*-3,4-oxa-2,5-dimethylhexane, 54644-32-5; *trans*-3,4-epithio-2,5-dimethylhexane, 101630-81-3.

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[12] This ordering is not analogous to that computed for the three CH_2O_2 isomers where the ring form dioxiirane lies 36 kcal/mol below the carbonyl oxide: Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180–7188. This prediction is supported by the observed stability of dioxiranes: Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847–2853.

[13] The zwitterion form is depicted only to indicate formal charge and not the lack of biradical character.

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[18] The identity of the trapping products was confirmed by independent synthesis of all isomers from the corresponding olefins. *trans*-3,4-Oxa-2,5-dimethylhexane: ^{1}H NMR ($CDCl_3$) δ 0.98 (dd, J_{ab} = 28.6, J_{ac} = 6.7 Hz, J_{ac} = 12 H), 1.47 (m, 2 H), 2.48 (d, J = 7.6 Hz), splitting of ring hydrogen ^{13}C satellite = 2.4 Hz; MS, *m/e* (relative intensity) M^+ not observed, 113 (1.6), 73 (23.7), 72 (18.1), 71 (10.5), 57 (28.7), 56 (100.0), 55 (35.2), 43 (47.6), 41 (89.1). *cis*-3,4-Oxa-2,5-dimethylhexane: ^{1}H NMR ($CDCl_3$) δ 1.04 (dd J_{ab} = 44.2 Hz, J_{ac} = 6.6 Hz, 12 H), 1.48 (m, 2 H) 2.62 (m, 2 H), splitting of ^{13}C satellite = 4.4 Hz; MS, *m/e* (relative intensity), M^+ not observed, 113 (1.6), 73 (25.0), 72 (17.3), 71 (9.9), 57 (29.6), 56 (100.0), 43 (43.9), 41 (76.7). *trans*-3,4-Thia-2,5-dimethylhexane: MS, *m/e* (relative intensity) 146 (M + 2, 3.2) 145 (M + 1, 4.8), 144 (M^+, 44.2), 111 (19.0), 101 (35.8), 88 (32.2), 69 (100.0), 55 (81.9), 41 (71.2). *cis*-3,4-Thia-2,5-dimethylhexane: MS, *m/e* (relative intensity), 146 (M + 2, 3.4) 145 (M + 1, 7.3), 144 (64.7), 112 (20.6), 101 (26.7), 88 (61.6), 69 (99.4), 55 (100.0), 41 (82.3).

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Synthesis of (+)-Avermectin B_{1a}

Stephen Hanessian,* Antonio Ugolini, Daniel Dubé,
Paul J. Hodges, and Christiane André

Département of Chemistry, Université de Montréal
Montréal, Québec, Canada, H3C 3V1

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The avermectins[1–3] are a group of exceedingly potent anthelmintic agents which appear to exert their insecticidal activity by interfering with invertebrate neurotransmission.[4–6] Any aspirations toward a total synthesis of this group of 16-membered macrocyclic lactones with unique structural, functional, and to-

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