was treated with boiling EtOH (5 mL) to yield 96 mg (55%) of raw **9** (mp 230–238 °C dec). Pure **9** (yellow) was obtained by recrystallization from glacial AcOH: mp 238–241 °C dec. IR (KBr): 1690 (CO). ^{1}H NMR (300 MHz, Me_2SO-d_6): δ 7.75 (d, 1 arom H, J = 8 Hz), 7.28 (d, 1 arom H, J = 8 Hz), 6.60 (s, 1 arom H), 6.45 (s, 1 olef H), 6.00 (s, 2 H, OCH_2O), 3.99, 3.91, and 3.87 (3 s, 9 H, 3 CH_3O), 2.81 (s, 3 H, CH_3N) 2.60 (m, 4 H). Anal. Calcd for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.06; H, 5.37; N, 6.72.

Compound **9** was also obtained from **12**: A solution of **12** (200 mg, 0.44 mmol), 6 mL of EtOH, and 2 mL of 2 N HCl was kept at room temperature for 72 h, and then it was poured on ice-cooled dilute NH_4OH (20 mL). After extractions with CH_2Cl_2 (2 × 10 mL), the combined organic layers were washed with H_2O (2 × 10 mL), dried, and evaporated to give 172 mg of a red-brown oil which was crystallized from MeOH to yield 117 mg (65%; mp 233–237 °C dec). This material was identical with material obtained by the procedure described above by TLC, mixed melting point, IR, and ^{1}H NMR.

5,6,7,8-Tetrahydro-1,2,13-trimethoxy-6-methyl-[1,3]dioxolo[4′,5′:4,5]benzo[*f*]indeno[1,2-*c*]-1,2-diazocin-14-one (10). A solution of **8** (1.0 g, 2.15 mmol) in 20 mL of anhydrous EtOH/HCl was refluxed for 4 h and then poured on 100 mL of ice-cooled saturated $NaHCO_3$ solution. The red precipitate was collected and recrystallized from EtOH to give 137 mg (16%) of pure **10**: mp 277–279 °C dec. IR (KBr): 1645 (CO). ^{1}H NMR (300 MHz, Me_2SO-d_6): δ 8.60 (br s, 1 H, NH), 7.31 (d, 1 arom H, J = 8 Hz), 6.93 (d, 1 arom H, J = 8 Hz), 6.49 (s, 1 arom H), 5.96 (s, 2 H, OCH_2O), 3.87, 3.83, and 3.80 (3 s, 9 H, 3 CH_3O), 2.73 (m, 4 H), 2.57 (s, 3 H, CH_3N). Anal. Calcd for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.05; H, 5.51; N, 6.81.

2,3-Dimethoxy-6-[1,4,5,6-tetrahydro-11-methoxy-4-methyl-[1,3]dioxolo[4′,5′:4,5][3,4]benzodiazocin-2-yl]benzoic Acid Ethyl Ester (12). A solution of **7** (17.5 g, 42.3 mmol) in 80 mL of EtOH and 10.5 mL of triethylamine was refluxed for 17 h. Then the volume of the resulting red solution was reduced in vacuo by ca. two-thirds. During this operation, crystallization took place. After cooling, 12.3 g (73%; mp 140–146 °C) of **12** was obtained. For analysis, a small sample was recrystallized from EtOH: mp 147–150 °C. IR (KBr): 1720 (ester), 1685 (C=N). ^{1}H NMR (60 MHz, $CDCl_3$): δ 7.25 (d, 1 arom H. J = 8 Hz), 6.86 (d, 1 arom H, J = 8 Hz), 6.21 (s, 1 arom H), 5.78 (s, 2 H, OCH_2O), 4.18 (q, 2 H, CH_2CH_3, J = 7 Hz), 4.02 (s, 2 H, $ArCH_2$), 3.84 (s, 6 H, 2 CH_3O), 3.58 (s, 3 H, CH_3O), 2.93 (s, 4 H), 2.78 (s, 3 H, CH_3N), 1.26 (t, 3 H, CH_3CH_2, J = 7 Hz). CI-MS: m/z 457 (M^+ + 1). Anal. Calcd for $C_{24}H_{28}N_2O_7$: C, 63.15; H, 6.18; N, 6.14. Found: C, 62.92; H, 6.32; N, 6.17.

6,7,8,9,15,15a-Hexahydro-3,4,14-trimethoxy-7-methyl-[1,3]dioxolo[4′,5′:4,5][3,4]benzodiazocino[2,3-*a*]isoindol-5-one (13). A mixture of **12** (3.0 g, 6.57 mmol), 900 mg of 10% Pt/C, and 150 mL of EtOH was hydrogenated at 40 °C and 50 psi for 24 h. The catalyst was filtered off, the filtrate was evaporated, and the residue (colorless foam) was crystallized from EtOH (yield 1.6 g; 59%). An analytical sample was obtained by recrystallization from EtOH: mp 165 °C. IR (KBr): 1680 (CO). ^{1}H NMR (60 MHz, $CDCl_3$): δ 7.02 (dd, 2 arom H, J = 8, 8 Hz), 6.25 (s, 1 arom H), 5.76 (s, 2 H, OCH_2O), 4.28 (m, 1 H, ArCH), 3.92 (s, 3 H, CH_3O), 3.83 (s, 6 H, 2 CH_3O), 3.27 (m, 2 H), 2.91 (s, 3 H, CH_3N), 2.65 (m, 4 H). CI-MS: m/z 413 (M^+ + 1). Anal. Calcd for $C_{22}H_{24}N_2O_6$: C, 64.07; H, 5.87; N, 6.79. Found: C, 64.07; H, 5.98; N, 6.78.

6,7,8,9,15,15a-Hexahydro-3,4,14-trimethoxy-7-methyl-[1,3]dioxolo[4′,5′:4,5][3,4]benzodiazocino [2,3-*a*]isoindole (14). Compound **13** (500 mg; 1.22 mmol) was transferred with anhydrous Et_2O from a Soxhlet apparatus to a stirred and refluxing mixture of 100 mg of LAH and 15 mL of Et_2O under N_2 within 4 h. The mixture was stirred under reflux for an additional hour, and then excess LAH was destroyed with 30 mL of saturated Na_2SO_4 solution. The Et_2O phase was separated after addition of 10 mL of H_2O, the aqueous layer was extracted with Et_2O (2 × 10 mL), and the combined organic layers were dried and evaporated. The resulting slightly brown foam was crystallized from EtOH to yield 425 mg (88%) of **14** (mp 148–152 °C). A small sample was recrystallized from EtOH: mp 152–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (d, 1 arom H, J = 8 Hz), 6.82 (d, 1 arom H, J = 8 Hz), 6.42 (s, 1 arom H), 5.88 and 5.86 (2 d, 2 H, OCH_2O, J = 0.8 Hz), 4.22 (m, 1 H, ArCH), 4.16 (s, 2 H, $ArCH_2N$), 3.86 (s, 3 H, CH_3O), 3.80 (s, 6 H, 2 CH_3O), 2.28 (s, 3 H, CH_3N). EI-MS: m/z 398 (M^+). Anal. Calcd for $C_{22}H_{26}N_2O_5$: C, 66.32; H, 6.58; N, 7.03. Found: C, 6.11; H, 6.58; N, 6.94.

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Registry No. **6**, 128-62-1; **7**, 103937-31-1; **8**, 129917-22-2; **9**, 129917-23-3; **10**, 129917-24-4; **11**, 129942-14-9; **12**, 129917-25-5; **13**, 129917-26-6; **14**, 129917-27-7; DNPH, 17508-17-7; DPH, 72804-96-7.

Mechanistic Implications of Pyrophosphate Formation in the Oxidation of *O*,*S*-Dimethyl Phosphoramidothioate

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The chemical oxidation of phosphorothiolates **1** has been the subject of a number of studies that have emphasized the identification of intermediates in the reaction sequence.[1-6] Interest in the process was initiated by the desire to identify the potent in vivo phosphorylating species that are proposed to form via oxidative bioactivation of thiophosphorus insecticides. Chemical oxidation (Scheme I) is believed to involve the initial formation of a reactive *S*-oxide (**2**), which rearranges to a phosphinyloxy sulfenate (**3**), possibly via a phosphoranoxide.[2,3] Subsequent oxidation of **3** ultimately produces the phosphinyloxy sulfonate **4**, which is stable in the absence of nucleophilic species.

When the oxidation is performed in the absence of an added nucleophilic species, in addition to **4**, a significant fraction of the symmetrical pyrophosphate **5** is observed.[3,6] Formation of **5** is assumed to result from the reaction of one of the species **2**–**4** with the free acid **6** (eq 1), in turn formed by hydrolysis of **2**, **3**, or **4** by adventitious water in nominally dry solvents.[7] While investigating the oxi-

(1) Bellet, E. M.; Casida, J. E. *J. Agric. Food Chem.* **1974**, *22*, 207–211.
(2) Segall, Y.; Casida, J. E. In *Phosphorus Chemistry*; Quin, L. D., Verkade, J., Eds.; ACS Symposium Series 171, American Chemical Society: Washington D.C., 1981; pp 337–340.
(3) Segall, Y.; Casida, J. E. *Tetrahedron Lett.* **1982**, *23*, 139–142.
(4) Segall, Y.; Casida, J. E. *Phosphorus Sulfur* **1983**, *18*, 209–212.
(5) Thompson, C. M.; Castellino, S.; Fukuto, T. R. *J. Org. Chem.* **1984**, *49*, 1696–1699.
(6) Bielawski, J.; Casida, J. E. *J. Agric. Food Chem.* **1988**, *36*, 610–615.
(7) Mixed anhydride **4** has been described as an exclusively sulfonating agent (refs 2 and 4) which could not therefore form **5** by reaction with **6**, or as both a phosphorylating and sulfonating agent (ref 6). In dry methanol, **4** is exclusively phosphorylating (Dabkowski, W.; Michalski, J.; Radziejewski, C.; Skrzypczynski, Z. *Chem. Ber.* **1982**, *115*, 1636–1643).

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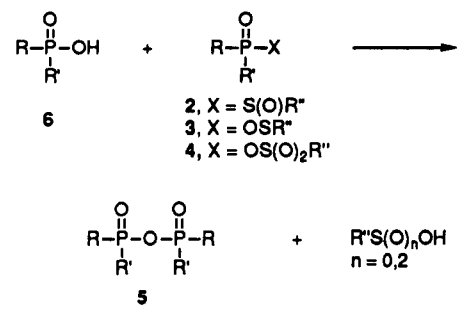
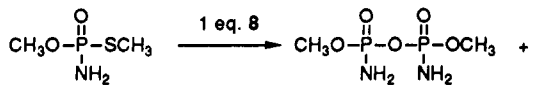
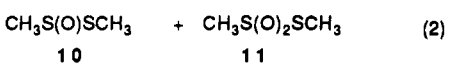


dation of phosphonothiolates,[8] we observed that the formation of pyrophosphates was enhanced by efforts to reduce the amount of water in the reaction, although this should reduce the formation of the intermediate acid. Hence the current study was undertaken.

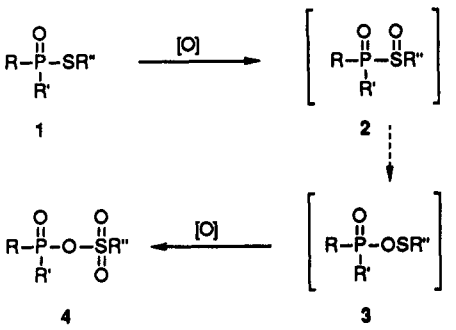
From a limited study of phosphono- and phosphorothiolate oxidation reactions, we found that pyrophosphate formation was greatest in the reaction of *O,S*-dimethyl phosphoramidothioate (**7**) with 2-(phenylsulfonyl)-3-(4-nitrophenyl)oxaziridine (**8**). Reaction of **7** with 1 equiv of **8** in dry, ethanol-free chloroform yielded *P,P'*-dimethyl diamidodiphosphate (**9**) in greater than 95% yield (50% conversion of **7**) after 2 h at 18 °C (eq 2). The identity



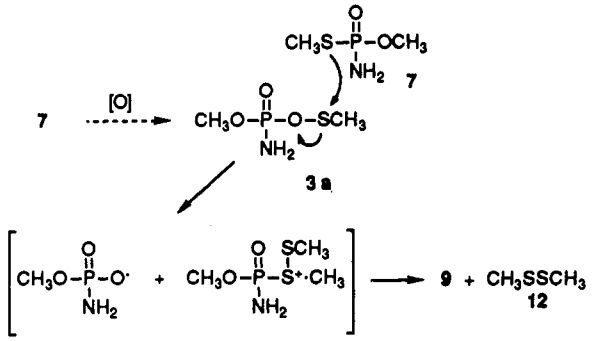


of the pyrophosphate was determined by its ^{31}P NMR spectrum (δ 1.21 and 1.43 for the diastereomers[9]), ^{1}H and ^{13}C NMR spectra,[10] GC/MS, and direct exposure probe MS of the reaction mixture (CI, M + 1 = 205). The *S*-methyl moiety was accounted for in the final reaction mixture as *S*-methyl methanethiosulfinate (**10**), *S*-methyl methanthiosulfonate (**11**), and a third unidentified product (^{1}H NMR: δ 3.22; ^{13}C NMR δ 38.3).[11] The structures of products **10** and **11** were confirmed by comparison of their NMR spectra (^{1}H and ^{13}C) and GC/mass spectra (CI) with authentic material prepared by oxidation of dimethyl disulfide.[12,13] Thiosulfonate **11** has previously been isolated from the *m*-chloroperbenzoic acid oxidation of **7**.[1,14] Neither methanesulfinic nor methanesulfonic acid were formed during the reaction. The absence of these acids is evidence that only one oxygen is transferred to the phosphorothiolate sulfur. Thus the involvement of more highly oxidized species in pyrophosphate formation can be excluded.

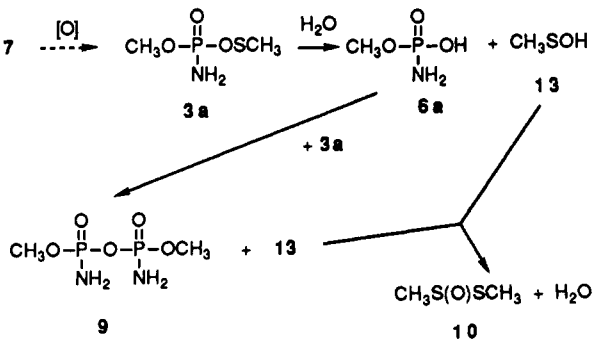
Scheme I



Scheme II



Scheme III



The concomitant formation of the dimethyl disulfide oxidation products **10** and **11** and pyrophosphate **9** suggested an alternate mechanism for the formation of **5** (Scheme II). Oxidation of **7**, followed by rearrangement, would first yield the mixed phosphoramidic/sulfenic acid anhydride **3a**. Subsequent nucleophilic attack upon the anhydride by the phosphorothiolate sulfur of a second molecule of **7** could then lead to the pyrophosphate and dimethyl disulfide. The susceptibility of the phosphorothiolate sulfur to oxidation by oxaziridine **8** is evidence of its nucleophilicity. The mechanism for oxidation by this reagent involves attack by a nucleophilic substrate on the electrophilic oxygen of the oxaziridine ring.[15] The oxidation of other phosphorothiolates by peracids suggests that the nucleophilicity of the sulfur in **7** is not unusual.[1-6] Oxidation of bivalent sulfur in organic compounds by peracids also involves attack upon electrophilic oxygen by nucleophilic sulfur.[16]

The presence of dimethyl disulfide (**12**) required by Scheme II was confirmed by GC/MS, but its concentration

(8) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K. *J. Am. Chem. Soc.* **1990**, *112*, 6621–6627.

(9) The ^{31}P chemical shift for **9**, presumed to have formed (although no supporting evidence for its presence was reported), in the 3-chloroperbenzoic acid oxidation of **7** has previously been reported as a single line at δ −6.53 or δ −5.74 (ref 3). In our hands, oxidation of **7** with 3-chloroperbenzoic acid resulted in a mixture of products, including **9**. The ^{31}P chemical shifts of diastereomeric **9** in this reaction solution were δ 1.6 and δ 1.2.

(10) NMR data for **9** (diastereomers): ^{13}C NMR δ 53.98 (d, $^{2}J_{POC}$ = 6 Hz), 54.02 (d, $^{2}J_{POC}$ = 6 Hz); ^{1}H NMR δ 3.84 (d, $^{3}J_{POCH}$ = 11.9 Hz), 3.86 (d, $^{3}J_{POCH}$ = 11.9 Hz).

(11) The ^{1}H and ^{13}C chemical shifts of the unidentified product do not correspond to those reported for any of the products detected in the 3-chloroperbenzoic acid oxidation of *S*-methyl methanethiosulfinate (**11**) (ref 12), although we found that it is formed in the oxidation of dimethyl disulfide by **8**. This product is not amenable to GC separation as we were unable to detect it using GC/MS.

(12) Allen, P.; Brook, J. W. *J. Org. Chem.* **1962**, *27*, 1019–1020.

(13) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4039–4049.

(14) Eto, M.; Okabe, S.; Ozoe, Y.; Maekawa, K. *Pest. Biochem. Phys.* **1977**, *7*, 367–377.

(15) Davis, F. A.; Billmers, J. M.; Gosciniak, D. J.; Towson, J. C. *J. Org. Chem.* **1986**, *51*, 4240–4245.

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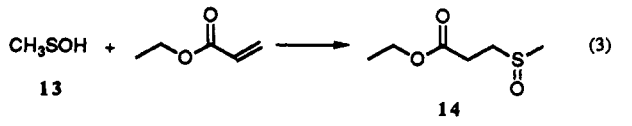
was insufficient for detection by ^1H NMR spectroscopy. In a separate experiment, dimethyl disulfide was found to react with 1 equiv of **8** in less than 15 min at 18 °C to give **10**. Addition of excess **8** resulted in formation of **11**. ^1H and ^{13}C NMR spectra of the reaction also revealed that the unidentified product formed from the *S*-methyl moiety in the oxidation of **7** is also present in the oxidation of dimethyl disulfide by **8**.

Scheme II is appealing because it accounts for all of the products formed in the reaction and does not require the involvement of water. Our procedure for the oxidation reaction must result in a very low concentration of water since the addition of 1 equiv of water to the reaction after all the oxidant was consumed and pyrophosphate formation had ceased resulted in hydrolysis of three quarters of the pyrophosphate formed within 1 h. Without the addition of water no hydrolysis is observed in the same period.

Provided a catalytic amount of water is present, the series of reactions shown as Scheme III also accounts for the products. As the final step of the sequence, methanesulfenic acid (**13**) dimerizes to *S*-methyl methanethiosulfinate (**10**), returning 1 equiv of water to the reaction. In all other respects, the scheme is identical with that previously described for pyrophosphate formation in peracid oxidation of phosphorothiolates.[3] Alkanesulfenic acids have been postulated as transient species in a variety of organic transformations, and their fleeting existence during the pyrolysis of alkanethiosulfonates has been confirmed by trapping as the addition product (**14**) with ethyl acrylate (eq 3).[17,18] In the absence of a trapping



agent, alkanesulfenic acids dimerize as shown in Scheme III.[17,18] The detection of dimethyl disulfide in the reaction is consistent with the reported disproportionation of **10** to dimethyl disulfide and **11**.[19]

Since formation of pyrophosphate **9** in Scheme III requires generation of the free acid **6a**, addition of a different phosphorus acid to the reaction should result in the formation of a mixed pyrophosphate. By itself, this would not prove the involvement of acid **6a** in the formation of the symmetrical pyrophosphate. However, we reasoned that if the free acid was involved then the presence of a pool of a different acid (nucleophile) should result in the accumulation of **6a** in solution. When reaction of **7** with 1 equiv of **8** was repeated with 0.2 equiv of isopropyl methylphosphonic acid (**15**) added to the solution, both the symmetrical and mixed pyrophosphates, **9** and **16**, respectively, formed. Identification of **16** relied upon its DEP/MS and NMR (^{31}P, ^{13}C, and ^1H) spectra.[20] In addition, acid **6a** accumulated in solution (Figure 1). After completion of the reaction, ^1H and ^{13}C NMR spectra of the reaction mixture indicated that *S*-methyl methanethiosulfinate (**10**), *S*-methyl methanthiosulfonate (**11**), and the unidentified product (^1H NMR: δ 3.22; ^{13}C NMR: δ 38.3) were present in approximately the same proportions observed in the reaction without the pool of free acid. Since the fate of the *S*-methyl moiety is the same in both reactions, a common pathway for formation of **9** and **16** is implicated.

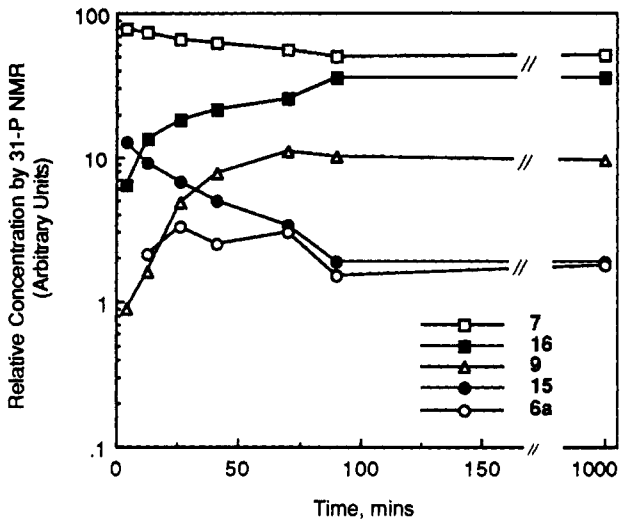
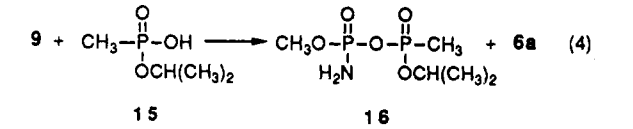


Figure 1. Product and reactant concentrations during the oxidation of *O,S*-dimethyl phosphoramidothioate (**7**) by **8** in the presence of 0.2 equiv of 2-methylethyl methylphosphonic acid (**15**).

The alternate explanation, that **16** forms via nucleophilic substitution of the symmetric pyrophosphate **9** by acid **15** (eq 4), was discounted for the following reasons. Firstly,



the presence of **16** soon after initiation of reaction and at a much higher concentration than **9** may be used to argue against this possibility (Figure 1). Secondly, when the above reaction was repeated with the same amount of free acid **15** added *after* all of the oxidant was consumed and pyrophosphate formation was complete, subsequent generation of the mixed pyrophosphate was slow. After 16 h, the concentration of the mixed pyrophosphate was only two-thirds that of **9**. Thus the involvement of the free acid **6a** in formation of the symmetrical pyrophosphate **9** has been demonstrated.

The products observed in the reaction with the added acid are also consistent with Scheme II, provided the added phosphorus acid could displace the phosphoramidate anion from the proposed transient ion pair. Demonstration of the involvement of methanesulfenic acid in the reaction is necessary to differentiate between the alternate pathways. To this end, the oxidation of **7** was repeated in the presence of 20 equiv of ethyl acrylate. An intense ion at *m/z* 165, which was absent in control experiments, was detected by direct exposure probe CI/MS of the reaction solution. This is consistent with the protonated molecular ion of ethyl 3-(methylsulfinyl)propionate (**14**), the methanesulfenic acid/ethyl acrylate adduct. Formation of **14** was confirmed by the ^1H and ^{13}C NMR spectra of the reaction mixture, which contained resonances identical with those obtained for an authentic sample of **14** prepared

(17) Block, E. *J. Am. Chem. Soc.* **1972**, *94*, 642–644.
(18) Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3929–3944.
(19) Douglass, I. B. *J. Org. Chem.* **1959**, *24*, 2004–2006.
(20) DEP/MS (CI) of **16**: M + 1 = 205. NMR data (diastereomers): ^{31}P NMR δ 22.9 (d, $^2J_{POP}$ = 24 Hz, CH_3POPNH_2), 22.95 (d, $^2J_{POP}$ = 24 Hz, CH_3POPNH_2), 1.5 (d, $^2J_{POP}$ = 24 Hz, CH_3POPNH_2), 1.1 (d, $^2J_{POP}$ = 24 Hz, CH_3POPNH_2); ^1H NMR δ 1.36 (d, $^2J_{HCH}$ = 6.4 Hz, 3 H, $(CH_3)_2CHOP$)), 1.37 (d, $^2J_{HCH}$ = 6.4 Hz, 9 H, $(CH_3)_2CHOP$)), 1.67 (d, $^2J_{PCH}$ = 18.2 Hz, 3 H, $POPCH_3$), 1.70 (d, $^2J_{PCH}$ = 18.2 Hz, 3 H, $POPCH_3$), 3.83 (d, $^3J_{POCH}$ = 12.0 Hz, 3 H, $POPOCH_3$), 3.84 (d, $^3J_{POCH}$ = 12.0 Hz, 3 H, $POPOCH_3$), 4.87 (m, 2 H, $POPOCH(CH_3)_2$); ^{13}C NMR δ 12.9 (d, $^1J_{PC}$ = 146 Hz, PCH_3), 13.1 (d, $^1J_{PC}$ = 146 Hz, PCH_3), 23.6 (d, $^3J_{POCC}$ = 4.5 Hz, $POCH{\cdot}CH_3{\cdot}CH_3$), 23.7 (d, $^3J_{POCC}$ = 4.5 Hz, $POCH{\cdot}CH_3{\cdot}CH_3$), 24.0 (d, $^3J_{POCC}$ = 4.5 Hz, 2 x $POCH{\cdot}CH_3{\cdot}CH_3$), 53.8 (d, $^2J_{POC}$ = 6 Hz, $POCH_3$), 53.9 (d, $^2J_{POC}$ = 6 Hz, $POCH_3$), 72.3 (d, $^2J_{POC}$ = 7.5 Hz, $POCH(CH_3)_2$), 72.4 (d, $^2J_{POC}$ = 7.5 Hz, $POCH(CH_3)_2$).

by thermal decomposition of methyl methanethiosulfinate (10) in ethyl acrylate.[17,18] Methanesulfenic acid has therefore been shown to form during the reaction. The involvement of the free acid **6a** and the transitory presence of methanesulfenic acid indicate that formation of the symmetric pyrophosphate **9** by oxidation of *O,S*-dimethyl phosphoramidothioate (**7**) occurs, at least in part, via the sequence of reactions given as Scheme III.

Trapping of the highly reactive methanesulfenic acid was expected to limit its concentration in solution, thereby preventing dimerization to **10** and subsequent oxidation to **11**. In turn, this removes water from the reaction manifold, thereby inhibiting formation of **9** by the mechanism shown in Scheme III. Although the methanesulfenic acid/ethyl acrylate addition product formed when the oxidation of **7** was performed with the trapping agent present, the major products from the *S*-methyl moiety of **7** were still the dimethyl disulfide oxidation products **10** and **11**. The dominant phosphorus-containing product in this reaction was pyrophosphate **9** (>95% yield, 45% conversion).

These observations suggest that formation of **9** also occurs via Scheme II. Support for this mechanism may be elicited from the oxidation of **7** by **8** in the presence of ethyl acrylate (20 equiv) and methanol (2.5 equiv). The major phosphorus product from this reaction is *O,O*-dimethyl phosphoramidate (**17**), formed by displacement of methanesulfenic acid from **3a** by methanol.[21] Formation of methanesulfenic acid was confirmed by the presence of **14** in the reaction solution. *S*-Methyl methanethiosulfinate (**10**) was not detectable by GC/MS in this solution. Thus, in the presence of ethyl acrylate, methanesulfenic acid does not dimerize. Formation of **10** in the oxidation of **7** by **8**, in the presence of ethyl acrylate, could not then have occurred by this process.

(21) Formation of **17** was confirmed by GC/MS (CI, M + 1 = 126) and multinuclear NMR: ^{31}P NMR δ 12.6 (septet, $^{3}J_{POCH}$ = 11.2 Hz) [lit. (Nielsen, M. L.; Pustinger, J. V.; Strobel, J. *J. Chem. Eng. Data* **1964**, *9*, 167–170), δ 15.2]; ^{1}H NMR δ 3.75 (d, $^{3}J_{POCH}$ = 11.2 Hz); ^{13}C NMR δ 53.3 (d, $^{2}J_{POC}$ = 5.6 Hz).

In summary, the formation of *P,P'*-dimethyl diamidodiphosphate (**9**) in the oxidation of *O,S*-dimethyl phosphoramidothioate (**7**) does not require the involvement of water. Scheme II provides a plausible mechanism for the pyrophosphate formation, consistent with all the experimental observations.

Experimental Section

O,S-Dimethyl phosphoramidothioate (**7**) (>98%) was obtained from the EPA Pesticide Repository and ethyl acrylate (>99%) from Chem Services. 2-(Phenylsulfonyl)-3-(4-nitrophenyl)oxaziridine (**8**) was prepared at Drexel University and chloroform was dried over 5A molecular sieves prior to use. 2-Methylethyl methylphosphonic acid (**15**) was available within the laboratory (CRDEC) and had a purity of greater than 95% by NMR.

Reactions were performed in 5-mm NMR tubes by mixing aliquots of standard chloroform solutions of the reactants, which were stored over molecular sieves. Typically, 8–10 mg of **7** was oxidized with ca. 1 equiv of **8**, giving a concentration of each reactant of about 0.05 M. ^{31}P, ^{1}H, and ^{13}C NMR were used to monitor the reactions. Identification of products was performed on separate solutions prepared in $CDCl_3$, using 4 mg of **7** with ca. 2 equiv of **8**, and in the case of **16**, ca. 1 equiv of **15** was also added. Spectra were recorded at probe temperature (ca. 20 °C). ^{31}P spectra were referenced to external 85% H_3PO_4, while ^{13}C and ^{1}H spectra were referenced to the solvent ($CHCl_3$, ^{13}C NMR: δ 77.2, ^{1}H NMR: δ 7.27; or $CDCl_3$, ^{13}C NMR: δ 77.0). Gas chromatography/mass spectrometry (GC/MS) was performed with a 25 m × 0.25 mm i.d. fused silica GB-1 column coated with 0.25-μm dimethylpolysiloxane (Analabs, North Haven, CT). Reagent gas used for CI analysis was methane at a source pressure of 0.6 Torr. The DEP filament for direct exposure probe MS was ramped from 0 to 1.0 A at 0.2 A/s.

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Supplementary Material Available: NMR spectra (^{31}P, ^{1}H, and ^{13}C) and CI DEP mass spectra of $CDCl_3$ solutions in which **9** and **16** are identified (11 pages). Ordering information is given on any current masthead page.