Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada and the University of Alberta for generous financial support. Grateful acknowledgments are also made to the Alexander von Humboldt-Stiftung, Bonn, FRG, for the award of a Feodor-Lynen-Stipendium to F.S. and to NSERC (Canada) for Undergraduate Summer Research Awards to M.J.B. and J.W.

Supplementary Material Available: Characteristic data (IR, NMR, MS, and elemental analysis) on compounds **4–6** (1 page). Ordering information is given on any current masthead page.

Generation and Trapping of *O*-Alkyl Metathiophosphates

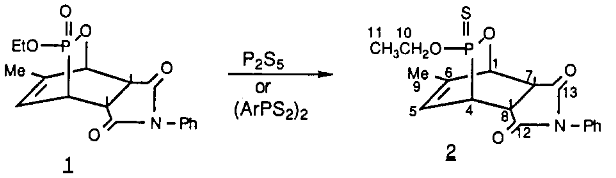
Louis D. Quin,* Narayan D. Sadanani, and Xiao-Ping Wu

Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003

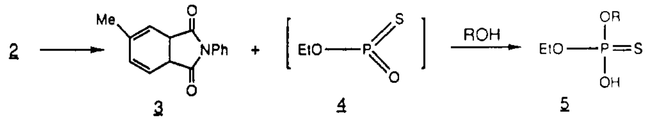
Received September 19, 1988
Revised Manuscript Received June 12, 1989

We have synthesized the first P-sulfides with the 2,3-oxaphosphabicyclo[2.2.2]octene ring system. These compounds are of interest since the P–O bridging unit might be eliminated to produce the first examples of the family of alkyl metathiophosphates, RO–P(S)O. This possibility is suggested from previously reported results with P-oxides in this series, whose fragmentation by both thermal[1] and photochemical[2] means to form alkyl metaphosphates has been studied. No previous attempts to generate alkyl metathiophosphates have been reported, although the anion (PSO_2^-) of the corresponding acid has been detected as a transient species in solution.[3,4] This anion appears to be more stable than PO_3^-, and a salt of the anion PS_3^- has actually been isolated and characterized.[5]

A precursor for O-ethyl metathiophosphate has structure **2**; it was prepared as a crystalline solid, mp 138–139 °C, isolated in 35–40% yield, by thionation of ester **1** (with retention of configuration[6]) with phosphorus pentasulfide or Lawesson's reagent, (p-$CH_3OC_6H_4PS_2)_2$. These reactions are best conducted at room temperature in CH_2Cl_2 to prevent loss of the P–O bridging unit; 5–6 days are required for complete reaction. Compound **2** has been characterized by elemental analysis (C, H, N) and by NMR spectral measurements.[7]



On being heated in dry toluene for 2 h at 110 °C, **2** was completely consumed in a fragmentation process that produced the known[1] dienic compound **3**, and hence is presumed to release the bridging unit as *O*-ethyl metathiophosphate (**4**). The complexity of the ^{31}P NMR spectrum of the reaction mixture suggested that **4** reacted immediately to form other products. However, when ethyl or isopropyl alcohols (about 1 equiv) were included in the reaction mixture as trapping agents, the ^{31}P NMR spectrum was totally different and possessed only one significant signal, in the region expected for an *O*,*O*-dialkyl thionophosphate (**5**), as would arise from a reaction of the alcohol with an initially generated metathiophosphate. Compound **5a** (lit.[8] δ ^{31}**P** 64) was isolated by chromatography on silica gel, with elution by methanol, and its structure confirmed through spectral studies.[9] Similarly, the new ester **5b** was synthesized and characterized.[10]



5a, R=Et, δ ^{31}P ($CDCl_3$) 63.9
5b, R=i-Pr, δ ^{31}P ($CDCl_3$) 61.2
5c, R=t-Bu, δ ^{31}P ($CDCl_3$) 56.5

Compound **2** (in dioxane or acetonitrile) was also fragmented efficiently on irradiation at 254 nm in the quartz apparatus described elsewhere.[2] The reaction was complete in a few hours at ambient temperatures (around 35 °C). When 1 equiv of ethanol or 2-propanol was present, the released phosphorus fragment was cleanly trapped, as in the thermal fragmentation, as **5a** and **5b**, respectively. From *tert*-butyl alcohol, thionophosphate **5c** was most efficiently formed when triethylamine[2] was also present.

The mechanism of these thermal and photochemical fragmentations (concerted or stepwise) has not yet been studied, but from the alcohol-trapping reactions the structure of the P-containing fragment at the time of its release from the carbon framework seems reasonably represented as that of a metathiophosphate. To provide confirmation of this proposal, we have prepared a metathiophosphate precursor with an optically active O-substituent. Our postulate was that a metathiophosphate with such a substituent would give two diastereomeric thionophosphates on attack of an alcohol, since a new chiral center is being created at phosphorus. The diastereomers should form in equal or nearly equal amounts, since the metathiophosphate is presumably planar and attack of the alcohol could occur at both faces with equal probability, except possibly for a small asymmetric induction effect. This postulate follows from the observation that the metaphosphate ion $^{16}O^{17}O^{18}OP^-$, when generated by the action of base on an aryl phosphate, gives a racemic mixture on reaction with an alcohol.[11] This is taken as proof of the existence of the planar metaphosphate ion as a free species. We therefore synthesized the (*S*)-*sec*-butyl ester **6** by the same procedure used for **2**, giving a mixture of diastereomers having δ ^{31}P NMR ($CDCl_3$) 86.50 and 87.05, and having the expected ^1H and ^{13}C NMR spectra and elemental analysis. When ester **6** was heated in toluene with ethanol present, the expected thionophosphate **8** was formed, as determined by ^{31}P, ^{13}C, and ^1H NMR analysis. However, the product was seen to be a 1:1 mixture of isomers; this was especially evident from

---

(1) Quin, L. D.; Marsi, B. G. *J. Am. Chem. Soc.* **1985**, *107*, 3389.

(2) Quin, L. D.; Pete, B.; Szewczyk, J.; Hughes, A. N. *Tetrahedron Lett.* **1988**, *29*, 2627.

(3) Harnett, S. P.; Lowe, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1416.

(4) Cullis, P. M.; Misra, R.; Wilkins, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1594.

(5) Roesky, H. W.; Ahlrichs, R.; Brode, S. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 82.

(6) Quin, L. D.; Osman, F. H.; Day, R. O.; Hughes, A. N.; Wu, X.-P.; Wang, L.-Q. *New J. Chem.* In press.

(7) Calcd for $C_{17}H_{18}NO_4PS$: C, 56.1; H, 4.99; N, 3.85. Found: C, 56.0; H, 5.08; N, 3.78. ^{31}P NMR ($CDCl_3$, 121.4 MHz) δ +86.1 (downfield from H_3PO_4); ^1H NMR ($CDCl_3$, 200 MHz, couplings confirmed by 2D COSY) δ 1.31 (t, 3 H, $^3J_{HH}$ = 7.0 Hz, H-11), 1.96 (d of d, 3H, J = 1.8 and 4.7 Hz, H-9), 3.62–3.72 (m, 1 H, H-4), 3.89–3.94 (m, 2 H, H-7,8), 4.13–4.30 (m, 2 H, H-10), 5.21 (d of m, 1 H, $^3J_{PH}$ = 21.4 Hz, H-1), 6.12 (m, 1 H, H-5), 7.1–7.5 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$, 50.31 MHz), δ 16.3 (J_{PC} = 5.7 Hz, C-11), 19.9 (J_{PC} = 2.6 Hz, C-9), 38.4 (s, C-8), 39.8 (J_{PC} = 93.9 Hz, C-4), 45.8 (J_{PC} = 8.8 Hz, C-7), 64.4 (J_{PC} = 6.2 Hz, C-10), 77.7 (J_{PC} = 5.7 Hz, C-1), 122.8 (J_{PC} = 12.9 Hz, C-5), 140.2 (J_{PC} = 13.3 Hz, C-6), 172.9 (s, C-13), 175.3 (J_{PC} = 22.8 Hz, C-12), C_6H_5 at 126.2, 129.1, 129.3, 131.3.

(8) Mlotkowska, B.; Zwierzak, A. P. *J. Prakt. Chem.* **1978**, *320*, 777.

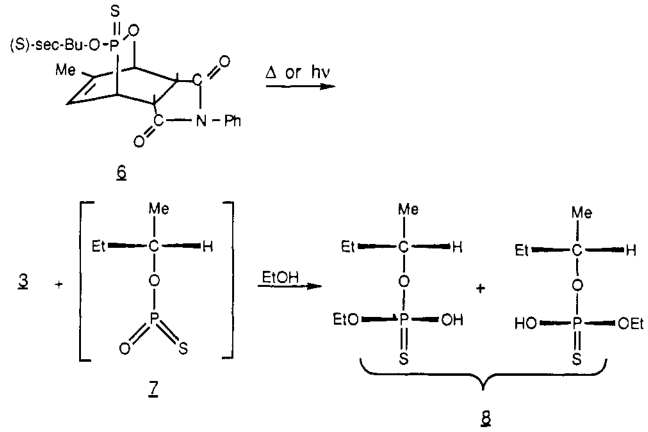
(9) Mass spectrum: calcd for M^+, 170; found m/z 170. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.29 (t, J_{HH} = 6.9 Hz, CH_3), 4.0 (m, CH_2); ^{13}C NMR ($CDCl_3$, 50.31 MHz) δ 16.2 (J_{PC} = 3.0 Hz, CH_3), 62.7 (J_{PC} = 4.0 Hz, CH_2).

(10) ^1H NMR (D_2O, 80 MHz) δ 1.17 (d, J = 6.4 Hz, Me_2C), 1.25 (t, J_{PH} = 7 Hz, CH_3CH_2), 3.7–4.2 (m, 2 H, OCH_2), 4.3–4.6 (m, 1 H, OCH); ^{13}C NMR ($CDCl_3$, 50.31 MHz), δ 16.2 (J_{PC} = 8.4 Hz, CH_3CH_2), 23.7 (J_{PC} = 4.0 Hz, CH_3CH), 24.0 (J_{PC} = 4.7 Hz, CH_3CH), 63.0 (J_{PC} = 5.3 Hz, CH_2), 71.7 (J_{PC} = 3.5 Hz, CH).

(11) Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 6126. Freeman, S.; Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3166.

0002-7863/89/1511-6852$01.50/0

the ^{31}P NMR (CDCl$_3$) spectrum, which consisted of two signals of equal intensity at δ 61.03 and 61.10 on a 300-MHz spectrometer. This product composition is that expected from planar metathiophosphate **7**; no other process (e.g., formation of a P(V) adduct by attack of ethanol on **6** followed by fragmentation) can be visualized that would give this stereochemical result. Furthermore, we obtained exactly the same stereochemical result when ester **6** was fragmented photochemically in the presence of ethanol, which constitutes proof that the same planar species **7** was generated in both the thermal and photochemical processes. Direct observation of a metathiophosphate remains desirable, however, and appropriate experiments are in progress.



Acknowledgment. This work was supported by grants from the Army Research Office and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Synthesis, Reactivity, and Crystal Structure of the First Methylenephosphonium Ion: A Severely Twisted Valence Isoelectronic Olefin

Alain Igau,[†] Antoine Baceiredo,[†] Hansjorg Grützmacher,[‡]
Hans Pritzkow,[‡] and Guy Bertrand*,[†]

Laboratoire de Chimie de Coordination du CNRS
205, route de Narbonne
31077 Toulouse Cêdex, France
Anorganische Chemisches Institut der Universität
Im Neuenheimer Feld 270
D-6900 Heidelberg, West Germany

Received March 13, 1989

In the course of the development of low coordinated heavier main group element chemistry, several types of phosphorus–carbon double-bonded derivatives (A,[1] B,[2] C,[3] D[4]) and of phosphorus cations (F,[5] G) have been structurally characterized. In contrast, no X-ray data are available concerning tricoordinated phosphorus cation H.[6] Methylenephosphonium ions (I) have only been postulated as transient intermediates[7] but never isolated.[8,9] This new class of phosphorus cation is of special interest since they are valence isoelectronic to olefins and have been computed to be planar with a short phosphorus–carbon bond length.[10] Here we wish to report the first example of an isolable methylenephosphonium salt, a molecule containing a short but strongly distorted phosphorus–carbon double bond.

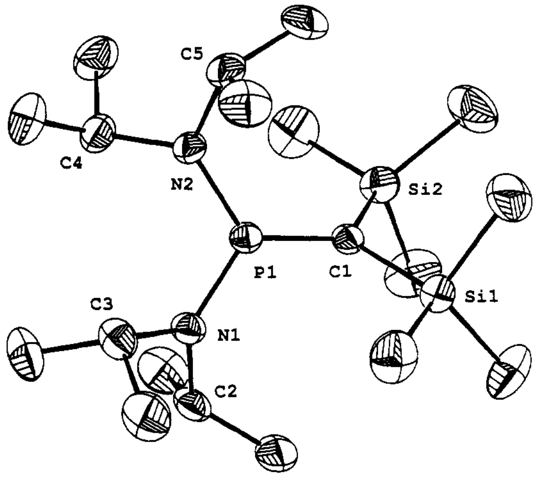
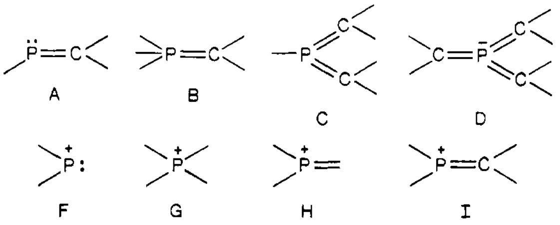


Figure 1. Thermal ellipsoid diagram (30% probability) of methylenephosphonium **2** showing the atom numbering scheme. Pertinent bond lengths (Å) and bond angles (deg) are as follows: P1–C1 1.620 (3), C1–Si1 1.875 (3), P1–N1 1.615 (3), C1–Si2 1.913 (3), P1–N2 1.610 (3); N1–P1–C1 123.4 (1), C2–N1–P1 121.0 (2), N2–P1–C1 124.4 (1), C3–N1–P1 123.1 (2), N2–P1–N1 112.2 (1), C2–N1–C3 115.6 (2), Si1–C1–P1 121.7 (1), C4–N2–P1 120.2 (2), Si2–C1–P1 119.3 (1), C5–N2–P1 124.4 (2), Si2–C1–Si1 119.1 (1), C4–N2–C5 115.1 (2).



Starting from the recently reported stable nucleophilic phosphinocarbene **1**,[11] a novel entry to the desired ion I was apparent. Addition of trimethylchlorosilane to **1** led to phosphorus ylide **3**[11a] suggesting that the use of silyl derivative containing a non-nucleophilic anion would afford **2**. Reaction of [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene (**1**) with trimethylsilyl triflate at room temperature gave clean conversion to methylenephosphonium ion **2** (yellow crystals extremely air sensitive, mp 80 °C dec, 70% yield).[12]

[†] Laboratoire de Chimie de Coordination du CNRS.

[‡] Anorganische Chemisches Institut der Universität.

(1) For reviews see: (a) Markovski, L. N.; Romanenko, V. D.; Rouban, A. V. *Acyclic Dicoordinated Phosphorus Derivatives*; Kiev-Science, 1988. (b) Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73. (c) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.

(2) For a review see for example: Bestmann, H. J.; Zimmermann, R. *Methoden der organischenchemie* (*Houben-Weyl*); Band E1, Thieme, Stuttgart, 1982.

(3) See for example: Appel, R.; Gaitzsch, E.; Dunker, K. H.; Knoch, F. *Chem. Ber.* **1986**, *119*, 535.

(4) Appel, R.; Gaitzsch, E.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 589.

(5) For a review see: Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.

(6) See for examples: (a) Rahil, J.; Haake, P. *J. Org. Chem.* **1981**, *46*, 3048. (b) Michalski, J.; Radziejewski, C.; Skrypczynski, Z.; Dabrowski, W. *J. Am. Chem. Soc.* **1980**, *102*, 1974. (c) Maier, L. *Z. Anorg. Allg. Chem.* **1966**, *345*, 29. (d) Marre, M. R.; Sanchez, M.; Wolf, R. *Phosphorus Sulfur* **1982**, *13*, 327. (e) Sanchez, M.; Marre, M. R.; Brazier, J. F.; Bellan, J.; Wolf, R. *Ibid.* **1983**, *14*, 331. (f) Mulliez, M.; Majoral, J. P.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1984**, 284.

(7) Van der Knaap, Th. A.; Bickelhaupt, E. *Tetrahedron Lett.* **1982**, *23*, 2037.

(8) Abstraction of chloride by AlCl$_3$ from a *P*-chloromethylenephosphorane was claimed by Appel et al.[9] to give a methylenephosphonium ion as characterized by ^{31}P NMR and elemental analysis. However, the relatively high field ^{31}P chemical shift of the product makes this assignment unlikely.

(9) Appel, R.; Schmitz, R. *Chem. Ber.* **1983**, *116*, 3521.

(10) Lohr, L. L.; Schlegel, H. B.; Morokuma, K. *J. Phys. Chem.* **1984**, *88*, 1981.

(11) (a) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. (b) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem.* **1989**, *101*, 617.