Hypervalent Phosphorus Compounds with Sulfur-Containing Eight-Membered Rings. Nature of the Leaving Group on Hydrolysis to Acyclic vs Cyclic Phosphates[1,2]

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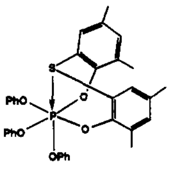
Reactions of phosphites with diols in the presence of *N*-chlorodiisopropylamine in ether solution led to new compounds formulated as the bicyclic tetraoxyphosphorane, $[S(Me_2C_6H_2O)_2]_2PNMe_2$ (**1**), the hexacoordinated pentaoxyphosphorane, $S[(t\text{-}Bu)_2C_6H_2O]_2P(Me_2C_3H_4O_2)(OCH_2CF_3)$ (**2**), with a P-S interaction indicated by ^{31}P NMR, and the two phosphates, $\{(CH_3CH_2CH_2)(CH)[t\text{-}Bu)_2C_6H_2OH]_2\}_2P(O)(OCH_2CF_3)$ (**3**) and $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$ (**4**), resulting from hydrolysis reactions. The X-ray structures of **1** and **4** were obtained, and all were characterized by NMR spectral measurements in solution. Phosphorane **1** possessed a trigonal bipyramidal geometry displaced 29% toward a rectangular pyramid. The lack of P-S coordination, potentially available from the two attached eight-membered ring systems, is attributable to strong P-N π bonding. X-ray analysis shows **4** to form as an acyclic phosphate rather than a cyclic phosphate. This is attributed to the presence of the poor OXyl leaving group. It is proposed that the hydrolysis process leading to acyclic and cyclic phosphates proceeds by way of a hexacoordinated intermediate that forms as a result of P-S coordination. Phosphorane **1** crystallizes in the monoclinic space group $C2/c$ with $a = 26.034(5)$ Å, $b = 15.230(2)$ Å, $c = 24.687(2)$ Å, $\beta = 131.31(1)°$, and $Z = 8$. Phosphate **4** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.971(4)$ Å, $b = 22.572(3)$ Å, $c = 10.800(2)$ Å, $\beta = 109.25(2)°$, and $Z = 4$. The final conventional unweighted residuals are 0.059 (**1**) and 0.035 (**4**).

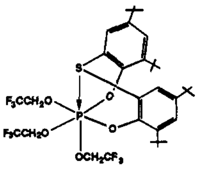
Introduction

Previous X-ray work[3-7a] on cyclic pentaoxyphosphoranes showed that a sulfur atom located in an eight-membered ring was capable of interacting with phosphorus such that a series of hexacoordinated structures resulted. The degree of octahedral character varied from 44.1% to 70.8% as the P-S distance decreased from 2.880(1) to 2.373(5) Å.[7] Representative examples **A**-**C** are shown as follows:[3,5,7a] In this class of compounds, of which there are six whose X-ray structures have been determined,[3-5,7a] sulfur coordination serves to increase the P-O bond distances.[7a] Compared to **D**, which is pentacoordinated and lacks P-S bonding,[3] the average P-O bond distance for the hexacoordinated oxyphosphoranes is 1.655(3) Å,[7a] whereas the average for **D** is 1.632(6) Å.[3]



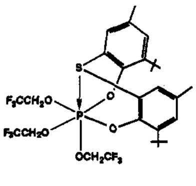
P-S = 2.880(1)Å

A[5]



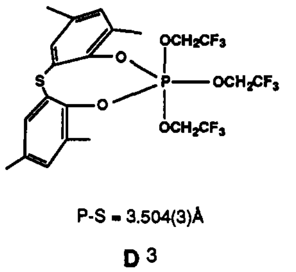
P-S = 2.504(3)Å

B[3]



P-S = 2.382(2)Å

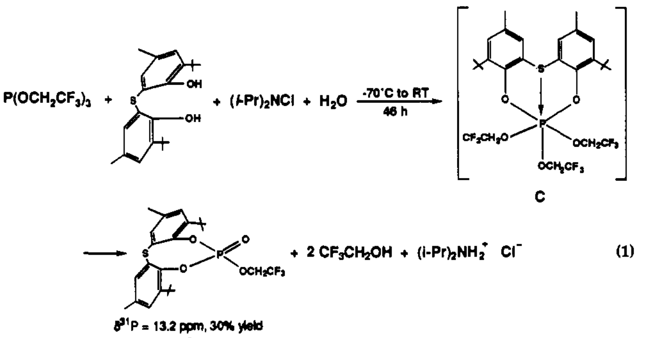
C[7]



P-S = 3.504(3)Å

D 3

It has been speculated that hydrolysis reactions of phosphites in the presence of sulfur in this type of ring system may very well proceed by way of hexacoordinated formulations that assume a catalytic role.[2] For example, we have found that the hydrolysis reaction depicted in eq 1occurs if moisture is not rigorously excluded.[7a] This process results in cyclic phosphate E_1[7a] postulated to form via the intermediate hexacoordinated state, **C**.[2] E_1 like **C** had its X-ray structure determined. In the absence of water, the reactants of eq 1 lead to oxidative addition over a period of 56 h yielding the hexacoordinated phosphorane **C** in 76% yield with a ^{31}P chemical shift of -82.2 ppm.[7a] The X-ray structure of the cyclic phosphate E_2 containing a diol as a hydrogen-bonded solvate also has been obtained.[7a] The latter resulted from the



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[*] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

(1) (a) Pentacoordinated Molecules. 99. (b) Part 98: Deiters, J. A.; Holmes, R. R. Submitted for publication.

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(7) (a) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993,** *32,* 4360. (b) The degree of structural displacement from a square pyramid toward an octahedron is based on the distance of the phosphorus atom from the base plane of the square pyramid.[7a]

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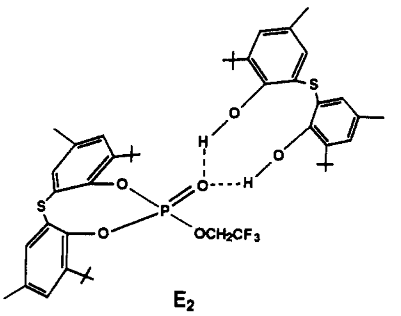
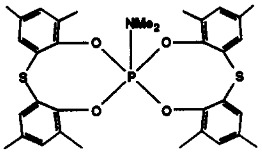
presnce of excess diol and a longer reaction time than that used for the formation of $\mathbf{E}_1$.



$\mathbf{E}_2$

In the present paper, we wish to report the effect of including two sulfur-containing rings in promoting P–S coordination in the presence of a P–N bond. For this purpose, the tetraoxyphosphorane $[S(Me_2C_6H_2O_2)_2]_2PNMe_2$ (**1**) was synthesized. It is reasoned that due to the presence of two potential sulfur donor atoms and a nitrogen atom capable of back-bonding P–O bond activation may be increased. Also of interest is the role that the leaving group takes in a hydrolysis process like that described in eq 1 in the presence of a sulfur-containing diol capable of cyclization. Tris(2,6-dimethylphenyl) phosphite, $P(OXyl)_3$, having a poorer leaving group compared to $P(OCH_2CF_3)_3$, was taken for this study. The resultant phosphate formed, $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$ (**4**),as well as the bicyclic phosphorane (**1**) was subjected to X-ray analysis and NMR characterization. In addition, the bicyclic pentaoxyphosphorane $S[(t\text{-}Bu)_2C_6H_2O]_2P(Me_2C_3H_4O_2)(OCH_2CF_3)$ (**2**) and the phosphate $\{(CH_3CH_2CH_2)(CH)[(t\text{-}Bu)_2C_6H_2OH]_2\}_2P(O)(OCH_2CF_3)$ (**3**) were synthesized and characterized by solution-state NMR spectral measurements. The latter compound, **3**, contained a $(CH_2CH_2CH_2)CH$ group in place of a sulfur atom.



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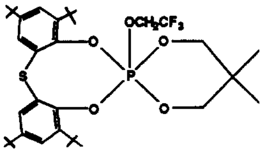

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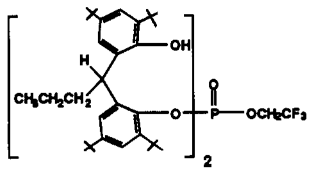

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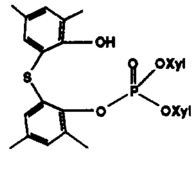

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Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, Eastman, or Fluka and used without further purification. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[8]

^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian XL 300 FT-NMR spectrometer and reported in ppm. ^1H and ^{19}F chemical shifts are recorded relative to tetramethylsilane and fluorotrichloromethane (external), respectively. Chemical shifts for ^{31}P NMR spectra were obtained by setting triphenyl phosphate[9] ($CDCl_3$) at −18.0 ppm and are referenced to 85% H_3PO_4 with negative shifts upfield. All NMR spectra were obtained at 23 °C.

Tris(dimethylamino)phosphine, $P(NMe_2)_3$, and tris(2,2,2-trifluoroethyl) phosphite, $P(OCH_2CF_3)_3$, were purchased from Fluka and Aldrich, respectively. Tris(2,6-dimethylphenyl)phosphite,[10] $P(OXyl)_3$, 2,2′-butylidenebis(4,6-di-*tert*-butylphenol),[11] and [thiobis(4,6-di-*tert*-butyl-*o*-phenylene)dioxy)](2,2,2-trifluoroethoxy)phosphine, $[(t\text{-}Bu)_4C_{12}H_4SO_2]POCH_2CF_3$,[4] 2,2′-thiobis(4,6-dimethylphenol),[12] and *N*-chlorodiisopropylamine[13] were prepared by literature methods. All the reactions were carried out in a dry nitrogen atomosphere using standard Schlenk-type glassware.[14]

Syntheses. Bis[thiobis(4,6-dimethyl-*o*-phenylene)dioxy](dimethylamino)phosphorane, $[S(Me_2C_6H_2O)_2]_2PNMe_2$ (1). To a mixture of tris(dimethylamino)phosphine (2.00 mL, 1.80 g, 11.0 mmol) and 2,2′-thiobis(4,6-dimethylphenol) (3.01 g, 11.0 mmol) in diethyl ether (100 mL) maintained at −70 °C was added dropwise a solution of *N*-chlorodiisopropylamine (1.70 mL, 1.63 g, 12.0 mmol) in diethyl ether (50 mL) over a period of 20 min with continuous stirring. The reaction was brought gradually to 25 °C and stirred at this temperature for 44 h. The solvent was removed under reduced pressure, and the resulting residue extracted with a 1:1 mixture (50:50 mL) of diethyl ether and hexane. Amine hydrochloride was filtered off, and colorless crystals of **1** were obtained by passing a slow stream of nitrogen over the filtrate: mp 138–140 °C; yield 2.38 g, 35%). ^1H NMR (toluene-d_8): 2.12–2.23 (m, 24H, CH_3), 3.20 (d, $^3J_{PH}$ = 10.6 Hz, 6H, NMe_2), 7.39–7.50 (m, 8H, H(Ar)). ^{31}P NMR (toluene-d_8): −76.48. Anal. Calcd for $C_{34}H_{38}NO_4PS_2$: C, 65.91; H, 6.14; N, 2.26. Found: C, 65.32; H, 6.19; N, 2.19.

[Thiobis(4,6-di-tert-butylphenylene)dioxy][(2,2-dimethylpropane-1,3-diyl)dioxy](2,2,2-trifluoroethoxy)phosphorane, $S[(t\text{-}Bu)_2C_6H_2O]_2P(Me_2C_3H_4O_2)(OCH_2CF_3)$ (2). The synthesis of **2** closely followed the general procedure used for **1** based on the reaction of a monocyclic phosphine. Quantities used were as follows: [thiobis(4,6-di-*tert*-butylphenylene)dioxy](2,2,2-trifluoroethoxy)phosphine[5] (1.00 g, 1.75 mmol), 2,2-dimethyl-1,3-propanediol (0.182 g, 1.75 mmol), *N*-chlorodiisopropylamine (0.300 mL, 0.276 g, 2.04 mmol), and diethyl ether (200 mL). The reaction was carried out for only 29 h. Colorless microcrystals of **2** were obtained by concentrating a solution of a 1:2 mixture (50:100 mL) of diethyl ether and hexane: mp 203 °C; yield 0.882 g, 75%. ^1H NMR ($CDCl_3$): 0.99 (s, 6H, $CH_2C(CH_3)_2$), 1.30 (s, 18H, $C(CH_3)_3$), 1.42 (s, 18H, $C(CH_3)_3$), 3.47 (br, 2H, OCH_2CF_3), 4.17 (d, $^3J_{P-H}$ = 11.7 Hz, 4H, OCH_2), 7.40 (s, 2H, H(Ar)), 7.60 (s, 2H, H(Ar)). ^{31}P NMR ($CDCl_3$): −82.00. Anal. Calcd for $C_{35}H_{52}F_3O_5PS\cdot 1.5n$-hexane: C, 65.92; H, 9.10. Found: C, 66.04; H, 8.40.

$\{(CH_3CH_2CH_2)(CH)[(t\text{-}Bu)_2C_6H_2OH]_2\}_2P(O)(OCH_2CF_3)$ (3). The synthesis of **3** followed the general procedure used for **1** although water entered the reaction. Quantities used were as follows: Tris(2,2,2-trifluoroethyl) phosphite (1.60 mL, 2.38 g, 7.24 mmol), 2,2′-butylidenebis(4,6-di-*tert*-butylphenol) (3.37 g, 7.24 mmol), *N*-chlorodiisopropylamine (1.30 mL, 1.18 g, 8.70 mmol), and diethyl ether (300 mL). The reaction was carried out for 120 h. Colorless crystals of **3** were obtained from a solution of 1:3 mixture of (100:300 mL) diethyl ether and hexane: mp 144 °C; yield 2.91 g, 38%. ^1H NMR ($CDCl_3$): 0.93 (t, $^3J_{HH}$ = 9.2 Hz, 6H, CH_3), 1.29 (s, 36H, *t*-Bu), 1.38 (s, 36H, *t*-Bu), 2.02–2.20 (m, 8H, CH_2), 4.40 (t, $^3J_{HH}$ = 9.4 Hz, 1H, CH), 4.67 (m, 2H, OCH_2), 4.80 (t, 1H, CH), 5.80 (s, 2H, OH), 7.13–7.26 (m, 8H, H(Ar)). ^{19}F NMR ($CDCl_3$): −75.5 (t, $^3J_{H-F}$ = 9.7 Hz, OCH_2CF_3). ^{31}P NMR ($CDCl_3$): −11.17. ^{31}P NMR (toluene-d_8): −10.43. Anal. Calcd for $C_{66}H_{100}O_6F_3P$: C, 73.57; H, 9.36. Found: C, 74.1; H, 9.3.

[(2-((1-Hydroxy-4,6-dimethyl-2-phenyl)thio)-4,6-dimethylphenyl)oxy]bis(2,6-dimethylphenoxy)phosphine Oxide, $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$ (4). The synthesis of **4** followed the general procedure used for **1** with water entering the reaction as with **3**. Quantities used were as follows: Tris(2,6-dimethylphenyl) phosphite (1.00 g, 2.54 mmol), 2,2′-

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Table 1. Crystallographic Data for Compounds **1** and **4**

	compd	
	1	**4**
formula	$C_{34}H_{38}O_4NS_2P$	$C_{32}H_{35}O_5SP$
fw	619.788	562.671
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
a, Å	26.034(5)	12.971(4)
b, Å	15.230(2)	22.572(3)
c, Å	24.687(2)	10.800(2)
β, deg	131.31(1)	109.25(2)
V, Å^3	7353(4)	2985(2)
Z	8	4
T, °C	23 ± 2	23 ± 2
λ, Å	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.120	1.252
μ, cm^{-1}	2.129	1.920
$R(F_o)^a$	0.059	0.035
$R_w(F_o)^a$	0.103	0.046

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

thiobis(4,6-dimethylphenol) (0.695 g, 2.54 mmol), *N*-chlorodiisopropylamine (0.40 mL, 0.39 g, 2.9 mmol) and diethyl ether (150 mL). The reaction was carried out for 40 h. Colorless crystals of **4** were obtained by concentrating a solution of a mixture of diethyl ether and hexane (50:50 mL): mp 179–180 °C; yield 1.03 g, 72%. ^1H NMR ($CDCl_3$): 2.10, 2.16, 2.23 (s, 12H, $OC_6H_3(CH_3)_2$), 2.37 (shoulder, 12H, CH_3), 6.44 (s, 1H, OH), 6.80–7.10 (m, 10H, H(Ar)). ^{31}P NMR ($CDCl_3$): –16.29. ^{31}P NMR (toluene-d_8): –15.69. Anal. Calcd for $C_{32}H_{35}O_5PS$: C, 68.30; H, 6.22. Found: C, 67.09; H, 6.69.

X-ray Experimental Section

All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum Kα radiation. Details of the experimental procedures have been described previously.[15]

Crystals were mounted in thin-walled glass capillaries which were sealed as a precaution against moisture sensitivity. Data were collected using the θ–2θ scan mode with $3° \le 2\theta_{Mo K\bar{\alpha}} \le 43°$ for **1** and $3° \le 2\theta_{Mo K\bar{\alpha}} \le 45°$ for **4**. No corrections were made for absorption. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least squares.[16] All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data are summaried in Table 1.

X-ray Study for $[S(Me_2C_6H_2O)_2]_2PNMe_2$ (1). The colorless crystal used for the study was cut from a clear region imbedded in an opaque mass of platelike crystals and had dimensions of 0.35 × 0.45 × 0.45 mm. A total of 3194 independent reflections ($+h,+k,\pm l$) was collected.

The 42 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers (ideal positions for aromatic H atoms, regularized difference Fourier positions for methyl hydrogen atoms). Residual density on a difference Fourier synthesis ($\rho_{max} = 0.817$ e/Å^3) suggested the presence of an Et_2O of solvation disordered about an inversion center (crystals from a diethyl ether/hexane mixture). Although the R factors decreased appreciably upon introduction of atoms in these locations, the atoms would not refine and were subsequently omitted from the final refinement. The final agreement factors (Table 1) were based on the 2675 reflections with $I \ge 3\sigma_I$.

X-ray Study for $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$ (4). The colorless crystal used for the study was obtained by cleaving a distorted octahedral crystal along an apparent twin plane. This crystal was roughly a rectangular pyramid with a base of 0.38 × 0.50 mm and a height of 0.30 mm. A total of 3416 independent reflections ($+h,+k,\pm l$) was collected.

The 39 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as described for **1**, except for the hydroxyl hydrogen atom which was located on a difference Fourier map and refined isotropically. The final agreement factors (Table 1) were based on the 2322 reflections with $I \ge 3\sigma_I$.

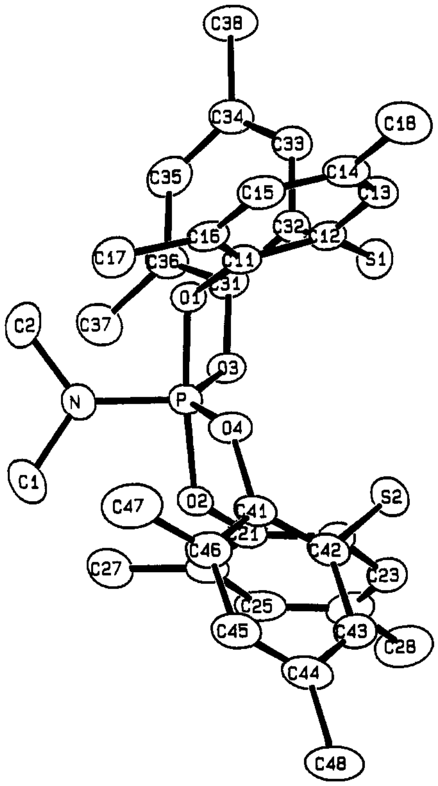

Figure 1. ORTEP plot of $[S(Me_2C_6H_2O)_2]_2PNMe_2$, **1**, with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Atomic Coordinates and B Values (Å^2) in Crystalline $[S(Me_2C_6H_2O)_2]_2PNMe_2$ (**1**)[a]

atom[b]	x	y	z	B_{equiv}[c]
S1	0.29488(9)	–0.0485(1)	0.8743(1)	4.57(6)
S2	0.10770(9)	–0.0792(2)	0.7329(1)	5.41(6)
P	0.18362(8)	0.0978(1)	0.71953(9)	3.46(5)
O1	0.2547(2)	0.1325(3)	0.8005(2)	3.4(1)
O2	0.1129(2)	0.0531(3)	0.6436(2)	3.6(1)
O3	0.2251(2)	0.0136(3)	0.7235(2)	3.7(1)
O4	0.1442(2)	0.1123(4)	0.7494(2)	4.3(1)
N	0.1826(3)	0.1829(4)	0.6779(3)	4.5(2)
C1	0.1202(4)	0.2187(6)	0.6093(4)	6.3(3)
C2	0.2416(4)	0.2386(6)	0.7073(4)	6.1(3)
C11	0.2717(3)	0.1313(5)	0.8662(3)	3.7(2)
C12	0.2938(3)	0.0530(5)	0.9069(3)	3.8(2)
C21	0.1003(3)	–0.0324(5)	0.6194(3)	3.8(2)
C22	0.0947(3)	–0.0991(5)	0.6538(3)	4.2(2)
C31	0.2955(3)	0.0057(5)	0.7690(3)	3.8(2)
C32	0.3346(3)	–0.0211(5)	0.8398(3)	3.7(2)
C41	0.0757(3)	0.0969(6)	0.7136(3)	4.3(2)
C42	0.0518(3)	0.0113(6)	0.7039(3)	4.6(2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Results

The atom-labeling scheme for **1** is given in the ORTEP plot of Figure 1. Selected atomic coordinates are given in Table 2, and selected distances and angles are given in Table 3. The corresponding materials for **4** are given in Figure 3 and in Tables 4 and 5. Complete tables of atomic coordinates, distances and angles, anisotropic thermal parameters, and hydrogen atom parameters for both compounds are provided as supplementary material.

Discussion

Synthesis. All syntheses appear to initially involve an oxidative addition reaction of a phosphite with a diol in the presence of *N*-chlorodiisopropylamine in ether solution. The ready removal of Me_2N groups as gaseous dimethylamine is a factor favoring

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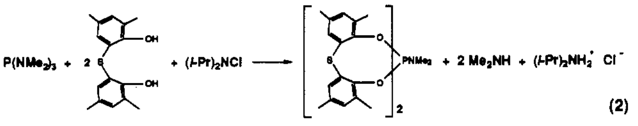
(16) The function minimized was $\sum w(|F_o| - |F_c|)_2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

Table 3. Selected Distances (Å) and Angles (deg) for $[S(Me_2C_6H_2O)_2]_2PNMe_2$ (**1**)[a]

Distances			
S1–C12	1.751(8)	P–N	1.644(7)
S1–C32	1.77(1)	O1–C11	1.37(1)
S2–C22	1.77(1)	O2–C21	1.378(9)
S2–C42	1.776(9)	O3–C31	1.384(7)
P–O1	1.678(3)	O4–C41	1.392(8)
P–O2	1.677(4)	N–C1	1.472(8)
P–O3	1.637(6)	N–C2	1.46(1)
P–O4	1.625(7)	S1–S2	3.700(2)
P–S1	3.652(3)	P–S2	3.485(4)
Angles			
C12–S1–C32	101.8(4)	O3–P–N	113.2(4)
C22–S2–C42	100.3(4)	O4–P–N	114.9(4)
O1–P–O2	173.5(3)	P–O1–C11	130.2(5)
O1–P–O3	90.6(2)	P–O2–C21	129.8(3)
O1–P–O4	87.0(3)	P–O3–C31	125.8(4)
O1–P–N	92.6(2)	P–O4–C41	128.1(5)
O2–P–O3	86.7(2)	P–N–C1	124.1(6)
O2–P–O4	90.4(3)	P–N–C2	124.6(1)
O2–P–N	93.9(2)	C1–N–C2	110.9(7)
O3–P–O4	131.9(3)		

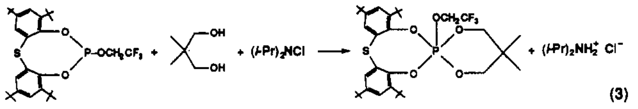
[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

the formation of the bicyclic derivative, **1**, rather than stopping at the monocyclic stage. Formation of the cyclic phosphoranes, **1** and **2**, is illustrated in eqs 2 and 3,respectively. The formation of the phosphates, **3** and **4**, is illustrated in eqs 4 and 5, respectively. All reactions were conducted in diethyl ether solution with yields varying between 35% and 75%. Similar to that postulated for the mechanistic route displayed in eq 1 for the formation of the cyclic phoshate E_1, it is proposed that the hydrolysis processes for the formation of the acyclic phosphates **3** and **4** do so by way of a hexacoordinated intermediate involving P–S coordination.



1

(2)



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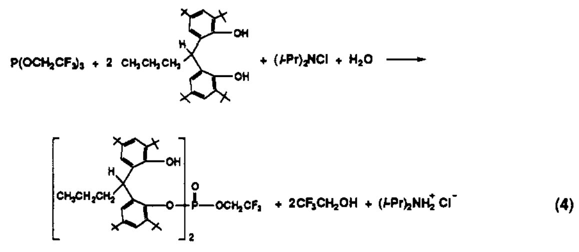
(3)



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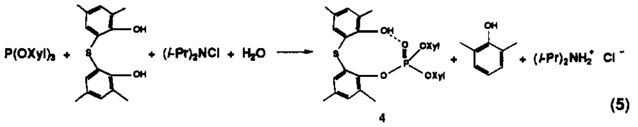
(4)



4

(5)

The spirocyclic phosphorane **1** was found to be reactive in chlorinated solvents. For example, its ^{31}P NMR in $CDCl_3$ solution showed multiple peaks in the region +10.00 to −16.95 ppm along with a less intense peak at −76.50 ppm, while the toluene-d_8 solution of the same sample showed a single resonance at −76.48 ppm. We observed this behavior previously with the monocyclic pentaoxyphosphorane A and two related members in $CDCl_3$ solution.[5]

Table 4. Selected Atomic Coordinates in Crystalline $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$ (**4**)[a]

atom[b]	x	y	z	B_{equiv}[c]
S	0.07577(7)	0.06712(4)	0.76320(8)	3.45(2)
P	0.31924(7)	0.10257(4)	0.69577(8)	3.61(2)
O1	0.2001(2)	0.1155(1)	0.6012(2)	3.63(5)
O2	0.3840(2)	0.1516(1)	0.6490(2)	4.18(6)
O3	0.3482(2)	0.0442(1)	0.6359(2)	3.89(5)
O4	0.3358(2)	0.1015(1)	0.8356(2)	4.34(6)
O5	0.2443(2)	0.0980(1)	1.0281(2)	4.56(6)
C1	0.1295(2)	0.1583(2)	0.6281(3)	3.33(8)
C2	0.0658(2)	0.1409(2)	0.7026(3)	3.10(7)
C3	−0.0080(3)	0.1807(2)	0.7214(3)	3.56(8)
C4	−0.0187(3)	0.2372(2)	0.6679(3)	4.02(9)
C5	0.0456(3)	0.2530(2)	0.5944(3)	4.32(9)
C6	0.1214(3)	0.2143(2)	0.5715(3)	3.93(8)
C11	0.1411(3)	0.0881(2)	1.0279(3)	3.59(8)
C12	0.0528(3)	0.0769(1)	0.9148(3)	3.35(8)
C13	−0.0505(3)	0.0686(2)	0.9232(3)	4.09(9)
C14	−0.0697(3)	0.0712(2)	1.0420(4)	4.38(9)
C15	0.0210(3)	0.0808(2)	1.1541(3)	4.77(9)
C16	0.1258(3)	0.0894(2)	1.1502(3)	4.42(9)
C21	0.4958(3)	0.1654(2)	0.7137(3)	4.33(9)
C31	0.3507(3)	−0.0139(2)	0.6876(3)	3.68(8)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 5. Selected Distances (Å) and Angles (deg) for $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$ (**4**)[a]

Distances			
S–C2	1.778(3)	O1–C1	1.426(4)
S–C12	1.772(4)	O2–C21	1.422(4)
P–O1	1.573(2)	O3–C31	1.421(4)
P–O2	1.570(3)	O4–H1	1.78(5)
P–O3	1.567(3)	O5–C11	1.356(4)
P–O4	1.453(2)	O5–H1	1.00(5)
C1–C2	1.388(5)	H1–O4	1.78(5)
C11–C12	1.394(4)	O5–O4	2.714(4)
Angles			
C2–S–C12	102.1(2)	P–O1–C1	123.5(2)
O1–P–O2	100.1(1)	P–O2–C21	124.3(2)
O1–P–O3	101.9(1)	P–O3–C31	126.2(2)
O1–P–O4	117.0(1)	P–O4–H1	139.(1)
O2–P–O3	103.5(1)	C11–O5–H1	118.(2)
O2–P–O4	115.8(1)	O5–H1–O4	155.(3)
O1–C1–C2	118.1(3)	O5–C11–C12	123.8(3)
S–C2–C1	119.6(3)	S–C12–C11	119.5(3)
O3–P–O4	116.2(1)		

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 3.

Structural Considerations for 1 and 2. The geometry about the phosphorus atom in phosphorane **1** can be referred to a trigonal bipyramid (TBP) with the ring systems spanning axial–equatorial sites. Distortions away from ideal trigonal bipyramidal geometry lie on the Berry pseudorotation coordinate,[17] which connects this TBP to a rectangular pyramid (RP) with four basal oxygen atoms and the nitrogen atom in an apical position. By use of the dihedral angle method to assess displacement,[18-20] the geometry is displaced 29.0% (29.2% with unit vectors) from the TBP toward the RP. In addition to the local near-C_{2v} geometry at the phosphorus

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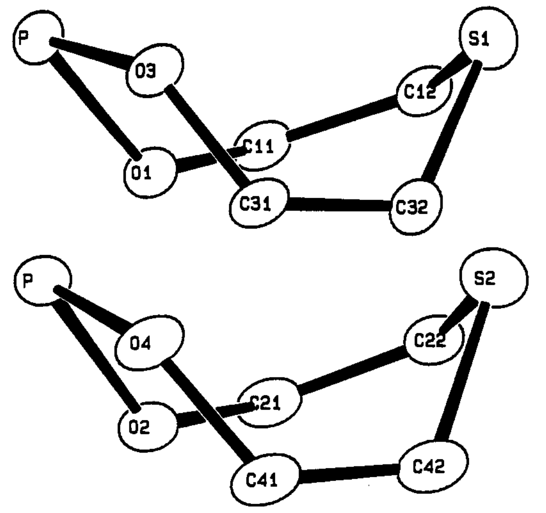


Figure 2. ORTEP plots showing the conformations of the eight-membered rings in **1**: (a, top) Ring containing S1; (b, bottom) ring containing S2.

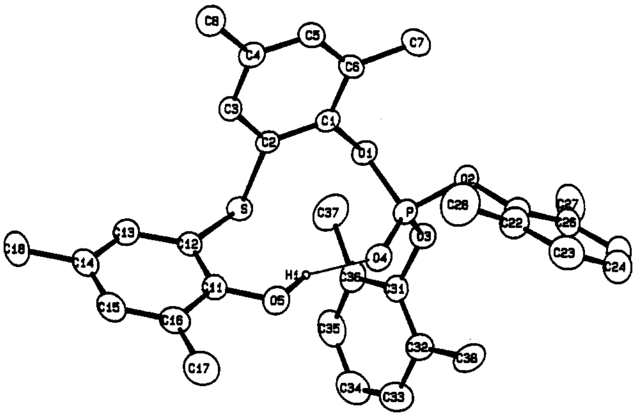
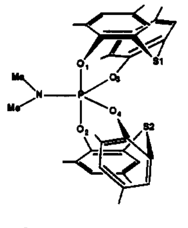


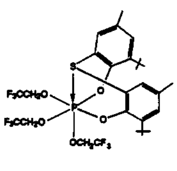
Figure 3. ORTEP plot of $S(Me_2C_6H_2)_2(OH)OP(O)(OXyl)_2$, **4**, with thermal ellipsoids at the 30% probability level. Hydrogen atoms, except for H1 which is shown as a sphere of arbitrary radius, are omitted for clarity. The hydrogen-bonding interaction is shown as a narrow line.

atom implied by this coordinate, the entire molecule has near-C_2 symmetry, with the pseudo-2-fold axis passing through the P–N bond. The two eight-membered rings are related by this 2-fold pseudo symmetry and, accordingly, have very similar conformations (Figure 2). P–S distances across these rings (3.652(3) and 3.485(4) Å) are long compared to those in phosphoranes containing the same ring system in which P–S bonding interactions have been observed,[3–5,7] 2.880(1)–2.373(5) Å, and show structural displacement toward an octahedron. Thus, there is no structural or electronic indication of a P–S donor interaction in **1**.

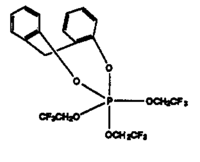
Examination of the P–O ring distances for **1** also supports this conclusion. The P–O axial bond distances for **1** are 1.678(3) Å (P–O1) and 1.677(4) Å (P–O2) while the P–O equatorial distances are 1.637(6) Å (P–O3) and 1.625(7) Å (P–O4). These compare with the hexacoordinated composition **C** (P–S = 2.362(2) Å), with the same eight-membered ring exhibiting P–O distances of 1.698(5) and 1.694(4) Å.[7] These are considerably longer than those for **1** as expected for a structure having increased coordination. The P–O bond distances for **1** are more comparable to those for **F**[3], which has a similar eight-membered ring but where the sulfur atom is replaced by a methylene group and, consequently, incapable of a bridge donor to phosphorus interaction. Here the P–O$_{ax}$ ring bond length is 1.660(3) Å and the P–O$_{eq}$ ring value is 1.602(4) Å.



1 (δ^{31}P = -76.5 ppm)



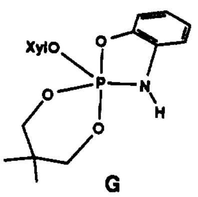
C[7] (δ^{31}P = -82.3 ppm)



F[3] (δ^{31}P = -78.3 ppm)

In solution the ^{1}H and ^{31}P NMR spectra are in agreement with the formulation for **1**. The ^{31}P chemical shift in particular indicates retention of the structural integrity in this phase. The value of −76.5 ppm is in the pentacoordinated range and very close to that for trigonal bipyramidal **F**. In this regard, pentaoxyphosphorane **2**, for which an X-ray structure was not successful, has a ^{31}P shift of −82.0 ppm. This value is in the range (−81.2 to −82.6 ppm) found for ^{31}P chemical shifts for the five hexacoordinated pentaoxyphosphoranes whose X-ray structures are known of the type **A**–**C**[3,5,7] that have one eight-membered ring. The introduction of a second ring normally causes a downfield shift.[21] Hence, a P–S interaction is indicated for **2** and a hexacoordinated structure is expected.

The P–N bond distance in **1** is relatively short, 1.644(7) Å, and may be responsible for the lack of attainment of the hexacoordinated state. This value compares with a P–N bond distance of 1.659(4) Å averaged over five tetraoxyphosphoranes having TBP structures of the type **G** where the composition of the phenyl ring varied.[22,23] The implication is that increased P–N π backbonding to phosphorus may negate the formation of a potentially weaker P–S interaction.

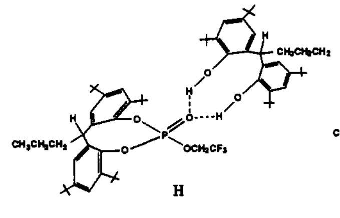


G

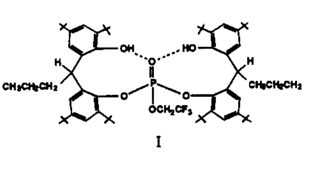
Structural Considerations for 3 and 4. In the acyclic phosphate **4**, the hydrogen atom of the hydroxyl group is nearly in the plane of the phenyl ring to which it is bound (torsion angle C12–C11–O5–H1 = 5(3)°). There is a hydrogen bonding interaction between the hydroxyl hydrogen atom, H1, and the phosphoryl oxygen atom of the phosphate, O4, which results in the formation of a ten-membered ring. The geometric details of the hydrogen bonding interaction are given in Table 4, where an O4 to O5 distance of 2.714(4) Å is listed, appreciably shorter than that expected on the basis of van der Waals radii.[24]

Concerning P–O bond distances (other than the shorter phosphoryl bond, P–O4 of 1.453(2) Å), they average 1.570(3) Å for the acyclic phosphate **4**. This compares with the average P–O bond distance value for the pentacoordinated molecule **1** of 1.654(5) Å.

The NMR data for **3** and **4** are consistent with phosphate formulations. In the case of **4**, this is in agreement with retention of the structure found by X-ray analysis. The ^{31}P chemical shift for both **3** and **4** are in range for four-coordinated phosphorus. However, in the absence of an X-ray study of **3**, one cannot easily differentiate between the structural form **H**,similar to **E$_2$** illustrated in the Introduction for a cyclic phosphate,[7] and the form **I** having the same composition as **H**. Structural representation **I** is favored for **3** on the basis of the fact that the hydrogen-



H

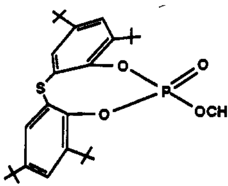


I

bonded solvate form E_2 was formed when a 1:2 mole ratio of phosphite to diol reactants was used, whereas E_1 formed when this mole ratio was 1:1. For the formation of **3**, a 1:1 mole ratio of reactants was used.

Hydrolyses. Cyclic vs Acyclic Phosphates. Acyclic phosphate **4** forms via the hydrolysis process expressed by eq 5. Most likely the acyclic phosphate formulation **I** would result by a similar hydrolysis process. Previously, our studies showed only cyclic phosphate products formed in hydrolysis reactions involving eight-membered rings. The reaction in eq 1 shows an example of this process yielding E_1. Others represented elsewhere in this paper are the cyclic phosphates E_2 and **J**. In these cases, the trifluoroethoxy group is the one undergoing hydrolytic cleavage. Two such groups are released to give the alcohol. In the present instance for the hydrolysis giving **4**, the phosphite used, $P(OXyl)_3$, has a poorer leaving group compared to that for $P(OCH_2CF_3)_3$. This effect is attributable to the enhanced electronegativity[21] of the trifluoroethoxy group. In the formation of the acyclic phosphate, **4**, only one OXyl group needs to be cleaved, as expressed in eq 5. It may be that, by employing groups of varying departing abilities, one can control whether a cyclic or an acyclic phosphate is produced. Relative to this rationale, since the phosphite used to prepare **3** is $P(OCH_2CF_3)$, containing a good leaving group, the cyclic phosphate product formulation **H** is suggested on this basis. At present, there is no sufficiently strong argument to suggest **H** vs **I** for **3** or *vice versa.*

Structural Details. Compared to previous compounds containing this ring system, the conformation of the eight-membered rings in phosphorane **1** is most like that found in the *syn* form of the phosphate **J**.[4] The rings of **1** have a twisted boatlike or twisted tub conformation. For the ring containing S1, the atoms forming the floor of the tub (O1, C11, C31, and C32) are coplanar to within ±0.050(7) Å. Atoms P, O3, S1, and C12 are displaced from this plane in the same direction by distances of 1.133(2), 1.074(5), 1.202(2), and 0.548(8) Å, respectively. Similarly, for the ring containing S2, atoms O2, C21, C41, and C42 are coplanar to within ±0.001(7) Å, with atoms P, O4, S2, and C22 displaced by distances of 1.283(2), 1.032(4), 1.269(2), and 0.514(7) Å, respectively.



J[4]

The dimethylamino group in **1** is not pyramidal but is nearly planar. Atoms N, P, C1, and C2 are coplanar to within ±0.024 Å, while the sum of the angles at nitrogen is 359.6(6)°. Back-bonding to the P atom would be best facilitated if the plane of the amino group were at an angle of 90° to the equatorial plane. The observed dihedral angle between the Me_2NP plane and the equatorial plane is 68.6(3)°, which corresponds at least in part to a rotation about the P–N bond. Alternatively, the dihedral angle between the plane of the NMe_2P group and the axial plane (P, N, O1, and O2 coplanar to within ±0.001(4) Å) is 23.4(7)°. This can be viewed as a rotation of the NMe_2 group about the P–N bond into a configuration which mitigates crowding between the methyl groups of the NMe_2 group and the axial oxygen atoms O1 and O2. This rotation also places the methyl groups at about equal distances from *ortho* methyl groups of the cyclic ligands. Close contacts in this region of the molecule are as follows: C2–O1, 2.64(1) Å; C2–C17, 3.54(2) Å; C2–C37, 3.57(1) Å, and C1–O2, 2.71(1) Å; C1–C27, 3.52(1) Å; C1–C47, 3.71(2) Å. Additional evidence of crowding in this area of the molecule is the enlarged P–N–C angles of 124.1(6) and 124.6(4)°.

Conclusion. The formation of the acyclic phosphate **4** vs the cyclic phosphates **E** and **J** during hydrolytic cleavage correlates with the use of a phosphite having a relatively poor leaving group. The presence of a P–N bond in the bicyclic oxyphosphorane **1** appears responsible in inhibiting P–S coordination, presumably by P–N π back-bonding. Formation of a hexacoordinated state via a P–S interaction in a hydrolysis process, as detailed in eq 1, appears to be a reasonable postulate for the formation of acyclic phosphate **4** as well as for the cyclic phosphates **E** and **J**.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 91-22352) is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S4) and **4** (Tables S5–S8) (18 pages). Ordering information is given on any current masthead page.

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