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Toward Stabilizing Rectangular-Pyramidal Geometries in Non-Metals: Polycyclic Phosphorus Esters

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The preparation of the novel polycyclic phosphorus compounds $ZP(OCH_2)_2CHCHCH_2O(CH_2OR)$ and $ZP(OCH_2)_2C(CH_2)_xCCH_2O(CH_2OR)$ (Z = lone pair, O, S, Se, BH_3, and CPh_3^+, x = 1-4, and R = H and Z = lone pair, x = 1-4, R = C(O)Ph) are reported. Compounds containing Z = lone pair and R = H were found to undergo an acid-catalyzed rearrangement, yielding the isomeric phosphonates $O(H)POCH_2CHCH_2OCH_2CHCH_2O$ and $O(H)POCH_2C(CH_3)_xCCH_2OCH_2CH_2O$. A possible pathway for this rearrangement is discussed. Over a temperature range of 223-350 K, the compounds possessing a pendant alcohol group (R = H) displayed no tendency to give the corresponding phosphorane even under deprotonating conditions. The molecular structures of $(HOCH_2)_2C(CH_2)_3C(CH_2OH)_2$, an isomer of $O(H)POCH_2C(CH_2)_2CCH_2OCH_2CH_2O$, $Ph_3C(O)POCH_2C(CH_2OH)(CH_2)_3CCH_2O(CH_2OH)$, $OP(OCH_2)_2C(CH_2)_2CCH_2O(CH_2O)(CH_2OH)$, and $OP(OCH_2)_2C(CH_2)_3CCH_2O(CH_2OH)$ determined by X-ray means are presented. Crystallographic parameters for these compounds are space group $P\bar{1}$, a = 7.342 (3) Å, b = 11.857 (3) Å, c = 6.333 (2) Å, α = 100.47 (3)°, β = 115.57 (3)°, γ = 85.51 (4)°, and Z = 2; space group $C2/c$, a = 11.452 (8) Å, b = 6.451 (3) Å, c = 26.03 (5) Å, β = 93.03°, and Z = 8; space group $P2_1/c$, a = 15.638 (2) Å, b = 11.119 (3) Å, c = 17.404 (3) Å, β = 106.06 (1)°, and Z = 4; space grou $P2_1/n$, a = 7.022 (1) Å, b = 10.5157 (9) Å, c = 13.122 (2) Å, β = 103.340 (8)°, and Z = 4; and space group $P2_1/c$, a = 7.545 (3) Å, b = 11.133 (5) Å, c = 12.061 (3) Å, β = 91.14 (3)°, and Z = 4, respectively.

Introduction

Five-coordinate phosphorus species are often invoked as intermediates in nucleophilic,[2] free radical,[3] and hydrolysis reactions[4] of both tri- and tetracoordinate phosphorus compounds. A factor determining the products obtained in these reactions is the geometry of the intermediate. Two of the most important pentacoordinate phosphorus geometries are the trigonal bipyramid (TBP) and the square pyramid (SP).[5] The TBP geometry is by far the most common one found in pentacoordinate phosphorus species, appearing both in reactive intermediates and in isolable phosphorus compounds. Though several theories have been proposed to account for axial/equatorial exchange in isolable TBP compounds, the Berry pseudorotation mechanism is the most widely accepted.[6,7] This mechanism features a square-pyramidal intermediate whose formation can be inhibited by bulky substituents.[8] As reaction intermediates, the reactivities of TBP phosphorus species are dependent upon the nature of their substituents,[9] but it is likely that the apical position of the TBP is preferred for both an incoming nucleophile and for a leaving group.[4,10] Other non-metals such as silicon behave similarly.[11]

Because the SP geometry occurs as an intermediate in Berry pseudorotation, efforts to stabilize it in appropriate phosphorus compounds are worthy of pursuit. In comparison with compounds of TBP geometry, SP compounds are very rare. Only a few examples of compounds that contain greater than 70% SP structural characteristics are known,[12] and in all of these compounds, the phosphorus atom is contained within multiple four- and/or five-membered rings. In compounds containing multiple unsaturated five-membered rings, the SP geometry seems to be favored. Conformational energy calculations indicate that the SP geometry is normally slightly higher in energy than the TBP geometry but that factors such as ring strain can cause the TBP to rise in energy relative to the SP geometry.[13] Previously, others have prepared pentacoordinate phosphorus compounds containing two five-membered rings to determine the factors that influence their geometry.[14] In these systems, it is possible to obtain TBP, SP, or a mixture of both geometries, depending on the degree of saturation of the ring, the size and substitution of the ring, the size and electron-donating ability of the exocyclic phosphorus substituent, the nature of the ring atoms bound to phosphorus, and the degree of hydrogen bonding in the solid state.[12b,c,e,f] The same factors also determine the geometry of the analogous pentacoordinate compounds of As,[15] Sb,[16] Si,[17] Ge,[18] and Sn.[19] In

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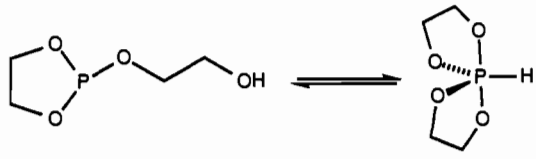
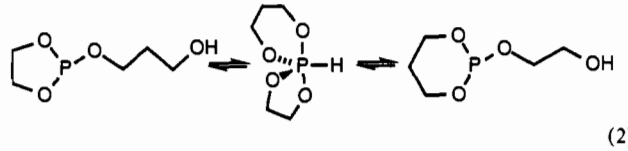
systems containing a six-membered ring or systems in which the exocyclic substituent is a hydrogen, the geometry is always TBP.[20] This demonstrates the importance of the ring strain energy and the nature of the exocyclic phosphorus substituent on the geometry in these systems.

Tautomeric equilibria as in reaction 1 have been known for many years.[21-25] Such equilibria between the trivalent and pentavalent forms of phosphorus are believed to be present in all



(1)

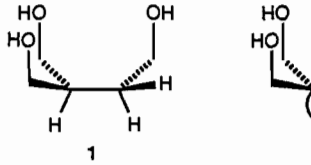
spiro(hydro)phosphoranes. Studies have recently been broadened to include spiro(hydro)phosphoranes that contain a six-membered ring.[26] Here the stability of the pentacoordinate tautomer is not as great and only one case is known, $MeOP(OCH_2CH_2CH_2O)[OC(CF_3)_2C(CF_3)_2O]$, in which this form is favored.[27] In all other instances, the tricoordinate tautomer is the only detectable isomer and the pentacoordinate tautomer is present only as an intermediate in the isomerization between the five- and six-membered rings containing phosphites shown in reaction 2. A factor complicating the investigation of these



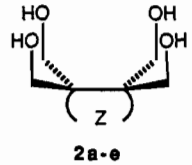
(2)

compounds is their tendency to undergo intermolecular transesterification reactions.

Recently, we have initiated a broad investigation of the capability of a set of novel quadrupedal ligands to constrain non-metal and metal complexes into unusual stereochemistries.[28] In applying this concept to potentially SP group 15 compounds, we chose **1** and **2a–e** for investigation. Compound **1** would serve as a pre-



1



2a-e

	Z
2a	H_2
2b	CH_2
2c	$(CH_2)_2$
2d	$(CH_2)_3$
2e	$(CH_2)_4$

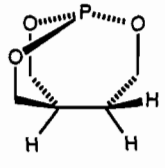


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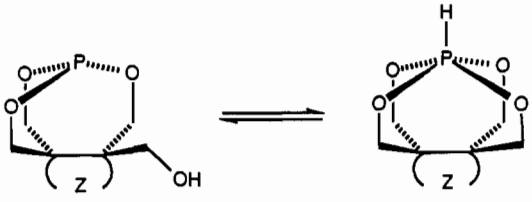
Table I. ^{31}P NMR Spectral Data for Compounds **3–5** and **7–20**[a]

	chem shift					
compd		a	b	c	d	e
3[b]	115.59					
4a–e[b]		113.99	111.73	114.58	111.45	113.23
5a–e[b]		12.09	15.21	14.32	12.00	12.45
		[715][e]	[722][e]	[717][e]	[720][e]	[722][e]
		11.38	14.72	13.97	11.39	11.67
		[695][e]	[699][e]	[698][e]	[701][e]	[700][e]
7a–e[c]		47.99	49.42	50.61	50.90	49.01
8[c]	35.23					
9[b]	30.07					
10a–d[b]		113.57	112.18	115.08	111.03	
11a–e[b]		−5.71	−5.80	−4.65	−5.29	−5.88
12a–c[b]		55.60	56.53	62.31		
13a–e[d]		61.22	61.77	62.84	61.78	61.20
		[1054][f]	[1054][f]	[1054][f]	[1050][f]	[1052][f]
14a–e[d]		106.24	105.92	107.13	106.73	106.79
		[97.12][g]	[95.69][g]	[94.20][g]	[97.44][g]	[97.83][g]
15[b]	−6.78					
16[b]	−6.15					
17[b]	−6.46					
18[b]	−5.23					
20[d]	107.04					
	[100.34][g]					
19[d]	60.91					
	[1054][f]					

[a] Chemical shifts are in ppm and coupling constants (in brackets) are in Hz. [b] In $CDCl_3$. [c] In CD_3CN. [d] Xylene/benzene-d_6. [e] ^1J(PH). [f] ^1J(PSe). [g] ^1J(PB).

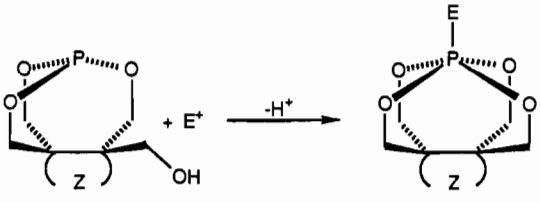
cursor to **3**, for example, which in turn would serve as a model for the tricoordinate form of **4a–e** in equilibrium 3. Here the



(3)

4a-e

tendency to chelate the pendant oxygen could also be expected to inhibit intramolecular transesterification. It should be noted that the framework of **2a–e** would be expected to yield SP geometries that are somewhat distorted toward rectangular pyramidal. Reaction of the trivalent compounds with positively charged electrophiles could potentially yield neutral pentacoordinate SP phosphorus derivatives as shown in reaction 4. SP species of the



(4)

4a-e

type proposed in reactions 3 and 4 would be the first containing saturated six- and seven-membered rings as well as the first with a proton as one of the substituents. The effect of the distance between pairs of alkoxy arms of the tetradentate system on the stability of the SP species could also be investigated by comparing compounds containing larger distances prepared from **2b**, for example, with smaller distances expected from **2d** and **2e**.

We report here the preparation of a variety of bicyclic tri- and tetracoordinate phosphorus compounds from **2a–e** and our attempts to prepare SP phosphorus compounds from these precursors. Whereas these attempts were not successful, it may be noted that our replacement of phosphorus by arsenic in the above

Table II. $^{1}H^{a}$ and $^{13}C^{b}$ NMR Spectral Data for Compound **4c**

atom label[c]	δ(^{1}H), ppm	proton coupling, Hz	δ(^{13}C), ppm	carbon coupling, Hz
a	3.51	10.38,[d] 5.30[e]	61.37	
a′	4.06	10.38,[d] 5.30[e]		
b	4.53	10.78,[d] 1.20[f]	72.25	<2.4[i]
		3.60[g]		
b′	3.99	10.78,[d] 3.60[b]		
c	4.05	4.40[d]	68.97	5.26[i]
c′	4.08	4.40[d]		
d	3.93	10.28,[d] 3.40[f]	68.52	5.02[i]
		3.60[g]		
d′	3.82	10.28,[d] 2.68[f]		
e			44.80	14.71[i]
f			49.16	5.01[i]
g			22.25	*j*
h			21.64	*j*
none	4.91	5.30[e]		
ring	2.10[h]			

[a] DMSO. [b] $CDCl_3$. [c] See Discussion. [d] ^{2}J(HH). [e] $^{3}J(H_aCOH) = {}^{3}J(H_{a'}COH)$. [f] ^{3}J(PH). [g] $^{4}JH_bH_d$. [h] Multiplet. [i] J(CP). [j] Singlet.

polycyclics recently does give rise to an SP system.[28]

Experimental Section

NMR spectra were obtained on Nicolet NT-300 (^{1}H), Bruker WM-200 (^{13}C), and Bruker WM-300 (^{31}P) instruments at room temperature. The COSY experiment was run on a Nicolet NT-300 spectrometer. All other two-dimensional experiments as well as the variable-temperature NMR measurements were performed on a Bruker WM-300 instrument. Chemical shifts are given in ppm (positive downfield) relative to internal Me_4Si (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P) standards. The ^{31}P NMR signals of the compounds described in this paper are presented in Table I. The ^{1}H and ^{13}C NMR data of compound **4c** are presented in Table II. For space considerations, ^{1}H and ^{13}C NMR and high-resolution mass spectral data not given in this section for new compounds are compiled in extensive tables in the supplementary material.

Compounds **1**[29] and **2a–e**[30,31] were prepared as previously described. All reactions were performed with strict exclusion of moisture. Solvents were dried by standard methods and distilled before use. All other chemicals were used as received. The yields of the syntheses that follow are presented in Table III.

1-Phospha-2,7,8-trioxabicyclo[3.2.2]nonane (3), 4-(Hydroxymethyl)-1-phospha-2,7,8-trioxabicyclo[3.2.2]nonane (4a), 4-(Hydroxymethyl)-1-phospha-2,8,9-trioxatricyclo[4.2.2.0^{4,6}]decane (4b), 4-(Hydroxymethyl)-1-phospha-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane (4c), 4-(Hydroxymethyl)-1-phospha-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (4d), and 4-(Hydroxymethyl)-1-phospha-2,11,12-trioxatricyclo-[7.2.2.0^{4,9}]tridecane (4e). The same general method was used to prepare all of these species. In a typical synthesis, a solution containing the appropriate alcohol (ca. 5.0 mmol) and $P(NMe_2)_3$ (ca. 5.1 mmol) in 40 mL of THF was heated to 65 °C under nitrogen for 3 h. The solution was allowed to cool to room temperature and the solvent removed under vacuum. The remaining solid residue was then extracted with 20 mL of chloroform and the chloroform extract placed on a silica gel chromatography column and eluted with ethyl acetate. Upon removal of solvent from the product-containing fractions, the white solid product was obtained.

4-Oxo-3,5-dioxa-4λ^5-phosphabicyclo[5.3.0]decane (5a), 4-Oxo-3,5,9-trioxa-4λ^5-phosphatricyclo[5.3.1.0]undecane (5b), 4-Oxo-3,5,9-trioxa-4λ^5-phosphatricyclo[5.3.2.0]dodecane (5c), 4-Oxo-3,5,9-trioxa-4λ^5-phosphatricyclo[5.3.3.0]tridecane (5d), 4-Oxo-3,5,9-trioxa-4λ^5-phosphatricyclo[5.4.3.0]tetradecane (5e), 3,7-Dioxabicyclo[3.3.0]octane (6a), 3,7-Dioxatricyclo[3.3.2.0]decane (6b), 3,7-Dioxatricyclo[3.3.3.0]undecane (6c), and 3,7-Dioxatricyclo[4.3.3.0]dodecane (6d). The preparation of **5a–e** was accomplished by the same general procedure. Compounds **6a–d** were also found to be products in all of these reactions, with the exception of the reaction producing **5b**; here no cyclic ether product was detected. In a typical reaction, a mixture of the appropriate alcohol (ca. 10.0 mmol) and $P(NMe_2)_3$ (ca. 10.1 mmol) was heated to 65 °C for 3 h under nitrogen. The resulting oily solid was subjected to sublimation at 0.1 Torr and 180 °C for 2 days. The sublimate was then collected and passed down a silica gel column using ethyl acetate as the eluent. Fractions containing first **6a–d** and then **5a–e**, respectively, were collected and the solvent removed under vacuum. Recrystallization of **5a–e** from ethanol gave the pure products. (**5c**, isomer A, ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.98 (m, 4 H, H_d and $H_{d'}$) 3.71 (d, $^{2}J(H_aCH_{a'}) = 9.13$ Hz, 2 H, H_a), 3.84 (d, $^{2}J(H_{a'}CH_a) = 9.13$ Hz, 2 H, $H_{a'}$), 3.95 (dd, $^{2}J(H_bCH_b) = 12.93$ Hz, $^{3}J(H_bCOP) = 19.07$ Hz, 2 H, $H_{b'}$), 4.66 (dd, $^{2}J(H_bCH_{b'}) = 12.93$ Hz, $^{3}J(H_bCOP) = 14.10$ Hz, 2 H, H_b), 6.83 (d, $^{1}J(H_cP) = 7.17$ Hz, 1 H, H_c). **5c**, isomer B, ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95 (m, 4 H, H_d and $H_{d'}$), 3.66 (d, $^{2}J(H_aCH_{a'}) = 9.31$ Hz, 2 H, H_a), 3.83 (d, $^{2}J(H_{a'}CH_a) = 9.31$ Hz, 2 H, $H_{a'}$), 4.04 (dd, $^{2}J(H_bCH_b) = 12.98$ Hz, $^{3}J(H_bCOP) = 17.16$ Hz, 2 H, $H_{b'}$), 4.34 (dd, $^{2}J(H_bCH_{b'}) = 12.98$ Hz, $^{3}J(H_bCOP) = 19.16$ Hz, 2 H, H_b), 6.95 (d, $J(H_cP) = 6.98$ Hz, 1 H, H_c).)

1-(Triphenylmethyl)-4-(hydroxymethyl)-1-phosphonia-2,7,8-trioxabicyclo[3.2.2]nonane Tetrafluoroborate (7a), 1-(Triphenylmethyl)-4-(hydroxymethyl)-1-phosphonia-2,8,9-trioxatricyclo[4.2.2.0^{4,6}]decane Tetrafluoroborate (7b), 1-(Triphenylmethyl)-4-(hydroxymethyl)-1-phosphonia-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane Tetrafluoroborate (7c), and 1-(Triphenylmethyl)-4-(hydroxymethyl)-1-phosphonia-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane Tetrafluoroborate (7d). To a solution of the appropriate compound **4a–d** (ca. 1.5 mmol) in 20 mL of THF was added triphenylcarbenium tetrafluoroborate (ca. 1.6 mmol). The solution was stirred for 3 h, and 10 mL of benzene was added to precipitate the phosphonium salt. After filtration and washing with benzene, the white solid product was left.

1-Methyl-4-(hydroxymethyl)-1-phosphonia-2,10,11-trioxatricyclo-[6.2.2.0^{4,8}]dodecane Tetrafluoroborate (8). To a solution of **4d** in THF was added solid $Me_3O^+BF_4^-$ in an NMR tube. Solid **8** formed upon removal of the solvent.

1,7-Bis(hydroxymethyl)-4-oxo-4-(triphenylmethyl)-3,5-dioxa-4λ^5-phosphabicyclo[5.3.0]decane (9). A mixture of **4d** (0.2182 g, 1.001 mmol) and triphenylcarbenium tetrafluoroborate (0.3584 g, 1.086 mmol) was stirred in 6 mL of THF for 30 min and then cooled to −50 °C. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 0.164 mL, 1.10 mmol) was then added portionwise. The suspension was then stirred at −50 °C for 15 min and allowed to warm to room temperature over 3 h. Water (0.036 mL, 2.0 mmol) was then injected to the mixture and the solution stirred for 10 h. The reaction mixture was poured into chloroform and the solution extracted with water (2 × 20 mL). The residue after concentration was chromatographed on silica gel to give **9** as a colorless oil. Recrystallization from chloroform–hexane (1:1) gave the white solid **9** (^{1}H NMR (300 MHz, $CDCl_3$): δ 1.5 (m, 6 H, H_c, $H_{c'}$, H_d and $H_{d'}$), 3.24 (dd, $^{2}J(H_{b'}CH_b = 12.83$ Hz, $^{3}J(H_{b'}COP) = 13.05$ Hz, 2 H, $H_{b'}$), 3.61 (d, $^{2}J(H_aCH_{a'}) = 11.80$ Hz, 2 H, H_a), 3.65 (d, $^{2}J(H_{a'}CH_a) = 11.80$ Hz, 2 H, $H_{a'}$), 4.13 (dd, $^{2}J(H_bCH_{b'}) = 12.83$ Hz, $^{3}J(H_bCOP) = 18.50$ Hz, 2 H, H_b), 7.35 (m, 15 H, Ph_3C). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): δ 17.99 (s, C_d), 28.92 (s, C_c), 51.87 (s, C_e), 62.28 (d, ^{1}J(CP) = 32.0 Hz, CPh_3), 63.98 (s, C_a), 70.61 (d, $^{2}J(C_bOP) = 7.4$ Hz, C_b), 127.99 (s, Ph_3C),

Table III. Yields of Compounds **3–20**

compd	yield, %	compd	yield, %
3	92.7	**11b**[a]	94.1
4a	32.9	**11c**[a]	88.8
4b	32.9	**11d**[a]	92.9
4c	51.6	**11e**[a]	88.9
4d	67.3	**11a**[b]	32.8
4e	43.3	**11c**[b]	1.8
5a	10.9	**11d**[b]	47.2
5b	30.5	**12a**	33.2
5c	9.20	**12b**	40.8
5d	9.26	**12c**	44.8
5e	20.9	**13a**	22.6
6a	39.5	**13b**	11.8
6b	15.8	**13c**	24.1
6c	37.0	**13d**	24.3
6d	16.7	**13e**	18.5
7a	79.3	**14a**	15.6
7b	74.2	**14c**	33.8
7c	85.6	**14d**	31.2
7d	85.0	**14e**	27.0
9	44.4	**15**	75.3
10a	52.6	**16**	27.6
10b	37.2	**17**	38.5
10c	44.4	**18**	88.0
10d	46.7	**19**	85.0
11a[a]	94.4	**20**	64.6

[a] Method 1. [b] Method 2.

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Table IV. Crystallographic Data for **2d**, **5c**, **9**, **11c**, and **11d**

compd	2d	5c	9	11c	11d
formula	$C_9H_{18}O_4$	$C_8H_{13}O_4P{\cdot}0.5H_2O$	$C_{28}H_{31}O_5P{\cdot}CHCl_3$	$C_8H_{13}O_5P$	$C_9H_{15}O_5P$
fw	190.24	213.17	597.91	220.16	234.19
space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, Å	7.342 (3)	11.452 (8)	15.638 (2)	7.022 (1)	7.545 (3)
b, Å	11.857 (3)	6.451 (3)	11.119 (3)	10.5157 (9)	11.133 (5)
c, Å	6.333 (2)	26.03 (5)	17.404 (3)	13.122 (2)	12.061 (3)
α, deg	100.47 (3)				
β, deg	115.57 (3)	93.03 (14)	106.06 (1)	103.340 (8)	91.14 (3)
γ, deg	85.51 (4)				
vol, Å^3	489.03 (24)	1920 (4)	2908.2	942.8 (2)	1012.85 (6)
Z	2	8	4	4	4
d_{calcd}, g/cm^3	1.29	1.47	1.37	1.55	1.54
cryst size, mm	0.2 × 0.3 × 0.2	0.25 × 0.25 × 0.40	0.40 × 0.40 × 0.20	0.35 × 0.38 × 0.28	0.20 × 0.18 × 0.35
μ, cm^{-1}	0.94	2.64	4.0	2.761	2.616
λ	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
temp., °C	25 ± 1	25 ± 1	20 ± 1	−20 ± 1	23 ± 1
R,[a] %	6.2	4.9	4.4	3.5	4.6
R_w,[b] %	7.7	5.5	5.6	4.4	5.0

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

130.96 (d, J(CCP) = 6.1 Hz, Ph_3C), 140.46 (d, J(CCP) = 6.4 Hz, Ph_3C).

4-[(Benzoyloxy)methyl]-1-phospha-2,7,8-trioxabicyclo[3.2.2]nonane (10a), 4-[(Benzoyloxy)methyl]-1-phospha-2,8,9-trioxatricyclo-[4.2.2.0^{4,6}]decane (10b), 4-[(Benzoyloxy)methyl]-1-phospha-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane (10c), and 4-[(Benzoyloxy)methyl]-1-phospha-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (10d). To a solution containing the appropriate compound **4a–d** (ca. 1.4 mmol), triethylamine (ca. 1.45 mmol), and DMAP (4-(dimethylamino)pyridine, ca. 0.144 mmol) in 10 mL of chloroform was added benzoyl chloride (ca. 1.45 mmol). The solution was stirred for 20 h and diluted with 10 mL of toluene and the chloroform removed under vacuum. The solution was then filtered and the solvent removed under vacuum. The resulting impure **10a–d** was subjected to silica gel chromatography using chloroform as the eluent to give pure **10a–d**.

1-Oxo-4-(hydroxymethyl)-1λ^5-phospha-2,7,8-trioxabicyclo[3.2.2]nonane (11a), 1-Oxo-4-(hydroxymethyl)-1λ^5-phospha-2,8,9-trioxatricyclo-[4.2.2.0^{4,6}]decane (11b), 1-Oxo-4-(hydroxymethyl)-1λ^5-phospha-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane (11c), 1-Oxo-4-(hydroxymethyl)-1λ^5-phospha-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (11d), 1-Oxo-4-(hydroxymethyl)-1λ^5-phospha-2,11,12-trioxatricyclo[7.2.2.0^{4,9}]tridecane (11e), and 1-Oxo-1λ^5-phospha-2,7,8-bicyclo[3.2.2]nonane (18). Two methods were used to prepare **11a–e** and **18**. The first was used to synthesize **11a–e** and **18**, while the second was used only to synthesize **11a**, **11c**, and **11d**. (1) In a typical reaction, a 1.2 M solution of *t*-BuOOH in toluene (ca. 2.9 mmol) was added dropwise to a solution of the appropriate compound **4a–e** or **3** (ca. 2.0 mmol) in 50 mL of toluene in an ice bath. Filtration gave the appropriate white solid **11a–e** or **18**, which was washed with toluene and air-dried. (2) To a cooled solution of 1,2,4-triazole (ca. 30.0 mmol) in 30 mL of dioxane was added dropwise $OPCl_3$ (ca. 10.0 mmol). Triethylamine (ca. 29.9 mmol) was added dropwise and the mixture stirred for 1 h. The reaction was then filtered and the filtrate slowly added dropwise to a solution of the appropriate alcohol (ca. 7.7 mmol) in 25 mL of pyridine. The solution was stirred for an additional 3 h and the solvent removed under vacuum at 60 °C. The solid residue was extracted with chloroform and placed in a freezer for 2 days to precipitate the remaining triazole. Solvent was removed from the resulting solution and the solid recrystallized from 2-propanol.

1-Thioxo-4-(hydroxymethyl)-1λ^5-phospha-2,7,8-trioxabicyclo[3.2.2]-nonane (12a), 1-Thioxo-4-(hydroxymethyl)-1λ^5-phospha-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane (12b), and 1-Thioxo-4-(hydroxymethyl)-1λ^5-phospha-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (12c). A suspension of **4a**, **4c**, and **4d** (ca. 0.9 mmol) and sulfur (ca. 1.5 mmol) in 25 mL of a 50:50 mixture of carbon disulfide and benzene was heated to 50 °C for 1 week. After solvent evaporation the solid residue was purified on silica gel with ethyl acetate to give **12a–c**.

1-Selenoxo-4-(hydroxymethyl)-1λ^5-phospha-2,7,8-trioxabicyclo-[3.2.2]nonane (13a), 1-Selenoxo-4-(hydroxymethyl)-1λ^5-phospha-2,8,9-trioxatricyclo[4.2.2.0^{4,6}]decane (13b), 1-Selenoxo-4-(hydroxymethyl)-1λ^5-phospha-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane (13c), 1-Selenoxo-4-(hydroxymethyl)-1λ^5-phospha-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (13d), 1-Selenoxo-4-(hydroxymethyl)-1λ^5-phospha-2,11,12-trioxatricyclo[7.2.2.0^{4,9}]tridecane (13e), and 1-Selenoxo-1λ^5-phospha-2,7,8-trioxabicyclo[3.2.2]nonane (19). In a typical reaction, a suspension of the appropriate compound **4a–e** or **3** (ca. 3.6 mmol) and finely divided red selenium (ca. 5.3 mmol) in 40 mL of toluene was heated to 80 °C for 4 days. The hot solution was filtered and the solvent removed under vacuum to give the appropriate white solid **13a–e** or **19**.

1-Borane-4-(hydroxymethyl)-1-phospha-2,7,8-trioxabicyclo[3.2.2]nonane (14a), 1-Borane-4-(hydroxymethyl)-1-phospha-2,8,9-trioxatricyclo[4.2.2.0^{4,6}]decane (14b), 1-Borane-4-(hydroxymethyl)-1-phospha-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane (14c), 1-Borane-4-(hydroxymethyl)-1-phospha-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (14d), 1-Borane-4-(hydroxymethyl)-1-phospha-2,11,12-trioxatricyclo[7.2.2.0^{4,9}]-tridecane (14e), and 1-Borane-1-phospha-2,7,8-trioxabicyclo[3.2.2]nonane (20). To a solution of the appropriate compound **4a–e** or **3** (ca. 3.0 mmol) in 40 mL of THF was slowly added dropwise a 1.00 M solution of THF·BH_3 in THF (ca. 3.2 mmol). After the solution was stirred for an additional 2 h, the solvent was removed under vacuum to give white solid **14a–e** or **20**.

4-[(Benzoyloxy)methyl]-1-oxo-1λ^5-phospha-2,10,11-trioxatricyclo-[6.2.2.0^{4,8}]dodecane (15). A pyridine (2.0 mL) solution of **11d** (0.0617 g, 0.263 mmol) was treated with benzoyl chloride (0.043 mL, 0.37 mmol) followed by addition of DMAP (0.0032 g, 0.026 mmol). After 2 days, the solution was diluted with 3 mL of toluene and evaporated to dryness. The residue was chromatographed on silica gel with ethyl acetate and recrystallized from chloroform–hexanes (1:1).

1-Oxo-4-(methoxymethyl)-1λ^5-phospha-2,10,11-trioxatricyclo-[6.2.2.0^{4,8}]dodecane (16). A suspension of sodium hydride (0.0233 g, 0.929 mmol; oil free) in 6.0 mL of dry dioxane was mixed with **11d** (0.1437 g, 0.6136 mmol) at room temperature and stirred until the evolution of hydrogen ceased (1 h). Dimethyl sulfate (0.064 mL, 0.0676 mmol) was then added and the mixture stirred for 10 h. After solvent removal under vacuum, the solid residue was extracted with chloroform and the chloroform-soluble material chromatographed on silica gel with ethyl acetate. Recrystallization from chloroform–hexane (1:1) gave **16**.

1-Oxo-4-[((butyldimethylsilyl)oxy)methyl]-1λ^5-phospha-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (17). To a solution of **11d** (0.1099 g, 0.4693 mmol) in 2.0 mL of dimethylformamide containing triethylamine (0.079 mL, 0.57 mmol) and DMAP (0.0030 g, 0.024 mmol) was added *tert*-butyldimethylsilyl chloride (0.0850 g, 0.564 mmol). The solvent was removed under vacuum and the residue purified on silica gel to give **17** after recrystallization from chloroform–hexane (1:1).

Reactions of 4a–e with Anhydrous Protic Acids. The reactions of the title phosphites were carried out with CF_3CO_2H and CF_3SO_3H in essentially the same manner. To a solution of the appropriate phosphite in THF was added 0.01 equiv of acid in THF. The solution was stirred for 12 h and monitored by ^{1}H NMR and ^{31}P NMR spectroscopies. In the case of H_3PO_3, 0.1 equiv of the acid was added to a solid sample of **4c** and the resulting mixture sublimed at 1.0 Torr and 120 °C. The sublimate was analyzed by ^{31}P NMR spectroscopy.

Reactions of 4a–e with Amines. Phosphites **4a–e** were reacted with pyridine, Et_3N, and DBU by using the same general procedure. To a solution of the appropriate phosphite in THF was added 0.01 equiv of base in THF. The solution was stirred for 12 h and monitored by ^{1}H and ^{31}P NMR spectroscopies.

Reaction of 4a–e with Water. To solutions containing **4a–e** in THF was added 0.01 equiv of H_2O in THF. Each solution was stirred for 12 h and monitored by ^{1}H NMR and ^{31}P NMR spectroscopies.

X-ray Crystallography. Crystals were mounted on glass fibers (**9**, **11c**) or inside thin-walled Lindemann capillaries (**2d**, **5c**, **11d**). Geometric and intensity data were gathered by automated four-circle diffractometers

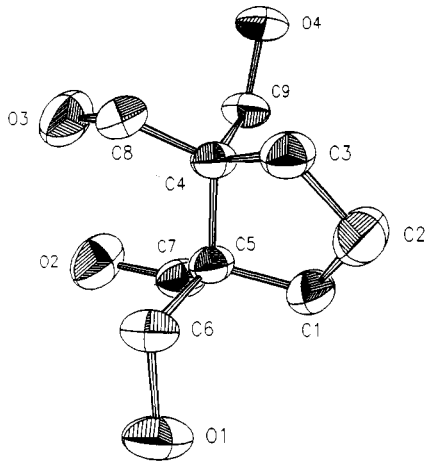


Figure 1. ORTEP drawing of **2d**, with ellipsoids at the 50% probability level.

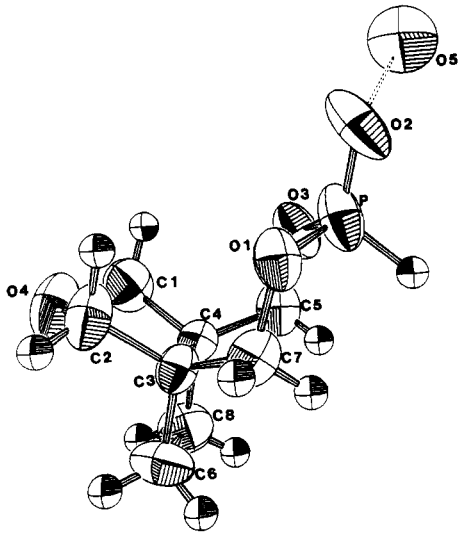


Figure 2. ORTEP drawing of **5c**, with ellipsoids at the 50% probability level.

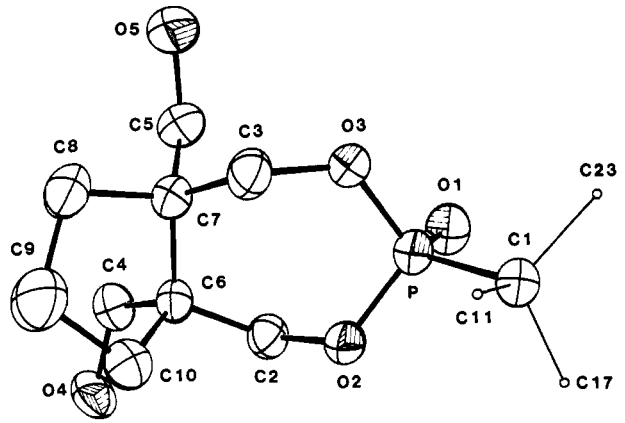


Figure 3. ORTEP drawing of **9**, with ellipsoids at the 50% probability level. The phenyl rings have been reduced to single carbon atoms for clarity.

using routine procedures. Important crystal data and data-collection parameters are provided in Table IV. During data collection for each crystal, standard reflections were measured at regular intervals to check for sample and instrument stability. For each crystal, the lattice dimensions and Lauc group were verified by normal-beam axial photographs. For **9**, azimuthal scans of several reflections with Eulerian angle χ near 90° were used as the basis of an empirical absorption correction. The monitor reflections for **9** decreased in intensity by an average of 9.1%; therefore, an anisotropic decay correction was applied.

For each structure, the majority of the initial atomic positions were determined by direct methods. The structures were developed and refined

Table V. Selected Bond Distances and Angles in **2d**[a]

	Bond Distances (Å)		
O(1)–C(6)	1.429 (4)	C(4)–C(8)	1.527 (4)
O(2)–C(7)	1.426 (4)	C(4)–C(9)	1.538 (4)
O(3)–C(8)	1.425 (4)	C(5)–C(6)	1.538 (4)
O(4)–C(9)	1.429 (4)	C(5)–C(7)	1.528 (4)
	Bond Angles (deg)		
C(2)–C(1)–C(5)	106.7 (2)	C(1)–C(5)–C(6)	110.0 (2)
C(1)–C(2)–C(3)	106.0 (3)	C(1)–C(5)–C(7)	109.5 (2)
C(2)–C(3)–C(4)	106.9 (2)	C(4)–C(5)–C(6)	110.1 (2)
C(3)–C(4)–C(5)	102.4 (2)	C(4)–C(5)–C(7)	116.1 (2)
C(3)–C(4)–C(8)	109.6 (2)	C(6)–C(5)–C(7)	108.5 (2)
C(3)–C(4)–C(9)	109.9 (2)	O(1)–C(6)–C(5)	112.6 (2)
C(5)–C(4)–C(8)	116.2 (2)	O(2)–C(7)–C(5)	112.0 (2)
C(5)–C(4)–C(9)	110.1 (2)	O(3)–C(8)–C(4)	112.1 (2)
C(8)–C(4)–C(9)	108.5 (2)	O(4)–C(9)–C(4)	112.5 (2)
C(1)–C(5)–C(4)	102.4 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Bond Distances and Angles in **5c**[a]

	Bond Distances (Å)		
P–O(2)	1.447 (7)	O(2)···O(5)	2.685 (9)
P–O(1)	1.569 (5)	P–O(3)	1.558 (6)
O(1)–C(7)	1.449 (10)	O(3)–C(5)	1.456 (10)
C(7)–C(3)	1.483 (11)	C(5)–C(4)	1.500 (11)
C(3)–C(6)	1.515 (12)	C(4)–C(8)	1.533 (12)
C(3)–C(2)	1.516 (11)	C(4)–C(1)	1.517 (12)
C(2)–O(4)	1.414 (11)	C(1)–O(4)	1.412 (12)
C(3)–C(4)	1.561 (10)	C(6)–C(8)	1.515 (14)
	Bond Angles (deg)		
O(3)–P–O(1)	108.3 (3)	C(1)–O(4)–C(2)	104.2 (7)
O(1)–P–O(2)	111.3 (4)	O(3)–P–O(2)	111.1 (4)
P–O(1)–C(7)	121.2 (5)	P–O(3)–C(5)	120.3 (5)
O(1)–C(7)–C(3)	111.6 (6)	O(3)–C(5)–C(4)	112.3 (7)
C(7)–C(3)–C(2)	113.9 (6)	C(5)–C(4)–C(1)	113.5 (7)
C(3)–C(6)–C(8)	89.9 (7)	C(4)–C(8)–C(6)	89.2 (7)
C(3)–C(2)–O(4)	104.8 (7)	C(4)–C(1)–O(4)	104.5 (7)
C(7)–C(3)–C(6)	114.2 (7)	C(5)–C(4)–C(8)	113.3 (7)
C(6)–C(3)–C(2)	114.9 (7)	C(8)–C(4)–C(1)	115.0 (7)
C(4)–C(3)–C(7)	118.3 (6)	C(3)–C(4)–C(5)	119.5 (6)
C(4)–C(3)–C(2)	102.3 (6)	C(3)–C(4)–C(1)	103.2 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

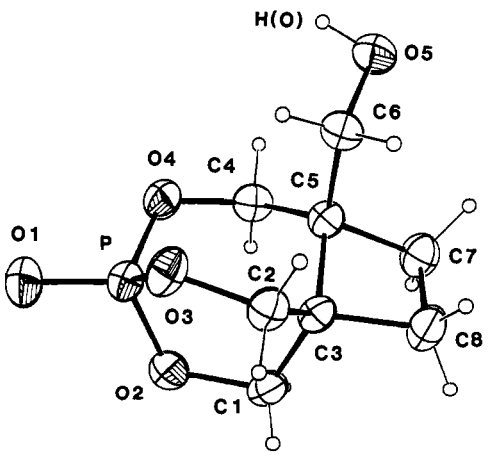


Figure 4. ORTEP drawing of **11c**, with ellipsoids at the 50% probability level.

in sequences of Fourier maps and least-squares refinements. The refinement packages used were ALLS[32a] (**2d**, **5c**, **11d**), SHELX-76[32b] (**9**), or

(32) (a) Lapp, R. L.; Jacobson, R. A. U.S. Department of Energy Report IS-4708; Iowa State University: Ames, IA, 1979. (b) Sheldrick, G. M. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University: Delft, The Netherlands, 1978. (c) *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1988.

Table VII. Selected Bond Distances and Angles in **9**[a]

Bond Distances (Å)			
P-O(1)	1.457 (2)	C(4)-C(6)	1.551 (6)
P-O(2)	1.574 (3)	C(5)-C(7)	1.541 (5)
P-O(3)	1.568 (3)	C(6)-C(7)	1.559 (5)
P-C(1)	1.857 (4)	C(6)-C(10)	1.536 (5)
O(2)-C(2)	1.470 (5)	C(7)-C(8)	1.558 (5)
O(3)-C(3)	1.463 (5)	C(8)-C(9)	1.524 (6)
O(4)-C(4)	1.424 (5)	C(9)-C(10)	1.527 (6)
O(5)-C(5)	1.421 (5)	C(2)-C(6)	1.515 (5)
		C(3)-C(7)	1.522 (6)

Bond Angles (deg)			
O(1)-P-O(2)	114.8 (1)	C(2)-C(6)-C(10)	113.6 (3)
O(1)-P-O(3)	109.8 (2)	C(4)-C(6)-C(7)	110.1 (3)
O(1)-P-C(1)	113.2 (2)	C(4)-C(6)-C(10)	109.1 (3)
O(2)-P-O(3)	104.9 (1)	C(7)-C(6)-C(10)	102.7 (3)
O(2)-P-C(1)	104.4 (2)	C(3)-C(7)-C(5)	108.9 (4)
O(3)-P-C(1)	109.3 (2)	C(3)-C(7)-C(6)	113.8 (3)
P-O(2)-C(2)	115.7 (2)	C(3)-C(7)-C(8)	104.8 (3)
P-O(3)-C(3)	125.5 (2)	C(5)-C(7)-C(6)	113.8 (3)
O(2)-C(2)-C(6)	113.4 (3)	C(5)-C(7)-C(8)	112.5 (3)
O(3)-C(3)-C(7)	113.6 (3)	C(6)-C(7)-C(8)	102.6 (3)
O(4)-C(4)-C(6)	112.2 (3)	C(7)-C(8)-C(9)	106.4 (3)
O(5)-C(5)-C(7)	111.1 (3)	C(8)-C(9)-C(10)	107.2 (3)
C(2)-C(6)-C(4)	104.4 (2)	C(6)-C(10)-C(9)	104.4 (3)
C(2)-C(6)-C(7)	117.0 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VIII. Bond Distances and Angles in **11c**[a]

Bond Distances (Å)			
P-O(1)	1.463 (1)	O(5)-H(0)	0.93 (4)
P-O(2)	1.563 (1)	C(1)-C(3)	1.521 (2)
P-O(3)	1.564 (2)	C(2)-C(3)	1.522 (2)
P-O(4)	1.572 (1)	C(3)-C(5)	1.573 (3)
		C(3)-C(8)	1.555 (2)
O(2)-C(1)	1.468 (2)	C(4)-C(5)	1.499 (3)
O(3)-C(2)	1.472 (2)	C(5)-C(6)	1.539 (2)
O(4)-C(4)	1.475 (2)	C(5)-C(7)	1.555 (2)
O(5)-C(6)	1.415 (2)	C(7)-C(8)	1.546 (3)

Bond Angles (deg)			
O(1)-P-O(2)	113.25 (8)	C(1)-C(3)-C(8)	109.0 (1)
O(1)-P-O(3)	111.08 (8)	C(2)-C(3)-C(5)	116.2 (1)
O(1)-P-O(4)	110.66 (8)	C(2)-C(3)-C(8)	121.2 (2)
O(2)-P-O(3)	106.18 (18)	C(5)-C(3)-C(8)	88.3 (1)
O(2)-P-O(4)	106.97 (7)	O(4)-C(4)-C(5)	110.7 (1)
O(3)-P-O(4)	108.44 (8)	C(3)-C(5)-C(4)	115.6 (1)
P-O(2)-C(1)	118.3 (1)	C(3)-C(5)-C(6)	111.8 (1)
P-O(3)-C(2)	120.5 (1)	C(3)-C(5)-C(7)	87.6 (1)
P-O(4)-C(4)	120.3 (1)	C(4)-C(5)-C(6)	111.2 (2)
C(4)-C(5)-C(7)	118.9 (1)		
C(6)-C(5)-C(7)	109.7 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

CAD4-SDP[32c] (**11c**). Scattering factors were obtained from the usual sources.[33] Hydrogen atoms were used in calculated positions with fixed temperature factors for **2d** and **11d**. For **5c** and **11c** the hydrogen positional parameters were refined with fixed temperature factors, except for the hydroxyl hydrogen atom on **11c**, for which an isotropic temperature factor was also refined. The hydroxyl H atoms in **9** were also freely refined, while the other hydrogen atoms were used in calculated positions; one common temperature factor was refined for the phenyl hydrogen atoms, and another, for the alkyl hydrogen atoms. For **2d** and **5c**, the choice of the centric space groups were suggested by intensity statistics and confirmed by successful refinement.

Data pertinent to the least-squares refinements are summarized in Table IV. Selected bond lengths and angles for **2d**, **5c**, **9**, **11c**, and **11d** are given in Tablex V–IX. The ORTEP diagrams are presented in Figures 1–5.

(33) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table IX. Bond Distances and Angles in **11d**[a]

Bond Distances (Å)			
P(1)-O(1)	1.459 (3)	C(2)-C(6)	1.524 (5)
P(1)-O(2)	1.557 (2)	C(3)-C(6)	1.513 (5)
P(1)-O(3)	1.561 (3)	C(4)-C(5)	1.539 (5)
P(1)-O(4)	1.546 (3)	C(5)-C(6)	1.564 (5)
O(2)-C(3)	1.472 (4)	C(5)-C(7)	1.543 (5)
O(3)-C(1)	1.465 (5)	C(6)-C(9)	1.557 (5)
O(4)-C(2)	1.462 (4)	C(7)-C(8)	1.522 (5)
O(5)-C(4)	1.423 (4)	C(8)-C(9)	1.519 (6)
C(1)-C(5)	1.512 (5)		

Bond Angles (deg)			
O(1)-P(1)-O(2)	113.0 (2)	C(1)-C(5)-C(6)	115.1 (3)
O(1)-P(1)-O(3)	111.4 (2)	C(1)-C(5)-C(7)	109.0 (3)
O(1)-P(1)-O(4)	112.6 (2)	C(4)-C(5)-C(6)	110.5 (3)
O(2)-P(1)-O(3)	106.3 (1)	C(4)-C(5)-C(7)	109.5 (3)
O(2)-P(1)-O(4)	105.9 (1)	C(6)-C(5)-C(7)	102.2 (3)
O(3)-P(1)-O(4)	107.1 (1)	C(2)-C(6)-C(3)	107.7 (3)
P(1)-O(2)-C(3)	119.4 (2)	C(2)-C(6)-C(5)	115.2 (3)
P(1)-O(3)-C(1)	119.4 (2)	C(2)-C(6)-C(9)	109.1 (3)
P(1)-O(4)-C(2)	121.1 (2)	C(3)-C(6)-C(5)	112.3 (3)
O(3)-C(1)-C(5)	113.4 (3)	C(3)-C(6)-C(9)	108.6 (3)
O(4)-C(2)-C(6)	111.0 (3)	C(5)-C(6)-C(9)	103.7 (3)
O(2)-C(3)-C(6)	112.5 (3)	C(5)-C(7)-C(8)	104.7 (3)
O(5)-C(4)-C(5)	109.9 (3)	C(7)-C(8)-C(9)	106.3 (3)
C(1)-C(5)-C(4)	110.1 (3)	C(6)-C(9)-C(8)	107.4 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

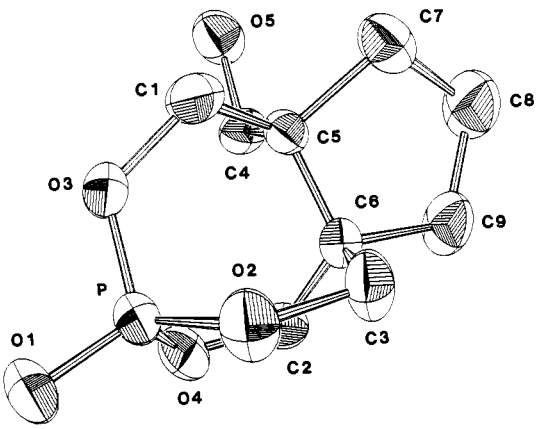
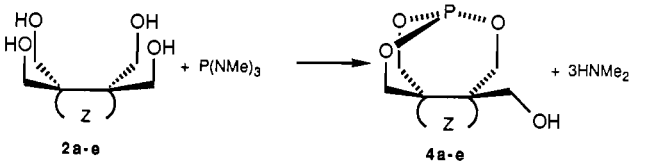


Figure 5. ORTEP drawing of **11d**, with ellipsoids at the 50% probability level.

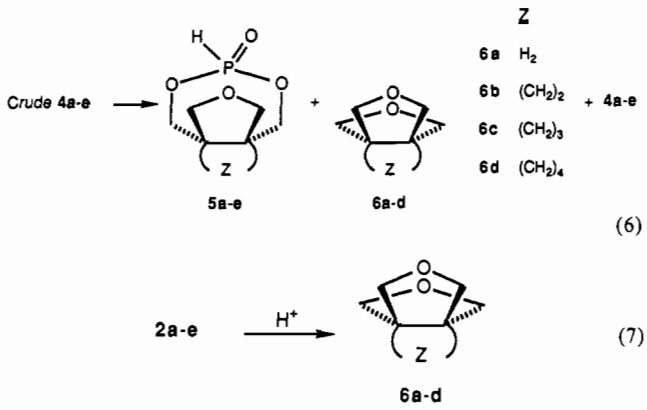
Results and Discussion

Synthetic Pathways. Phosphites **3** and **4a–e** could be prepared by the reaction of the appropriate alcohol with $P(NMe_2)_3$ in THF as shown in reaction 5 for **4a–e**. Reaction 5 could be performed



(5)

both with or without solvent. Initially the purification of the phosphites proved to be much more difficult than anticipated. Although ^{31}P and ^{1}H NMR spectroscopy of the crude product prior to sublimation showed the phosphite to be the major phosphorus-containing product of the reaction, attempts to purify the phosphite by sublimation (0.1 Torr, 180 °C) also gave the new compounds **5a–e** and the known tricyclic ethers **6a–d** shown in reaction 6. Due to stereochemistry about the phosphorus atom, compounds **5a–e** appear as pairs of diastereomers (vide infra). Compounds **6a–d** were previously prepared by reaction of the tetraalcohols **2a** and **2c–e** with catalytic amounts of acid as shown in reaction 7.[28] Only ca. 1% of the sublimate was found to be

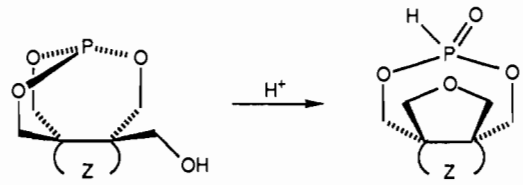


(6)

(7)

in the form of the phosphite ester, and the polymeric residue contained no detectable phosphite ester.

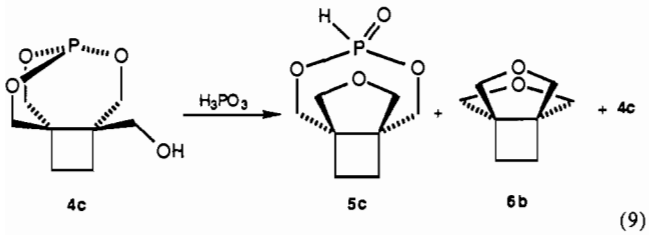
The phosphonates **5a–e** could also be prepared by reaction of the chromatographically purified phosphite esters with trace amounts of anhydrous acids as shown in reaction 8. Monitoring



(8)

the acidic solutions by ^{31}P NMR and ^{1}H NMR spectroscopy showed that rearrangement of the phosphite to phosphonate began almost immediately. Solutions containing small amounts of water were also found to promote the formation of the phosphonate species while solutions containing dry solvent showed no signs of rearrangement. In solutions containing pyridine, Et_3N, or DBU, no phosphonate or cyclic ether products could be detected.

In order to determine whether acid was playing a role in the rearrangement in solid samples of **4a–e** subjected to sublimation, a mixture containing purified **4c** and a small amount of freshly prepared phosphorous acid was heated under vacuum (1.0 Torr, 120 °C). The resulting sublimate was a mixture containing **4c** (32%), **5c** (45%), and **6b** (23%) as shown in reaction 9. Moreover,

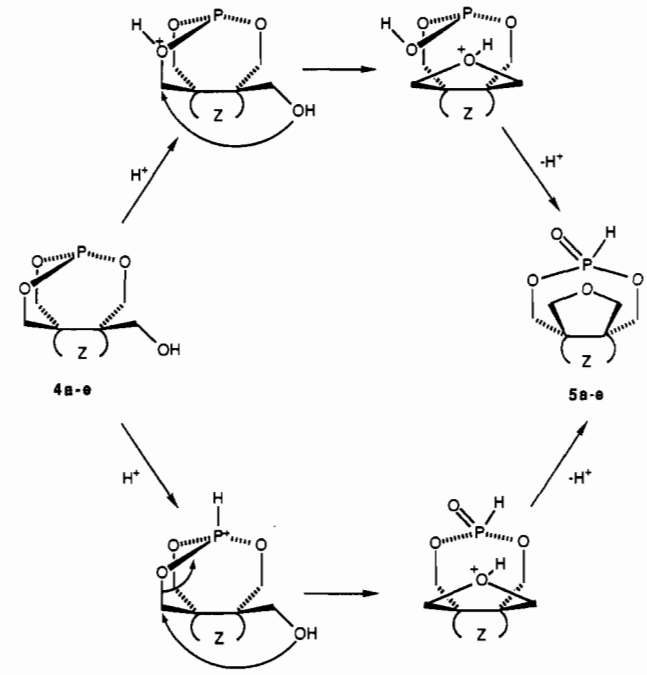


(9)

purified samples of **4a–e** were sublimed at 0.01 Torr and 85 °C without change, while at 5.0 Torr and 85 °C, they sublimed as roughly an 80/20 mixture of phosphite and phosphonate, as shown by ^{1}H and ^{31}P NMR spectroscopies. These data suggest a competitive acid-catalyzed rearrangement for the formation of **5a–e** and acid-assisted pyrolysis of the phosphonate to give **6a–d** and presumably HPO_2 polymer.

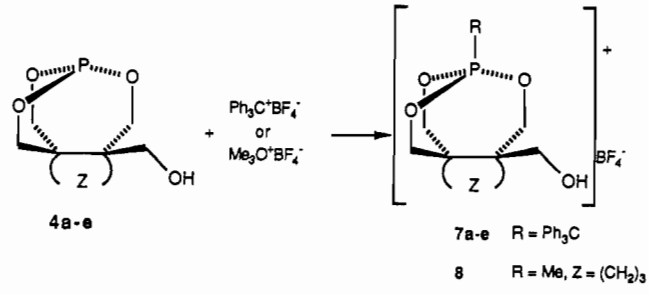
A possible pathway for the acid-catalyzed rearrangement of **4a–e** is shown in Scheme I. In the first step of the upper pathway, an esteratic oxygen is protonated. Such a protonated intermediate is similar to one proposed in the acid-catalyzed hydrolysis of phosphite and phosphate esters.[34] As in the reactions of the tetraalcohols with acid to form diethers **6a–d**,[29] the protonation of this oxygen forms a (POH) leaving group, rendering the adjacent carbon atom more susceptible to nucleophilic attack in the second step. The POH function rearranges in the next step, and the cyclic ether group loses the remaining proton. The lower

Scheme I



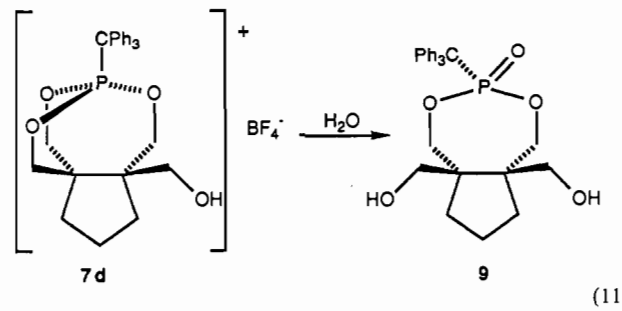
pathway involves an initial intermediate protonated at phosphorus (the more active of the two pathways in the acid-catalyzed hydrolysis of phosphite esters[33]). As in the upper pathway in Scheme I, nucleophilic attack of the carbon by the adjacent alcohol function gives the cyclic ether and forms a P=O bond.

We consider the lower pathway in Scheme I probably to be of lesser importance, based on the results of reactions of **4a–e** with electrophiles. In reactions of the phosphite esters with $Ph_3C^+BF_4^-$, alkylation takes place exclusively at phosphorus to give **7a–e** and **8** as shown in reaction 10. These species, similar to the phos-



(10)

phorus-protonated intermediate in Scheme I, do not undergo spontaneous rearrangement to form the corresponding phosphonates, indicating that the C–O bond is not sufficiently activated (at least not by carbenium ions) for nucleophilic attack by the adjacent alcohol group. In the presence of water, however, **7d** slowly forms **9** in reaction 11, demonstrating that nucleophilic



(11)

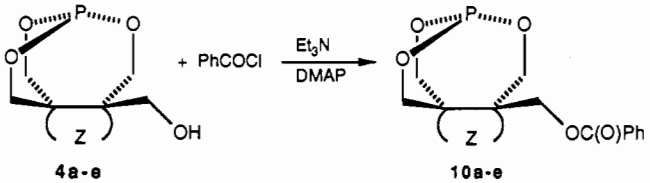
attack on the C–O–P carbon is possible, but that it is relatively slow. Nucleophilic reactions of analogous species protonated at phosphorus are probably also slow, supporting the upper pathway

(34) Westheimer, F. H.; Huang, S.; Coritz, F. *J. Am. Chem. Soc.* **1988**, *110*, 181.

in Scheme I as the dominant one.

Because phosphite esters are well-known to transesterify in the presence of alcohols rather than afford an ether and a phosphonate (as do **4a–e** in the presence of anhydrous acid), we added anhydrous trifluoroacetic acid to methanol or ethanol solutions of the bicyclic phosphite $P(OCH_2)_3CMe$. Monitoring the mixtures by ^{31}P NMR revealed virtually no change compared with the acid-free solution. It is therefore suggested that nucleophilic attack of the oxygen of the pendant alcohol group on the indicated carbon of protonated **4a–e** in Scheme I is facilitated by formation of a five-membered ring intermediate, which eventually forms the five-membered ether ring of **5a–e**. Solution evidence for hydrogen bonding of the oxygen of the pendant alcohol group with the hydrogens of the vulnerable carbon in **4a–e** (Scheme I) is given in the next section.

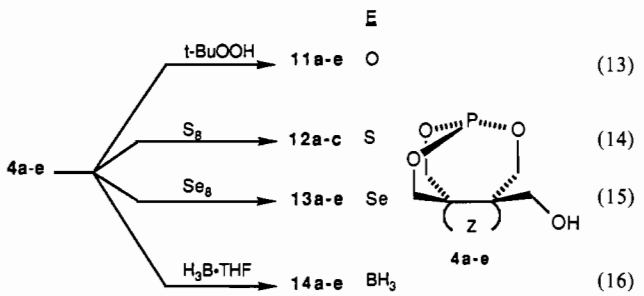
In an attempt to trap pentacoordinate species possibly formed in the equilibrium envisioned in reaction 4, compounds **4a–e** were reacted with PhC(O)Cl in the presenc e of Et_3N and catalytic amounts of DMAP (reaction 12). In this reaction, the penta-



4a-e **10a-e** (12)

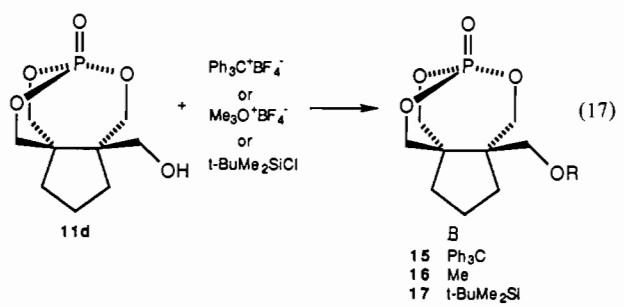
coordinate tautomer would be deprotonated and the resultant anion would be expected to react with the PhC(O)Cl to yield a pentacoordinate compound. However, the benzoate derivatives **10a–e** were isolated instead.

The phosphate (**11a–e**), thiophosphate (**12a–c**), selenophosphate (**13a–e**) and BH_3 (**14a–e**) derivatives of the corresponding parent compounds **4a–e** were synthesized as shown in reactions 13–16.



The phosphates **11a–d** could also be prepared by reaction of tris(triazolyl)phosphine oxide with the appropriate tetraalcohol **2a–d**.

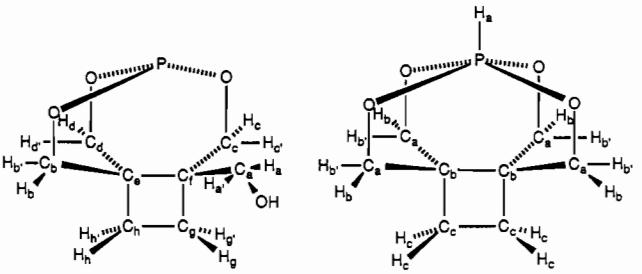
Attempts to trap a pentacoordinate species by derivatization of the phosphate oxygen of **11d** with electrophiles (with concomitant deprotonation and coordination of the alkoxy arm) resulted in the isolation of tetracoordinate phosphorus compounds **15–17** as shown in reaction 17.



(17)

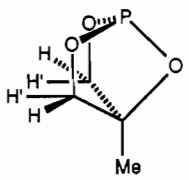
Spectroscopic Studies. ^{31}P NMR data for the compounds synthesized herein are tabulated in Table I. Because of space considerations, tables of ^{13}C and ^1H NMR data with assignments are given in the supplementary material. These assignments were made on the basis of a detailed NMR analysis of **4c** to be discussed shortly.

All of the protons of the tricoordinate and pentacoordinate forms of **4c** are labeled as follows:



The higher symmetry of the pentacoordinate form requires the ^1H NMR spectrum of this compound to exhibit a simple ABX pattern. The proton spectra of **4a–e** and their derivatives, however, are very complex owing to the presence of the pendant alcohol group, which renders all of the protons in these compounds inequivalent. The complexity of the spectra of these compounds rules out the square-pyramidal structure as the dominant form in solution. In order to determine whether detectable amounts of the square-pyramidal tautomer were present, it was necessary to assign the ^1H NMR shifts and couplings in these compounds, and **4c** was chosen for this purpose.

A useful model for the interpretation of the ^1H NMR spectra is phosphite ester **3**. In this compound and its derivatives, the absence of the pendant alcohol group increases the symmetry of the molecule, simplifying the proton NMR spectrum and its analysis. Comparison of the coupling constants and proton chemical shifts in **3** with those of the previously investigated bicyclic phosphorus compound **21**,[35] which is of similar symmetry,



21

confirmed the ^1H NMR assignments. A common feature of **21** and **3** is the smaller value of $^3J(POCH)$ in comparison with $^3J(POCH')$.[35] This effect has also been found in derivatives of **4a–e**.

To interpret the ^1H NMR spectra of **4a–e** and their derivatives, the complete assignment of the spectrum of **4c** was accomplished with the help of several NMR techniques. The region of the ^1H NMR spectrum of **4c** containing methylene protons a–d is shown in Figure 6. The chemical shift of proton a was identified by its $^3J(HOCH_a)$ value using DMSO-d_6 as the solvent. To determine which signals in the one-dimensional ^1H NMR spectrum were coupled, a COSY[36] experiment was performed (Figure 7). From these data, the positions of protons a, b, b′, d and d′ could be tentatively assigned as shown in the figure. The resonances of protons a′, c, and c′ were found to overlap. This experiment was also useful in detecting the four-bond "W" coupling between protons b and d, also observed in rigid bicyclic systems containing protons in a "W" orientation.[37] To unambiguously establish the chemical shifts of protons a–d, a ^1H–^{13}C correlated two-dimensional NMR spectrum using bilinear pulses[38] was obtained. For each carbon atom of the molecule, this technique (which allows suppression of coupling in the ^1H–^{13}C chemical-shift-correlation maps) gave a one-dimensional decoupled ^1H NMR spectrum of

(35) Bertrand, R. D.; Verkade, J. G.; White, D. W.; Gagnaire, D.; Robert, J. B.; Verrier, J. *J. Magn. Reson.* **1970**, *3*, 494.
(36) Derome, A. E. In *Modern NMR Techniques for Chemistry Research*; Baldwin, J. E., Ed.; Pergamon: Elmsford, NY, 1987.
(37) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981; p 209.
(38) Rutar, V.; Wong, T. C.; Guo, W. *J. Magn. Reson* **1985**, *64*, 849.

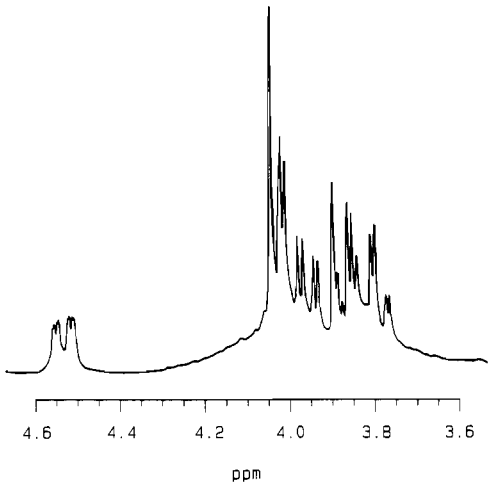


Figure 6. ^{1}H NMR spectrum of the methylene proton region of **4c**.

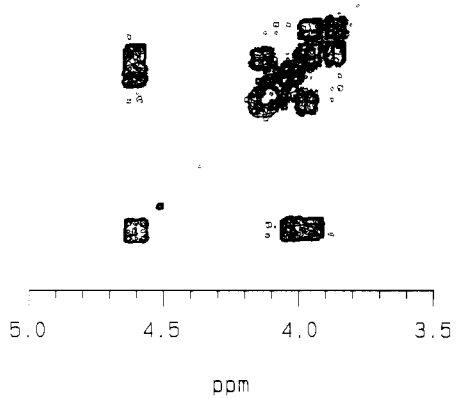
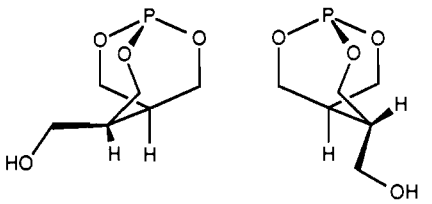


Figure 7. Representation of the COSY NMR experiment with **4c**.

the protons bound to that carbon atom. From these data the chemical shifts of protons a′, c, and c′ were obtained and the assignments of protons a, b, b′, d, and d′ were confirmed. Two-dimensional indirect J spectroscopy with a selective spin flip,[39] an NMR experiment that allows the direct measurement of geminal couplings without resolution of the complete coupling pattern, allowed the determination of the geminal proton couplings of the eight methylene protons of interest, as well as of the four methylene protons of the cyclobutane ring. These coupling values were then employed in conjunction with data from a normal ^{1}H–^{13}C NMR correlated two-dimensional NMR experiment[36] to determine all of the remaining proton–proton and proton–phosphorus couplings. The ^{1}H and ^{13}C NMR assignments for **4c** are given in Table II. With the assignment of **4c** complete, the interpretation of the ^{1}H NMR spectra of the remaining compounds was straightforward (see supplementary material). No signals assignable to a square-pyramidal compound appeared in the ^{1}H NMR spectra of any of these compounds.

Several trends in coupling constants and chemical shifts are found in the NMR data. As in other phosphorus compounds, the values of ^3J(PH) depend on the derivatization at phosphorus, and they show little variation among compounds with identical phosphorus functionality. Similarities can also be found in the proton–proton couplings of phosphorus derivatives of the same tetraalcohol. The functionality on phosphorus, or on the oxygen of the free arm, has little effect on the position and the line shape of the methine protons of the derivatives of **4a** or of the protons of the monocyclic rings in derivatives of **4b–e**. In **4a** and its derivatives, the methine protons appear in the range 2.6–1.6 ppm, similar to observations for derivatives of **3**, while the ring protons of **4b**, **4c**, **4d**, and **4e** and their derivatives appear at ca. 2.3–2.0, 2.4–1.9, 2.1–1.5, and, 2.2–1.6 ppm, respectively. This indicates that little change occurs in the geometry of the carbon backbone of these compounds upon derivatization of the phosphorus atom. The "W" coupling, $^4J(H_bH_d)$ observed in **4c** is present in the ^{1}H NMR spectra of all of the derivatives of **4a–e** and is a further indication of the rigid nature of these compounds.

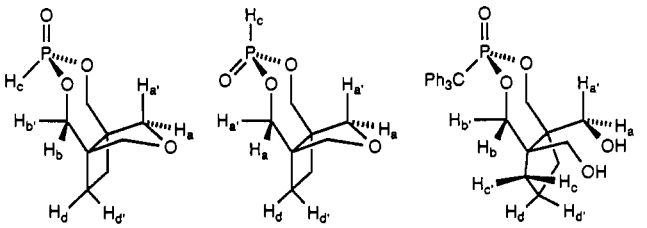
Compounds containing a carbocyclic ring (i.e., **4b–e** and their derivatives) reveal that the chemical shift of proton b appears significantly downfield with respect to the other seven methylene protons in this region of the spectrum. On the other hand, **4a** and its derivatives do not exhibit this effect and the chemical shift of proton b appears within the range of shifts of the other methylene protons. The major difference between compounds such as **4a** and **4b–e** can be seen in conformations A and B for **4a**. Two



A B

conformations (A and B) are available to **4a** while only the one resembling A is possible for **4b–e** owing to the carboxylic ring in these compounds. Steric arguments suggest that conformation B should be preferred in **4a**, with the alcoholic arm nearly eclipsing the methine proton. The presence of the carboxylic ring in **4b–e** places the alcoholic arm in closer proximity to proton b, permitting hydrogen bonding to the oxygen of the alcohol group and consequently causing the NMR resonance of proton b to move to lower field.

Compounds **5c** and **9**, shown below, yield ^{1}H NMR spectra indicative of the conformational equilibria present in 1,3,2-dioxaphosphepanes and 1,3,2-dioxaphosphepenes in solution.[40] In the case of **5c**, the presence of a pair of diastereomers is readily apparent from the pairs of similar, yet inequivalent, proton signals in the mixture. The similarity of the $^3J(POCH_b)$ and $^3J(POCH_{b'})$ values in the pair of **5c** diastereomers and in compound **9** shows



5c **9**

that conformational flipping interchanges the axial and equatorial environments of these protons rapidly on the NMR time scale. Dioxaphosphepanes not undergoing conformational exchange exhibit differences in their ^3J(POCH) values of 10 Hz or greater.[39] In the case of **9** this conformational exchange is probably a twist–twist equilibrium since the five-membered ring is flexible and would tend to resist formation of an eclipsed conformation around the two quaternary carbons, which would be required for chair or boat forms of the seven-membered ring. For compound **5c**, the energy difference between the planar and puckered forms of cyclobutane is small, allowing the possibility for both a chair and a twist conformation of the 1,3,2-dioxaphosphepane ring. In dioxaphosphepanes believed to exhibit a chair–chair equilibrium, however, protons H_b and $H_{b'}$ do not appear to be coupled, unlike in **5c** in which $^2J(H_bCH_{b'})$ is ca. 12.9 Hz. These values are comparable to $^2J(H_bCH_{b'})$ in twist–twist equilibrating dioxaphosphepanes whose coupling constants are ca. 11.8 Hz.[40] On the basis of these comparisons, both isomers of **5c** appear to be undergoing a twist–twist conformational equilibrium in solution.

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Table X. Selected Bond Distances and Angles in **25**,[a] **26**,[b] and **27**[c]

	25	**26**[d]	**27**
	Bond Distances (Å)		
P–O(1)	1.445 (2)	1.464 (16)	
P–O(2)	1.594 (2)	1.576 (17)	1.60 (2)
P–O(3)	1.577 (2)	1.567 (12)	1.59 (2)
P–O(4)	1.577	1.567 (12)	1.56 (2)
O(2)–C(1)	1.492 (4)	1.456 (23)	1.47 (4)
O(3)–C(2)	1.478 (2)	1.453 (17)	1.48 (4)
O(4)–C(3)	1.478 (2)	1.453 (17)	1.52 (4)
	Bond Angles (deg)		
O(1)–P–O(2)	121.9 (1)	115.4 (10)	
O(1)–P–O(3)	115.8 (1)	114.6 (6)	
O(1)–P–O(4)	115.8 (1)	114.6 (6)	
O(2)–P–O(3)	97.4 (1)	103.2 (6)	105 (11)
O(2)–P–O(4)	97.4 (1)	103.2 (6)	103 (11)
S–P–O(2)			113 (1)
S–P–O(3)			114 (1)
S–P–O(4)			114 (1)
O(3)–P–O(4)	105.1 (1)	104.2	106 (0)
P–O(2)–C(1)	95.3 (2)	115.2 (12)	114 (17)
P–O(3)–C(2)	105.8 (1)	115.3 (9)	112 (17)
P–O(3)–C(2)	105.8 (1)	115.3 (9)	114 (17)

[a] See ref 56. [b] See ref 57. [c] See ref 58. [d] Distances are average values of two orientations in the crystal.

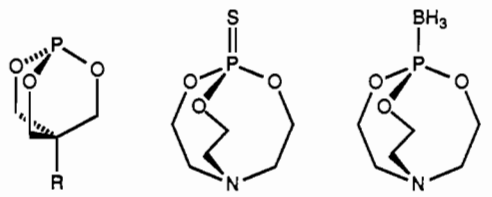
The ^{13}C NMR data also demonstrate the lack of symmetry in **4a–e**. All of the carbon atoms of **4c** are inequivalent in the tricoordinate form (Table II) while in the pentacoordinate configuration form only three types of carbons would be present. From the straightforward ^{13}C NMR assignment of **3** and information gained from the two-dimensional NMR experiments described above for **4c**, the ^{13}C NMR spectrum of the latter compound was assigned. An INADEQUATE NMR experiment[36] performed on **4c**, which allows the observation of carbon–carbon couplings and indicates the connectivity in the carbon backbone of the molecule, confirmed these assignments.

In **4a–e** and its derivatives, smaller ^2J(POC) couplings were observed for carbon b (<2.4 Hz) than for either carbons c (ca. 4.5 Hz) or d (ca. 5.5 Hz). This phenomenon and the fact that carbon b appears further downfield than the other carbon resonances are probably the result of the interaction of the alcoholic arm with proton b and hence indirectly with carbon b. Similarly, the value of ^3J(POCC) was always much greater for bridgehead carbon e (ca. 13 Hz) than that of bridgehead carbon f (<2.4 Hz). It has been shown that, all other factors being equal, the larger the number of bond pathways through which two nuclei can couple, the greater the coupling value.[41] Thus carbon e in **4a–e** is connected to the phosphorus by two three-bond paths, while carbon f is connected by only one such pathway. In none of the ^{13}C NMR spectra of the compounds reported here are peaks detected indicating the presence of pentacoordinate species. Moreover, variable-temperature ^{13}C NMR spectroscopy of **4c** showed no evidence of exchange of the alcohol group or the formation of pentacoordinate species up to 100 °C.

The ^{13}C NMR spectrum of **9** is consistent with the structure proposed for this compound. As in **4a–e** and their derivatives, the methylene carbon containing the alcohol group appears at lower field than the methylene carbons of the seven-membered ring. Also, ^3J(POCC) is not observed for **9** because the bridgehead carbon is part of a single three-bond pathway similar to that for carbon f in **4a–e** and their derivatives discussed above, for which detectable $^3J(POCC_f)$ coupling was also not observed.

^{31}P NMR spectroscopy has been used to investigate tautomeric equilibria of tricoordinate phosphorus compounds with pentacoordinate species (see Introduction). The chemical shifts of such tricoordinate species appear in the range 140–130 ppm while their pentacoordinate tautomers display signals between −30 and −45 ppm.[21–25] Compound **3** and its derivatives exhibit chemical shifts similar to those of their corresponding counterparts among **4a–e** and their derivatives (Table I) demonstrating that the presence of the pendant alcohol group has little effect on the phosphorus atom. The same is true for each of the other chemical shifts in Table I, with each type of phosphorus compound displaying ^{31}P resonances normally associated with such species.[42] This result strongly supports the absence of a five-coordinate phosphorus tautomer in these systems.

In the case of compounds **13a–e** and **19**, their P–Se coupling constants[43] allowed a ranking of the relative Lewis basicity of the corresponding phosphite esters **4a–e** and **3**. On the basis of the values of ^1J(PSe) presented in Table I, all of the phosphites have similar basicities, indicating that the presence of a carbocyclic ring in the system has little effect on the phosphorus-containing portion of the molecule. Comparison of the P–Se coupling constants with those of known compounds[44] shows **3** and **4a–e** to be slightly less basic than the bicyclic compounds of type **22**. The



22 **23** **24**

fact that identical types of phosphorus functionalities have similar chemical shifts suggests little change in the geometry around phosphorus in going from derivatives of **3** to corresponding derivatives of **4a–e**.

Description of the Structures. Tetraalcohol **2d**, whose structure is shown in Figure 1, is engaged in a high degree of intermolecular hydrogen bonding between alcohol groups. All of the bond distances (Table V) are well within the normal range.[45] The conformation of the five-membered ring is the half-chair form, which causes the pairs of arms on carbons 4 and 5 to be staggered. All of the C–O bond distances (average 1.427 Å) and the O–C–C bond angles (average 112.3°) are the same within experimental error, as are the hydrogen bond lengths (average 2.660 Å). All of the C–C bond lengths (average 1.537 Å) are likewise the same within experimental error with the exception of the C(4)–C(5) bond distance (1.576(4) Å), which is slightly elongated (0.04 Å) in relation to the other C–C bonds. This bond length is similar to, although slightly longer than, distances determined from molecular mechanics calculations and conformational analysis of 2,2-dimethylbutane (1.5478 Å),[46] 2,3-dimethylbutane (1.552 Å),[47] and tricyclo[3.3.2.0]decane (1.556 Å).[48] Because of the lengthening of the C(4)–C(5) bond, the C(1)–C(5)–C(4) and C(3)–C(4)–C(5) bond angles (102.4 (2)°) are smaller than the other three angles of the five-membered ring (average 106.7°). This elongation may also be in part due to steric effects resulting from the presence of four groups on adjacent carbon atoms of the ring. The remaining bond angles around C(4) and C(5) are all similar (average 109.3°) with the exception of C(4)–C(5)–C(7) (116.1 (2)°) and C(5)–C(4)–C(8) (116.2 (2)°), which are larger by 6.9°. In light of the fact that O(2) and O(3) are hydrogen bonded to one another within the same molecule, the 116° bond angles may be the result of the optimization of hydrogen bonding between O(2) and O(3).

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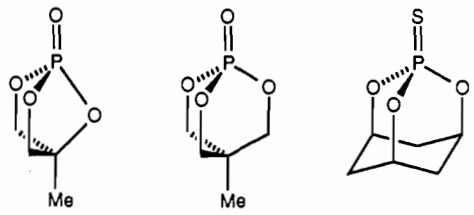
Phosphate **11c**, shown in Figure 4, contains only slight deviations from the C–C distances found in **2d**. In the slightly puckered four-membered ring, the elongation of the C(3)–C(5) bond is of the same magnitude as the corresponding bond length in **2d** and probably results from steric effects due to the substitution on the four-membered ring. The phosphorus atom in **11c** is in a roughly tetrahedral environment of oxygens with a slight twist of the OPO_3 group, with respect to the axis defined by P and the midpoint of C(3) and C(5), similar to the twist of this group found in **23**[49] and **24**.[50] The O–P–O bond angles containing the phosphoryl oxygen are slightly larger (average 111.66°) than those containing only cage oxygen atoms (average 107.19°), and this deviation from tetrahedrality is common in structures of acyclic, monocyclic, and bicyclic phosphate esters.[51]

Selected structural data for the two related bicyclic compounds (**25**[52] and **26**[53]) and one tricyclic compound (**27**)[54] are presented in Table X for comparison with **11c**. The decrease in strain in



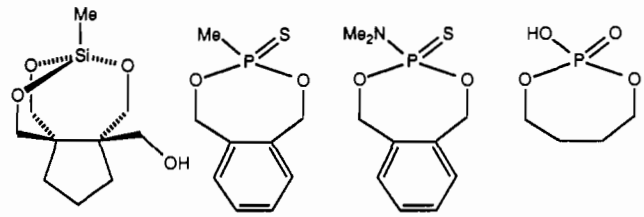
25 **26** **27**

going from highly strained **25** to the less strained **26** and **27** is evident from the P–O–C bond angles, which in unstrained acyclic systems are ca. 120°.[55] For **25** these values are much lower (average 102.3°) than for **26** (average 115.3°) and **27** (average 113°). Comparison of these values with the analogous angles in **11c** (average 119.7°) reveals little if any strain present in this region of the molecule. In conjunction with the NMR evidence showing that **4c** and **22** have nearly the same basicity, this lack of strain in **11c** gives support to the postulate[55] that the relatively low basicity of bicyclic phosphite esters compared with that of their acyclic analogues results primarily from the constrained orientation of the lone electron pairs of the three oxygen atoms relative to the phosphorus lone pair, rather than strain in the molecule.[56]

The P=O bond distance in **11c** is typical of acyclic, monocyclic, and bicyclic phosphates.[50] Although this P=O bond length is in the typical range, the phosphoryl oxygen hydrogen bonds to the alcohol group of an adjacent molecule. It is interesting that the intermolecular hydrogen bonding observed in the solid state become intramolecular in solution, with the alcohol oxygen interacting with proton b as indicated by the NMR spectra of **11c**.

The structure of the phosphate **11d** (Figure 5) is similar to that of **11c** and also to that of the methylsilyl analogue **28**.[57] With the exception of a slight reduction of the P–O(3) and P–O(4) distances, the distances found in the structure of **11d** are equivalent to those of **11c** within experimental error. Examination of the bond angles found in Table IX shows that there are many small differences between the structures of **11c** and **11d**. The angles containing the carbon atoms of the cyclic ring in **11d** are all distorted in comparison with those of **11c**, as is expected in going from a cyclobutane to a cyclopentane derivative. The twist chair conformation of the five-membered ring in **11d** leads to staggering of the four substituents on the ring. Phosphate **11d**, like **11c**, engages in hydrogen bonding between the phosphoryl oxygen and the alcohol group of an adjacent phosphate molecule.

The structure of one of the diastereoisomers of **5c** (Figure 2) contains a 1,3,2-dioxaphosphepane ring which is in a chair conformation similar to that found in **29** and **30**.[58] As in **29** and



28 **29** **30** **31**

30, wherein the aromatic ring provides rigidity, the presence of the chair form of the seven-membered ring in **5c** stems from the planarity of the cyclobutane ring. The presence of this form in the crystal structure demonstrates the low energy difference between the planar and puckered conformations of the cyclobutane ring as well as the small difference in energy between the chair and twist forms of the seven-membered ring, the latter conformation being preferred by **5c** in solution as demonstrated by its ^1H NMR spectrum (vide supra). In contrast, **31** exhibits a twist–boat conformation of the seven-membered ring in the solid state.[59] The P=O, P–O, O–C, and C–C bond distances in **5c** compare well with those of **29–31**, as well as with those of other cyclic phosphonate compounds.[51] As a result of the use of nonanhydrous solvent in the recrystallization of **5c**, a water molecule is present in the unit cell, whose oxygen is hydrogen bonded to two nearby phosphoryl oxygens and to two nearby phosphonate hydrogen atoms in a roughly tetrahedral manner.

The structure of **9** reveals a 1,3,2-dioxaphosphepane ring in a twist–chair conformation. Although calculations and NMR data suggest this form to be the most stable of the possible conformations of cycloheptane,[60] **9** represents the first structurally characterized 1,3,2-dioxaphosphepane to exhibit this conformation. The presence of this orientation is probably the result of the higher degree of flexibility of the cyclopentane ring in comparison with that of the cyclobutane ring in **5c**, which forces eclipsing around the bridgehead carbons. The relatively high estimated standard deviations in the P–O, O–C, and C–C distances of the seven-membered ring make comparisons of these bond lengths with those of the compounds **29–31** unreliable. Unlike **5c** and **29–31**, compound **9** possesses variations among pairs of P–O–C and C–C–C angles that are outside experimental error (Table VII). Since the pairs of P–O–C, O–C–C, and C–C–C bond angles in the twist–boat conformation of **31** (which are the same within experimental error) bear the same relationship as those in **5c**, the differences in these angles in **9** are probably not due to distortion inherent in the twist–chair form of the 1,3,2-dioxaphosphepane system. The triphenylmethyl group itself shows no sign of distortion and the three C(1)–C distances and C–C(1)–C bond angles are the same within experimental error. The triphenylmethyl group, however, is so large that only one of the alcohol groups of an adjacent molecule can hydrogen bond to the phosphoryl oxygen. Since the remaining alcohol function cannot approach the

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phosphoryl oxygen, it is hydrogen bonded to the phosphoryl-bound alcohol group of another molecule. This dissymmetry may account for distortion of the 1,3,2-dioxaphosphepane ring in **9**.

Conclusions. The tricyclic phosphorus compounds **4a–e** and their derivatives do not equilibrate to form detectable quantities of pentacoordinate phosphorus species. Although nucleophilic attack of the pendant alcoholic oxygen on phosphorus is not favored, such attack at a neighboring OC carbon in **4a–e** is catalyzed by protonic acids, giving rise to isomeric phosphonates **5a–e** via an unusual Arbuzov-like rearrangement. Solution ^1H and ^{13}C NMR of **4a–e** and their derivatives are consistent with the postulate that hydrogen bonding occurs between the oxygen of the pendant alcohol and a hydrogen on a neighboring OC carbon. The relatively low Lewis basicity of phosphite esters of types **3** and **4a–e** is a conformational effect rather than the result of strain.

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Supplementary Material Available: Tables of positional parameters, hydrogen atom parameters, and anisotropic thermal parameters for **2d**, **5c**, **9**, **11c**, and **11d**, bond distances for **2d** and **11c**, bond angles for **2d**, **9**, and **11c**, high-resolution mass spectral data, and ^1H and ^{13}C NMR data (61 pages); tables of calculated and observed structure factors (32 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Heterobimetallic Complexes with Bridging Acyl Groups: $(CO)_4Fe(\mu\text{-}C(R)O)M(CO)_4$ (R = Ph, Me; M = Re, Mn)

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The reaction of $[(CO)_4Fe(C(O)R)][NMe_4]$ (**1a**, R = Ph; **1b**, R = Me) and $[(CO)_4ReBr]_2$ (**2**) in THF at 0 °C results in the formation of $(CO)_4Fe(\mu\text{-}C(R)O)Re(CO)_4$ (**4a**, R = Ph; **4b**, R = Me) in yields of 40–46%. The analogous derivative of manganese from **1a** and $[(CO)_4MnBr]_2$ (**3**) proved to be thermally unstable. The structures of **4a** and **4b** were determined by single-crystal X-ray diffraction analysis. Compound **4a** crystallizes in a triclinic space group $P\bar{1}$ with $Z = 4$. The cell dimensions are $a = 15.674$ (1) Å, $b = 14.986$ (1) Å, $c = 7.768$ (1) Å, $\alpha = 107.90$ (1)°, $\beta = 90.02$ (1)°, and $\gamma = 70.98$ (1)°. The final structure was refined to $R_F = 3.3\%$ and $R_{wF} = 4.9\%$ on 5297 reflections with $I > 3\sigma(I)$. Compound **4b** was also found to be triclinic, space group $P\bar{1}$ with $Z = 2$ and $a = 8.177$ (1) Å, $b = 9.869$ (1) Å, $c = 9.212$ (1) Å, $\alpha = 106.59$ (1)°, $\beta = 108.18$ (1)°, and $\gamma = 76.38$ (1)°. The structure was refined to $R_F = 1.6\%$ and $R_{wF} = 2.4\%$ on 2235 reflections with $I > 3\sigma(I)$. The Fe–Re distances are 2.841 (1) Å in **4a** and 2.861 (1) Å in **4b**. These rather long bond distances as well as the thermal instability of the manganese analogue reflect a weakening of the M–M′ bond over those observed in phosphide-bridged analogues.

Introduction

Bimetallic heterogeneous catalysts have been shown to possess improved activity, selectivity, and stability over the corresponding homometallic systems.[1a] As a consequence, the physical and chemical properties of bimetallic and mixed-metal polynuclear transition-metal complexes became of interest;[1b,c] heteronuclear compounds may polarize and activate substrates differently from analogous homometallic systems and thus lead to enhanced chemical and/or catalytic properties under homogeneous conditions. Due to prevalence of heterolytic (ionic) cleavage of complexes with dissimilar metals, emphasis has been placed on the presence of bridging ligands. Extensive studies have appeared on diorganophosphide-bridged bimetallic complexes. Acyl groups have been also been observed as bridging ligands and would exert different electronic effects on the bridged metal atoms. However, this group of complexes has been the subject of relatively fewer studies.[2] In this paper we report the synthesis and characterization of some heterometallic acyl-bridged compounds by interaction of iron acyl metalates with electrophilic complexes of manganese or rhenium.

Results

The syntheses undertaken in this study are summarized in eqs 1 and 2. The reaction is followed by the disappearance of the

$$\underset{\textbf{1a, R = Ph; 1b, R = Me}}{[(CO)_4Fe(C(O)R)][NMe_4]} + \underset{\textbf{2}}{[(CO)_4ReBr]_2} \xrightarrow{\text{THF/0 °C}} \underset{\textbf{4a, R = Ph; 4b, R = Me}\\ \text{yields 46 or 40\%}}{(CO)_4Fe\{\mu\text{-}C(R)O\}Re(CO)_4} \quad (1)$$

$$\textbf{1a} + \underset{\textbf{3}}{[(CO)_4MnBr]_2} \xrightarrow{\text{PhMe/25 °C}} \underset{\textbf{5a}\\ \text{yield ca. 20\%}\\ \text{(thermally unstable)}}{(CO)_4Fe\{\mu\text{-}C(Ph)O\}Mn(CO)_4} \quad (2)$$

bands corresponding to **2** or **3** in the IR spectrum. The IR absorptions in the CO stretching region and the NMR spectra for **4a**, **4b**, and **5** are collected in Table I. The bridging acyl groups in these compounds are identified through their characteristic IR absorbances at 1470–1525 cm^{-1}. There is a larger difference in the acyl stretching absorption between the phenyl and methyl derivatives compared to the corresponding iron dimers $(OC)_3Fe\{\mu\text{-}C(R)=O\}_2Fe(CO)_3$ (ν(bridging acyl) = 1497 cm^{-1} for R = CH_3 and 1536 cm^{-1} for R = Ph).[2a] The ^{13}C NMR resonances for the acyl carbon of the bridging acyl groups appear at a typical[2] low-field position, 280–300 ppm. Two singlets of unequal peak height are observed in the carbonyl region of the ^{13}C NMR spectrum for **4a**. The one at lower peak height (189.7 ppm) is assigned to the four CO groups on Re on the basis of two ob-

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