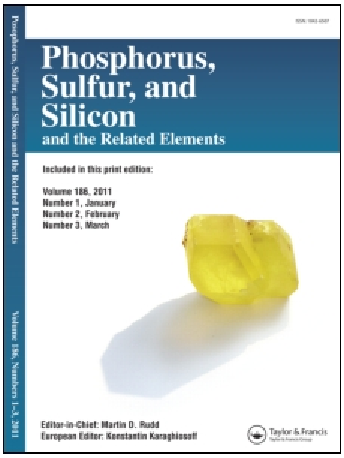

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NOVEL HIGH-YIELD TRANSESTERIFICATION AND TRANSAMINATION ROUTES TO $P(OCH_2)_3CCH_3$ AND $P[N(CH_3)CH_2]_3CCH_3$, RESPECTIVELY

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NOVEL HIGH-YIELD TRANSESTERIFICATION AND TRANSAMINATION ROUTES TO $P(OCH_2)_3CCH_3$ AND $P[N(CH_3)CH_2]_3CCH_3$, RESPECTIVELY

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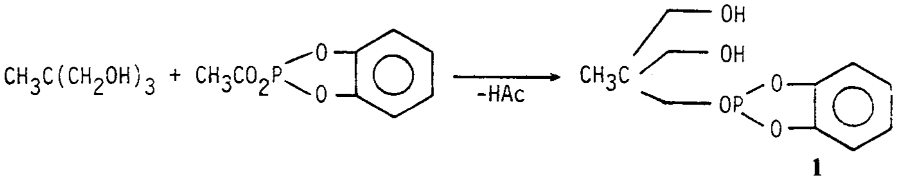
High yields (93–96%) in a one-step syntheses of $CH_3C(CH_2OP(o\text{-}O_2C_6H_4))_3$ (**3**), $CH_3C(CH_2OPOCH_2C(CH_3)_2CH_2O)_3$ (**4**) and $CH_3C(CH_2N(CH_3)POCH_2C(CH_3)_2CH_2O)_3$ (**5**) are reported. Compounds **4** and **5** at 100–110° give $P(OCH_2)_3CCH_3$ (**2**) and $P(N(CH_3)CH_2)_3CCH_3$ (**7**) in 97 and 96% yield, respectively, plus the diphosphite $(CH_3)_2C(CH_2O)_2POCH_2C(CH_3)_2CH_2OP(OCH_2)_2C(CH_3)_2$ (**8**). Compound **8** was also characterized as its dithiophosphate derivative. Experiments designed to synthesize the adamantane-like $P(OCH)_3(CH_2)_3$ (**9**) and $P(CH_2O)_3P$ (**10**) in an analogous manner met with only partial success. The *tris*-phosphate analogue of **4** was also synthesized but it did not thermolyze to $OP(OCH_2)_3CCH_3$ under the conditions used for **4** and **5** even after prolonged heating.

INTRODUCTION

In 1968 Nifanti'ev *et al.*[1] reported the formation of **1**[2] in reaction (1).



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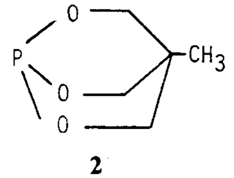
Upon attempted purification of this product on an alumina column, an 85% yield of **2** was realized. Using a 1 : 3 ratio of triol to phosphite in reaction (1), compound **3**[2]



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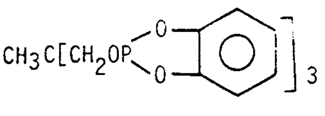

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was left as a residue after distillation of the theoretical amount of HAc, although on

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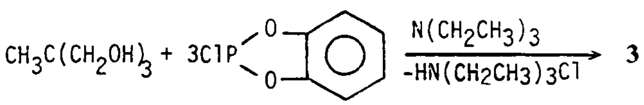
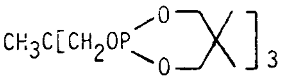
chromatography **2** was detected as a minor product. The rationale for the presence of **2** was that intermediate **1** underwent transesterification with elimination of **2**.



(2)

Herein we report the synthesis of **3** by reaction (2) and provide additional data for its characterization. In contrast to the earlier report,[1] however, **3** is found to yield **2** in 71% yield as the only product eluted with benzene from an alumina or silica gel column. We further show that **3** produces **2** in refluxing toluene. Also reported are syntheses of **4**–**6** using reactions analogous to that shown in reaction (2).



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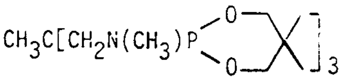

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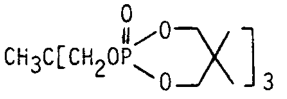

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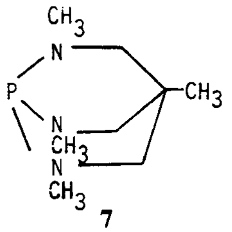
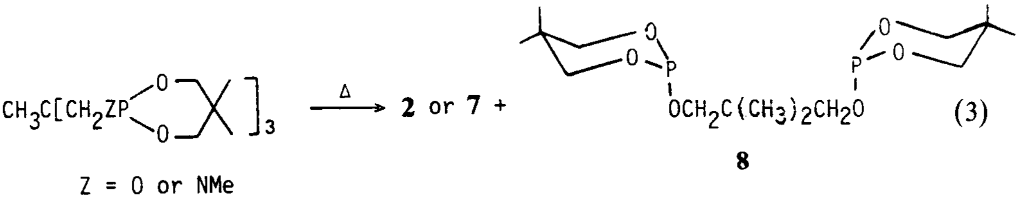


7

When heated, intermediates **4** and **5** readily give **2** and **7** in overall isolated yields of 93% and 89%, respectively, thus providing syntheses which rival previously published yields of 85%[3,4] and 90%,[5] respectively, for these cages. The other product of the thermal disproportionation of **4** and **5** is shown to be the diphosphite **8**:



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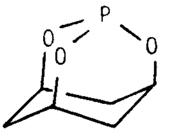
(3)

The formation of **9** and **10** via similar thermolyses of intermediates **11** and **12**, respectively, is discussed.



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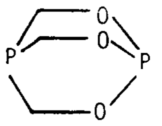

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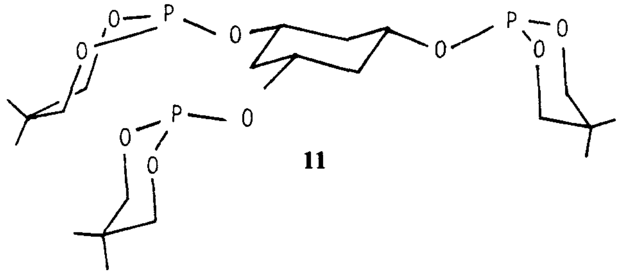

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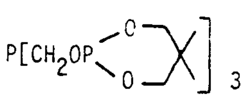

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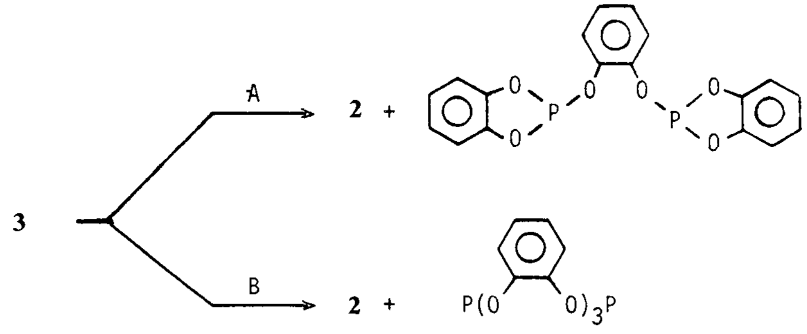
RESULTS AND DISCUSSION

New Synthetic Routes to Bicyclic 2 and 7

The *tris*-P(III) derivatives **3**, **4** and **5** are realized in 93–96% yield by reaction of the appropriate phosphorochloridite with $CH_3C(CH_2OH)_3$ to form **3** and **4** and with $CH_3C(CH_2NHCH_3)_3$ to synthesize **5**. Whereas **3** is an oil, **4** and **5** are white solids. All three compounds show ^1H nmr spectra consistent with their formulations, single peaks in their ^{31}P nmr spectra and peaks in their mass spectra associated with their parent ions. We do not detect bicyclic phosphite **2** as even a minor product in the synthesis of **3** as did earlier workers upon chromatography of their reaction product.[1] Since we find that **2** is the only product to elute upon column chromatography of **3** in yields of 71%, our results to some extent contradict those of the earlier report.[1] The earlier workers suggest that **2** results from transesterification of the intermediate **1**. Because we find no evidence for **1** in our synthesis of **3**, the ready conversion of **3** to **2** on chromatography could be attributed to the presence of adventitious water on the column material. Since the silica gel and alumina had been heated under vacuum and immediately packed into columns using dried benzene, however, we feel that insufficient water would be present to hydrolyze **3** to **1**. On the other hand, when a stoichiometric (1 : 1) amount of H_2O is added to a solution of **3** in $(CD_3)_2CO$ at room temperature, the $C\underline{H}_2$ ^1H nmr doublet associated with **2** develops. (Other products were not identifiable from this crude experiment.) Thus H_2O apparently can react with **3** to form an intermediate hydrolysis product such as **1**, which can then transesterify to **2**.

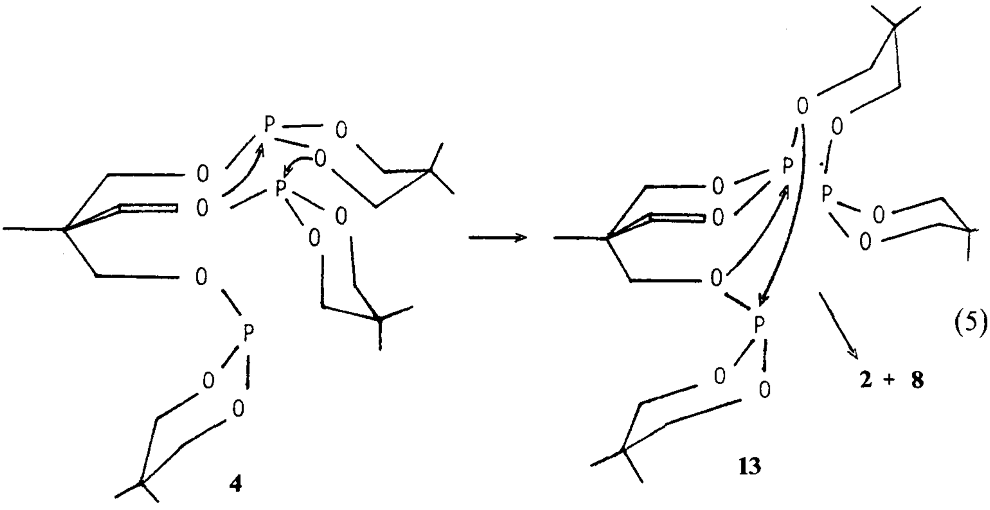
Thermolyses

Transesterification of **3** directly to **2** does occur under thermal conditions. Thus **3** in refluxing toluene for 16 hours shows a ^{31}P chemical shift (+91 ppm) characteristic of **2**.[16] The two pathways for the thermal decomposition of **3** shown in reaction (4) can be envisioned.[18] Since neither ^{31}P nor ^1H nmr spectral data were helpful in differentiating these two pathways, the thermolysis of **4** described in the Experimental Section was carried out. In this experiment, observation of the ^1H nmr spectral characteristics of the chair form of the phosphite rings[19] in the thermolysis product **8** would point to pathway A. Thus **8** would display three types of $C\underline{H}_3$ resonances (axial, equatorial and acyclic) while the bicyclic compound resulting from pathway B would be expected to give rise to only one $C\underline{H}_3$ proton resonance. The isolation and characterization of **8**, its further characterization as its dithiophosphate derivative



(4)

(see Experimental) and the absence of evidence for the bicyclic product demanded by pathway B suggest that pathway A is the major one. This is not unreasonable since pathway A involves fewer bond cleavages and there is no obvious stability factor favoring the bicyclic product of pathway B. Pathway A for **4** probably involves formation of **13** shown in reaction (5), although no ^{31}P nmr evidence for this intermediate was observed. The mechanism of formation of **13** (and its subsequent decomposition) is likely to involve two nucleophilic attacks of oxygen on phosphorus in a stepwise or simultaneous fashion and the stereochemistry of these processes may involve conformers of the six member rings other than the thermodynamically most stable one[20] shown.



(5)

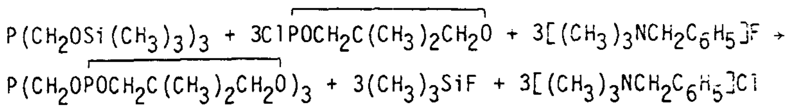
The synthesis of **2** via thermolysis of **4** rivals in yield that reported earlier by us utilizing the transesterification of $P(OCH_3)_3$ by $CH_3C(CH_2OH)_3$ with which an 85% yield of **2** was realized.[3,4] The synthesis of **4** in 96% yield followed by its thermolysis and recovery of 97% of the theoretical amount of **2** results in an overall yield of 93% in a new synthesis of **2**.

Thermolysis of the *tris*-phosphoramidite **5** results in a transamination reaction analogous to the transesterification shown in reaction (4). The 96% yield of the bicyclic aminophosphine **7** produced in this reaction coupled with the 93% yield in which **5** is made provides an overall yield of 89% for **7**. Although we previously reported the synthesis of **7** to proceed in 90% yield,[17] the expense and air sensitivity of $P(N(CH_3)_2)_3$ used in the reaction with $CH_3C(CH_2NHCH_3)_3$ renders the synthesis of **7** by the route reported here worthy of consideration.

Compounds **4** and **5** both melt irreversibly, which is consistent with their thermolytic instability as discussed above. By contrast the *tris*-phosphate **6** melts reversibly and is unchanged upon heating to 110°C at 1 torr over a period of several days. Thus, **6** does not form $CH_3C(CH_2O)_3PO$ and the diphosphate analogue of **8** under these conditions.

Attempted Syntheses of **10** *and* **11**

Recent interest in the bridging ligand **10**[21] prompted an attempt to improve its rather temperamental synthesis and the mediocre yields (20–30%) realized under the best of conditions.[14] Because $P(CH_2OH)_3$ made from $[P(CH_2OH)_4]Cl$ is contaminated with varying amounts of $OP(CH_2OH)_3$ and $CH_3(O)P(CH_2OH)_2$[11,22] we decided to purify the $P(CH_2OH)_3$ by distillation of the $P(CH_2OSi(CH_3)_3)_3$ derivative obtained by trimethylsilylation of the mixture.[13] This was followed by reaction of the $P(CH_2OSi(CH_3)_3)_3$ with $ClPOCH_2C(CH_3)_2CH_2O$ in the presence of a fluoride ion as an initiating nucleophile. Thus after formation of Me_3SiF (which was detected in the trapped gases by ^1H nmr spectroscopy) the resulting alkoxide ion presumably could attack the phosphorus in $ClPOCH_2C(CH_3)_2CH_2O$ to form **12** according to reaction (6). The reaction mixture, however, was shown by ^{31}P nmr spectroscopy to contain **10** along with several other phosphorus-containing products.



$$P(CH_2OSi(CH_3)_3)_3 + 3ClPOCH_2C(CH_3)_2CH_2O + 3[(CH_3)_3NCH_2C_6H_5]F \rightarrow P(CH_2OPOCH_2C(CH_3)_2CH_2O)_3 + 3(CH_3)_3SiF + 3[(CH_3)_3NCH_2C_6H_5]Cl \qquad (6)$$

12

Thus **12** or some partially phosphorylated intermediate apparently easily decomposes to **10**. Attempts to sublime **10** out of the reaction mixture were only partially successful owing to co-sublimation of $H(O)POCH_2C(CH_3)_2CH_2O$ in amounts considerably larger (16 : 1 as shown by ^1H nmr) than **10**. The monocyclic phosphorus acid diester may arise from incomplete drying of the $[(CH_3)_3NCH_2C_6H_5]F$. The relatively small amount of **10** which sublimed and our failure to separate it from the phosphorus acid diester contaminant appears to render this synthetic route to **10** impractical.

An attempt to synthesize and isolate **11** as an intermediate to **9** also met with only partial success. Reaction of $ClPOCH_2C(CH_3)_2CH_2O$ with *cis-cis*-1,3,5-trihydroxycyclohexane produced an oil in which the adamantane-like **9** is a major product according to ^{31}P nmr spectroscopy (+137.1 ppm[16]) while the other two resonances are consistent with the presence of **11** (+122.6 ppm) and diphosphite **8** (+121.1 ppm). Attempts to sublime **9** out of the mixture failed. The ease with which **9** forms under the mild reaction conditions employed while **2** forms from **4** only on thermolysis is indicative of a low activation energy for transesterification (perhaps owing to less steric crowding in **11** compared to **4**) and a greater thermodynamic stability of **9** compared to **2** (owing to the presence of chair-form rings in the former compound rather than boat-form rings in the latter).

EXPERIMENTAL

All solvents were reagent grade or better and were further purified by distillation from an appropriate drying agent. *Tetrakis*(hydroxymethyl)phosphonium chloride was obtained as an 85% aqueous solution from ROC/RIC and was converted to a hygroscopic crystalline solid as follows. Most of the water was removed by an azeotropic distillation with 1-propanol and the remaining oil was further dehydrated with 2,2-dimethoxypropane (Aldrich Chemical Co.). The solid $P(CH_2OH)_4Cl$ which forms was then recrystallized from 2-propanol. Triethylamine (Eastman Chemical Co.) was distilled from CaH_2 prior to use. 1,1,1-*Tris*(hydroxymethyl)ethane, 2,2-dimethyl-1,3-propanediol and benzyltrimethylammonium hydroxide (40% in methanol) were purchased from Aldrich Chemical Co. and were used as received. Pyrocatechol, phosphorus oxychloride and sulfur were used as received from Fisher Scientific Co. Phosphorus trichloride (Mallinckrodt Chemical Co.), chlorotrimethylsilane (Eastman Chemical Co.) and aqueous HF (J. T. Baker Chemical Co.) were used as received. Deuterated solvents for nmr spectroscopy were dried over 4 A molecular sieves before use.

The compounds $ClP(o\text{-}O_2C_6H_4)$,[6] $ClPOCH_2C(CH_3)_2CH_2O$,[6] $Cl(O)POCH_2C(CH_3)_2CH_2O$,[7] $CH_3C(CH_2NHCH_3)_3$,[8] *cis-cis*-1,3,5-trihydroxycyclohexane[9] and $[(CH_3)_3NCH_2C_6H_5]F$[10] were prepared according to procedures reported earlier.

Proton nmr spectra were obtained on a Varian EM360, EM360A, or EM360L spectrometer using appropriate deuterated compounds as solvents and using tetramethylsilane as an internal standard. ^{31}P nmr spectra were obtained from solutions in 10 mm tubes with a Bruker HX-90 spectrometer operating at 36.434 MHz in the Fourier transform mode while locked on the ^2H resonance of the deuterated solvent. The external standard was 85% H_3PO_4 sealed in a 1 mm capillary tube held coaxially in the sample tube by a Teflon vortex plug. The spectrometer was interfaced with a Nicolet Instruments 1080 minicomputer system. Mass spectra were obtained on an AEI MS-902 mass spectrometer. Low resolution and chemical ionization mass spectra were obtained on a Finnigan 4000 instrument.

$CH_3C(CH_2OP(o\text{-}O_2C_6H_4))_3$ **3**. A solution of 5.38 g (44.8 mmol) of $CH_3C(CH_2OH)_3$ and 13.60 g (134.4 mmol) triethylamine in 150 ml THF was added slowly, via a cannula, to 27.35 g (156.7 mmol) of neat $ClP(o\text{-}O_2C_6H_4)$. The temperature of the reaction mixture was maintained at 0°C throughout the addition period. Upon completion of the addition, the reaction mixture was warmed to room temperature and was stirred for fifteen hours. A Schlenk filtration was carried out to separate the white precipitate from the colorless solution. The precipitate was washed with two 75 ml portions of cold diethyl ether, dried *in vacuo*, and characterized by ^1H nmr and melting point to be triethylamine hydrochloride (17.76 g, 129.0 mmol). Solvent and excess phosphorochloridite were removed from the filtrate *in vacuo* to yield 22.73 g (42.56 mmol, 95%) of **3** as a viscous oil (^1H nmr ($CDCl_3$) 7.06 m, 12 H, C_6H_4, 3.15 d, $^3J_{PH} = 7$ Hz, 6 H, CH_2, 0.70 s, 3 H, CH_3; ^{31}P nmr ($(CD_3)_2CO$) + 128; mass spectrum (chemical ionization spectrum using CH_4 as the ionizing gas) $m/e = 535$ for $(P + 1)^+$). Attempts to obtain **3** as a crystalline product by chromatographic purification (silica gel/benzene, alumina/benzene) yielded the bicyclic phosphite **2** as the only product eluted from the column (yield, 71%).

$CH_3C(CH_2OPOCH_2C(CH_3)_2CH_2O)_3$ **4**. A solution of 2.36 g (19.6 mmol) of $CH_3C(CH_2OH)_3$ and 5.95 g (58.9 mmol) triethylamine in 100 ml THF was allowed to react with 9.93 g (58.9 mmol) of $ClPOCH_2C(CH_3)_2CH_2O$ by the method described above for **3**. Triethylamine hydrochloride (7.62 g, 55.4 mmol) was isolated from the reaction mixture by a Schlenk filtration. Vacuum evaporation of the solvent from the filtrate yielded 9.72 g (18.8 mmol, 96%) of **4** as a white solid (mp 95–97°C irreversible; ^1H nmr ($CDCl_3$) 3.3–4.3 m, 18 H, OCH_2, 1.25 s, 9 H, ring CH_3, 0.95 s, 3 H, acyclic, 0.75 s, 9 H, ring CH_3; ^{31}P nmr (CD_3CN) + 121.7; mass spectrum (chemical ionization spectrum using CH_4 as the ionizing gas) $m/e = 517$ for $(P + 1)^+$).

$CH_3C(CH_2N(CH_3)POCH_2C(CH_3)_2CH_2O)_3$ **5**. A solution of 1.49 g (9.33 mmol) of $CH_3C(CH_2NHCH_3)_3$ and 2.83 g (28.0 mmol) triethylamine in 80 ml diethyl ether was added dropwise at 0°C to a solution of 4.72 g (28.0 mmol) of $ClPOCH_2(CH_3)_2CH_2O$ in 100 ml ether. The resultant precipitate was isolated by filtration and identified as triethylamine hydrochloride (3.79 g, 27.5 mmol) by ^1H nmr. Solvent was removed from the filtrate *in vacuo* to yield 4.81 g (8.66 mmol, 93%) of **5** as a white solid (mp

112–118°C irreversible; ^1H nmr ($CDCl_3$) 2.9–4.2 m, 18 H, CH_2, 2.78 d, $^3J_{PH}$ = 5.5 Hz, 9 H, NCH_3, 1.24 s, 9 H, ring CH_3, 0.90 s, 3 H, acyclic CH_3, 0.74 s, 9 H, ring CH_3; ^{31}P nmr ($CDCl_3$) + 148.9; mass spectrum m/e = 555).

$CH_3C(CH_2O(O)POCH_2C(CH_3)_2CH_2O)_3$ **6**. To a solution of 4.18 g of $Cl(O)POCH_2C(CH_3)_2CH_2O$ (22.6 mmol) in 150 ml THF at 0°C was added a solution of 0.90 g of $CH_3C(CH_2OH)_3$ (7.5 mmol) and 2.3 g triethylamine (22.6 mmol) in 50 ml THF over a period of one hour. The reaction mixture was then warmed to room temperature and stirred an additional 16 hr. After cooling to −10°C, a Schlenk filtration was employed to separate triethylamine hydrochloride from the colorless filtrate. Vacuum distillation of the solvent from the filtrate gave **6** as a white solid which was recrystallized from diethyl ether. (mp 84–88°C reversible; ^1H nmr ($CDCl_3$) 3.5–4.3 m, 18 H, CH_2, 1.32 s, 9 H, cyclic CH_3, 1.08 s, 3 H, terminal CH_3, 0.90 s, 9 H, cyclic CH_3; ^{31}P nmr (CD_3CN) −1.6; mass spectrum (chemical ionization spectrum using CH_4 as the ionizing gas) m/e = 565 for $(P + 1)^+$).

cis,cis-$(CH_2)_3[HCOPOCH_2C(CH_3)_2CH_2O)]_3$ **11**. A suspension of 2.67 g (20.1 mmol) of *cis,cis*-1,3,5-trihydroxycyclohexane and 6.12 g (60.5 mmol) of triethylamine in 80 ml THF was added via cannula to a solution of 10.2 g (60.5 mmol) of $ClPOCH_2C(CH_3)_2CH_2O$ in 75 ml THF at 0°C. Upon completion of the addition, vigorous stirring was continued for 3 hr at 0°C, and for 72 hr at room temperature. The triethylamine hydrochloride, isolated from the colorless filtrate by Schlenk filtration, was dried *in vacuo* and characterized by ^1H nmr. Solvent was removed from the filtrate to leave a colorless oil (^{31}P nmr ($CDCl_3$) + 137.1, +122.6, +121.1 (minor)).

$P(CH_2OH)_3$. Neutralization of $[P(CH_2OH)_4]Cl$ with one equivalent of aqueous sodium hydroxide as described earlier[11] gave a mixture of $P(CH_2OH)_3$ and $OP(CH_2OH)_3$ (^{31}P nmr[12] (D_2O) −24 $P(CH_2OH)_3$, +48 $OP(CH_2OH)_3$) as an oil.

$P(CH_2OSi(CH_3)_3)_3$. Reaction of the above oil with excess chlorotrimethylsilane in benzene as described previously[13] gave a mixture of $P(CH_2OSi(CH_3)_3)_3$ and $OP(CH_2OSi(CH_3)_3)_3$ which could be separated by distillation. The phosphine is extremely pyrophoric and must be handled with strictly anaerobic techniques to avoid oxidation (bp 84–85°C/0.5 torr; ^{31}P nmr ($CDCl_3$) −26.3, −25.4[13]).

$P(CH_2OPOCH_2C(CH_3)_2CH_2O)_3$ **12**. Anhydrous $[(CH_3)_3NCH_2C_6H_5]F$ (2.20 g, 13.0 mmol) was stirred under nitrogen with 9 g of 4 Å molecular sieves in 15 ml dry THF at room temperature for 6 hr. The resulting fine suspension was then cooled to 0°C and a liquid nitrogen trap was assembled to trap condensibles in the effluent nitrogen purge from the reaction flask. A mixture of 1.5 g of $ClPOCH_2C(CH_3)_2CH_2O$ (8.8 mmol, ~ 200% excess) and 0.35 g of $P(CH_2OSi(CH_3)_3)_3$ (1.0 mmol) in 5 ml THF was added to the above suspension dropwise with vigorous stirring. After 10 hr the trapped effluent gases analyzed by ^1H nmr spectroscopy revealed the presence of $(CH_3)_3SiF$ (0.20 d, $^3J_{FH}$ = 8.0 Hz) and a small amount of THF. After stirring an additional 36 hr, a Schlenk filtration was carried out and the filtrate was evaporated to an oil *in vacuo*. Nmr characterization of the oil revealed it to be a mixture containing the bicyclic cage $P(CH_2O)_3P$, **10**[14] (^{31}P nmr ($CDCl_3$) +90.0, −67.0; ^1H nmr ($CDCl_3$) 4.54 dd, $^2J_{PH}$ = 8.8 Hz, $^3J_{PH}$ = 2.8 Hz) and other products giving rise to a complex set of resonances. In an attempt to isolate **10** from the mixture, a sublimation probe was placed over the oil. After evacuation of the system to 1.5 torr and heating to 50–60° for three hours, a white sublimate was washed from the probe using $CDCl_3$. The sublimate was identified as a mixture of $H(O)POCH_2C(CH_3)_2CH_2O$[15] and **10** in an approximate molar ratio of 16 : 1, respectively, by ^1H nmr integration. Further attempts at separation were unsuccessful.

Thermolysis of **4**. Triphosphite **4** (0.3273 g, 0.6338 mmol) was placed in a sublimation apparatus which was then purged with nitrogen by three purge/pump cycles. The decomposition was carried out for 16 hours at a pressure of 1 torr and an oil bath temperature of 100–105°C. After cooling, the sublimate was collected from the cold finger and characterized by ^1H and ^{31}P nmr[16] to be the bicyclic phosphite $CH_3C(CH_2O)_3P$, **2** (0.0911 g, 0.615 mmol, 97.1% yield). The residual colorless oil (0.2292 g) was tentatively identified as the diphosphite **8** based solely upon ^1H and ^{31}P nmr spectral data (^1H nmr ($CDCl_3$) 3.0–4.2 m, 12 H, OCH_2, 1.26 s, 6 H, cyclic CH_3, 0.97 s, 6 H, acyclic CH_3, 0.73 s, 6 H, cyclic CH_3; ^{31}P nmr ($CDCl_3$) + 121.7). Attempts to distill the oil resulted in decomposition.

The residual oil (1.0106 g) from a similar thermal decomposition was dissolved in 40 ml benzene, stirred with 1.00 g powdered sulfur, and refluxed for 23 hr. Stirring was continued at room temperature for an additional 36 hr followed by vacuum removal of the solvent to leave a yellow solid. Extraction of this residue with ether gave an ether-soluble white solid, which upon purification by column chromatography (silica gel/acetone, R_f = 0.76) was characterized as the dithiophosphate derivative of **8** (mp 148°C; ^1H nmr ($CDCl_3$) 3.63–4.47 m, 12 H, OCH_2, 1.23 s, 6 H, ring CH_3, 1.05 s, 6 H, non-ring CH_3, 0.95 s, 6 H, ring CH_3; ^{31}P nmr ($CDCl_3$) + 61.4; mass spectrum m/e = 432 parent ion).

Thermolysis of **5**. Triphosphoramidite **5** (0.75 g, 1.3 mmol) was placed in a 25 ml flask and inserted into a Kugelrohr oven, and the receiving bulb cooled to −75°C. The oven was heated to 110°C and the pressure was maintained at 25 torr. After 1 hr, the receiving flask contained 0.24 g of distillate which was characterized by ^1H and ^{31}P nmr[17] to be the bicyclic aminophosphine **7** (1.3 mmol, 96%). The residue in the distillation flask was characterized as the diphosphite **8** by its ^1H and ^{31}P nmr spectra (*vide supra*).

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REFERENCES

1. I. V. Fursenko, G. T. Bakhvalov and E. E. Nifant'ev, *J. Gen. Chem. USSR* (*Engl. Transl.*), **38**, 2445 (1968).
2. The constitution of this compound was inferred from elemental analysis.
3. C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).
4. J. G. Verkade, T. J. Huttemann, M. K. Fung and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).
5. B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton and J. G. Verkade, *Inorg. Chem.*, **6**, 173 (1967).
6. H. J. Lucas, F. W. Mitchell and C. N. Scully, *J. Am. Chem. Soc.*, **72**, 5491 (1950).
7. R. S. Edmundson, *Tetrahedron*, **21**, 2379 (1965).
8. R. D. Kroshefsky, R. Weiss and J. G. Verkade, *Inorg. Chem.*, **18**, 469 (1979).
9. H. Stetter and K. Steinacker, *Ber.*, **85**, 451 (1952).
10. I. Kuwajima, E. Nakamura and M. Shimizu, *J. Am. Chem. Soc.*, **104**, 1025 (1982).
11. M. Grayson, *J. Am. Chem. Soc.*, **85**, 79 (1963).
12. W. J. Vullo, *J. Org. Chem.*, **33**, 3665 (1968).
13. V. M. D'yakov, N. M. Kudyakov, M. G. Voronkov, R. K. Valetdinov and V. I. Glukhikh, *J. Gen. Chem. USSR* (*Engl. Transl.*), **49**, 694 (1974); *Zh. Obshch. Khim.*, **49**, 800 (1979).
14. J. W. Rathke, J. W. Guyer and J. G. Verkade, *J. Org. Chem.*, **35**, 2310 (1970).
15. D. W. White, G. K. McEwen, R. D. Bertrand and J. G. Verkade, *J. Mag. Res.*, **4**, 123 (1971).
16. J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).
17. B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton and J. G. Verkade, *Inorg. Chem.*, **6**, 173 (1967).
18. Although oligomer formation is also possible, such species would be expected to display middle and end-group ^{31}P NMR signals. The ^{31}P NMR spectra did not suggest this possibility. The diphosphite formed via pathway A in reaction (4) has been reported but only elemental analysis and cryoscopic molecular weight data were given (L. Anschütz and W. Broeker, *Ber. dtsch. Chem. Ges.*, **61**, 1264 (1928)).
19. D. W. White, R. D. Bertrand, G. K. McEwen and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 7125 (1970).
20. B. E. Maryanoff, R. O. Hutchins and C. A. Maryanoff, "Topics in Stereochemistry," N. L. Allinger and E. L. Eliel, Eds., Vol. 11, John Wiley and Sons, Inc., New York (1979), p. 187.
21. P. M. Stricklen, E. J. Volcko and J. G. Verkade, *J. Am. Chem. Soc.*, **105**, 2494 (1983).
22. S. J. Trippett, *J. Chem. Soc.*, 2813 (1961).