^{1}H NMR ($CDCl_3$) δ 1.44 (3 H, t, J = 7.0 Hz), 2.05–2.62 (2 H, m), 2.6–3.15 (2 H, m), 3.76 (2 H, br t), 4.32 (2 H, q, J = 7.0 Hz), 8.6 (1 H, br s).

Hydrolysis of 24. (a) 24a. Reaction of 0.783 g (5.23 mmol) of **24a** with 25 mL of water for 10 h gave, after removal of the water at 0.1 mmHg, 0.772 g (4.61 mmol) of **2** (88%).

(b) 24b. Reaction of 0.56 g (2.79 mmol) of **24b** with 25 mL of water for 10 h gave, after removal of the water at 0.1 mmHg, 0.531 g (2.42 mmol) of **2** (87%).

NMR Study of the Reaction Kinetics of 1. (a) Deuterolysis. In a typical experiment, 0.15 g (0.66 mmol) of 1 was placed in a 5-mm NMR tube. At time = 0 s, 0.5 mL of D_2O was added, via syringe, and the tube was shaken to dissolve 1. The signals at 6.82–7.32, 8.39, and 9.5 ppm were integrated every 60 s and utilized for the determination of the relative amounts of **12**, **14** and CH_3CHO.

(b) d_4 Methanolysis. In a typical experiment, 0.15 g (0.66 mmol) of 1 was placed in a 5-mm NMR tube. At time = 0 s, 0.5 mL of methanol-d_4 was added, via syringe, and the tube was shaken to dissolve 1. The signals at 6.82–7.32 and 5.2–5.7 ppm were integrated every 60 s and utilized for the determination of the relative ratios of **17** and **7**/**8**.

(c) In Acetone-d_6. In a typical experiment, 0.15 g (0.66 mmol) of 1 was dissolved in 0.5 mL of acetone-d_6. At time = 0 s, 0.2 mL of D_2O or methanol-d_4 was added, via syringe, and the tube was shaken. The signals at 6.82–7.3, 8.4, and 9.5 ppm were scanned every 300 s for the first hour and at odd intervals thereafter until the reaction was deemed complete.

Rate of Deuterolysis of 1 as a Function of pD. A total of 0.05 g (0.22 mmol) of 1 was weighed into a 5-mm NMR tube. At time = 0 s, 0.5 mL of a solution of the appropriate buffer, dissolved in D_2O, was added via syringe and the tube was shaken to dissolve 1. The signals at 6.8–7.3, 8.4, and 9.5 ppm were integrated every 30 s until the reaction was complete or had stopped. In this manner, the rate of deuterolysis of 1 as examined at pD = 1.6, 2.6, 3.6, 5.6, 6.6, 7.6, 8.6, and 9.6.

Registry No. 1, 86905-60-4; 2, 86905-61-5; 4, 88-12-0; 7, 86905-65-9; 8, 86905-67-1; 9, 86905-63-7; 23, 931-46-4; 24a, 90670-73-8; 24b, 24419-40-7; 2-deuterioacetaldehyde 2,4-dinitrophenylhydrazone, 90670-74-9; triethyloxonium tetrafluoroborate, 368-39-8; 2-pyrrolidinone, 616-45-5.

2,2,6,6-Tetramethyl-4-phosphorinanol: Synthesis and Conformational Analysis

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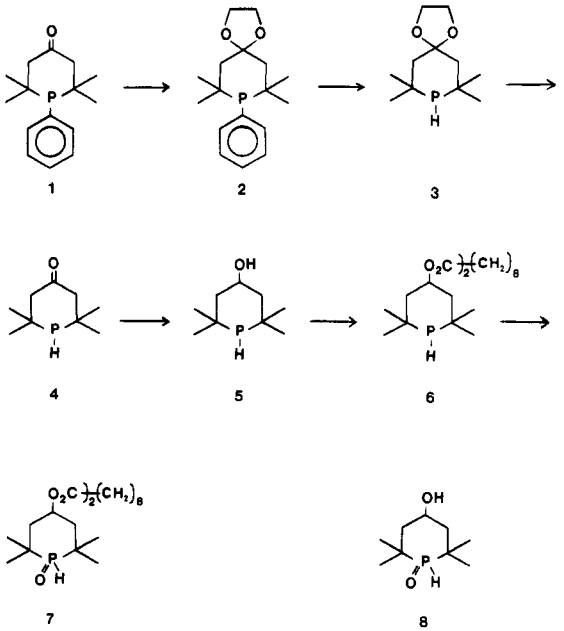
The synthesis and characterization of 2,2,6,6-tetramethyl-4-phosphorinanol (**5**) and its derivatives are described. The protection of the carbonyl group of 2,2,6,6-tetramethyl-1-phenylphosphorinan-4-one as the ethylene ketal, reductive removal of the 1-phenyl substituent with lithium metal in THF, and subsequent removal of the protecting group followed by hydride reduction gave **5**. A mild two-phase procedure for the oxidation of 1*H*-phosphorinanes to 1-oxo-1*H*-phosphorinanes is described. The ^{1}H NMR spectrum of **5** suggests that the ring has a biased conformation in solution where the proton on phosphorus assumes an axial ring position.

The chemistry of phosphorinanes continues to be an active area of research.[1] Quite recently, Berlin and coworkers reported the conformational analysis of C-alkylated phosphorinane derivatives.[2-4] Conformational studies on C-alkylated 1*H*-phosphorinanes would certainly be of interest in light of the high preferance for an axial P–H bond in the parent 1*H*-phosphorinane at room temperature.[5] Unfortunately, methodology previously did not exist for the preparation of alkyl-substituted 1*H*-phosphorinanes. We report herein the synthesis and characterization of the previously unreported 2,2,6,6-tetramethyl-4-phosphorinanol (**5**) and its corresponding derivatives.

Results and Discussion

Synthesis. Following the procedure of Welcher and Day,[6] the phosphorinane **1** was prepared by the condensation of phorone with phenylphosphine in a yield of 55% (distilled). The carbonyl group was protected by the acid-catalyzed condensation of **1** with ethylene glycol to give the ketal **2**.



Grim and Molenda have reported the preparation of lithium dialkylphosphides by the reduction of dialkyl-

(1) For a review, see: Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981; Chapter 3, Chapter 8 and references therein.
(2) Rampal, J. B.; Macdonell, G. D.; Edasery, J. P.; Berlin, K. D.; Rahman, A.; van der Helm, D.; Pietrusiewicz, K. M. *J. Org. Chem.* **1981**, *46*, 1156–1165.
(3) Rampal, J. B.; Berlin, K. D.; Edasery, J. P.; Satyamurthy, N.; van der Helm, D. *J. Org. Chem.* **1981**, *46*, 1166–1172.
(4) Rampal, J. B.; Satyamurthy, N.; Bowen, J. M.; Purdie, N.; Berlin, K. D. *J. Am. Chem. Soc.* **1981**, *103*, 7602–7609.
(5) Lambert, J. B.; Oliver, W. L., Jr. *Tetrahedron* **1971**, *27*, 4245–4254.
(6) Welcher, R. P.; Day, N. E. *J. Org. Chem.* **1962**, *27*, 1824.

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Table I. ^{1}H NMR[a] Spectral Data of Compounds 3, 5, and 6

compd	CH_3–C(2,6) equatorial	CH_3–C(2,6) axial	H(3,5) axial	H(3,5) equatorial	H(1) axial	H(4) axial
3	δ 1.03 d $^3J_{HCCp}$ = 14.0 Hz	δ 1.39 d of d $^3J_{HCCP}$ = 15.2 H $^4J_{HCCPH}$ = 1.8 H	δ 1.51 d $^2J_{HCH}$ = 13.8 Hz	δ 1.85 d of d $^2J_{HCH}$ = 13.8 Hz $^3J_{HCCP}$ = 4 Hz	δ 2.80 d of sept $^1J_{HP}$ = 167 Hz $^4J_{HPCCH}$ = 1.8 Hz	
5	δ 1.00 d $^3J_{HCCP}$ = 13.8 Hz	δ 1.03 d of d $^3J_{HCCP}$ = 15.0 Hz $^4J_{HCCPH}$ = 1.5 Hz	δ 1.27 d of d $^2J_{HCH}$ = 11 Hz $^3J_{HCCH}$ = 11 Hz	δ 1.87 d of d of d $^2J_{HCH}$ = 11 Hz $^3J_{HCCH}$ = 3.7 Hz $^3J_{HCCP}$ = 3.7 Hz	δ 2.53 d of sept $^1J_{HP}$ = 195 Hz $^4J_{HPCCH}$ = 1.5 Hz	δ 3.68 t of t $^3J_{HCCHa}$ = 11 Hz $^3J_{HCCHe}$ = 3.7 Hz
6	δ 0.98 d $^3J_{HCCP}$ = 13.6 Hz	δ 1.13 d of d $^3J_{HCCP}$ = 14.6 Hz $^4J_{HCCPH}$ = 1.8 Hz	δ 1.33 d of d $^2J_{HCH}$ = 12 Hz $^3J_{HCCH}$ = 12 Hz	δ 2.06 d of d of d $^2J_{HCH}$ = 12 Hz $^3J_{HCCH}$ = 4 Hz $^3J_{HCCP}$ = 4 Hz	δ 2.62 d of sept $^1J_{HP}$ = 197 Hz $^4J_{HPCCH}$ = 1.8 Hz	δ 5.25 t of t $^3J_{HCCHa}$ = 12 Hz $^3J_{HCCHe}$ = 4 Hz

[a] 80 MHz.

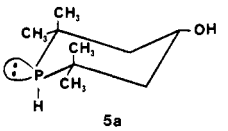
phenylphosphines with lithium metal in tetrahydrofuran (THF).[7] Under analogous conditions, the reduction of **2** with lithium metal in THF gave a deep red solution of the corresponding phosphide anion, which upon quenching with water gave the 1*H*-phosphorinane **3**. The IR spectrum of **3** showed an absorption at 2280 cm^{-1} assignable to the P–H stretching vibration. Interestingly in the ^{1}H NMR spectrum of **3**, a doublet of septets was observed at δ 2.80 which was assigned to the H(1) proton. A reasonable explanation which would account for this observation is that the H(1) proton is coupled to both the phosphorus atom and the protons on one equivalent pair of methyl groups (vide infra) with $^1J_{HP}$ = 167 Hz and $^4J_{HPCCH}$ = 1.8 Hz, respectively. The magnitude of $^1J_{HP}$ is that expected for the P(III) oxidation state.[8]

The ethylene ketal protecting group was removed by treatment of **3** with 3 M aqueous hydrochloric acid in THF to give **4**. The alcohol **5** was prepared by the reduction of **4** with lithium tetrahydroaluminate in a yield of 53% (distilled). Transesterification of **5** with dimethyl sebacate using lithium hydride as a catalyst gave the diester **6** (47% chromatographed yield). Flash chromatography of the crude transesterification residue also gave a small quantity of the 1-oxo derivative **8**, whose structure was based upon its IR, ^{1}H NMR, ^{31}P NMR, and mass spectra. The formation of **8** is attributed to fortuitous traces of atmospheric oxygen present either during transesterification or workup.

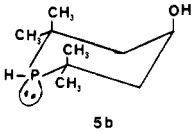
The attempted oxidation of **6** to the corresponding 1-oxo diester **7** with *m*-chloroperoxybenzoic acid in dichloromethane at 0 °C gave a complex residue which did not show the presence of a P–H bond in either its IR or ^{1}H NMR spectrum. Surprisingly, treatment of a solution of **6** in 2-propanol with molecular oxygen at 70 °C for 5 h did not lead to any detectable change as indicated by TLC. The desired conversion was accomplished by using a convenient two-phase oxidation technique. A toluene solution of **6** was stirred with dilute aqueous hydrogen peroxide to give **7**.[9] Although the clean formation of **7** by this two-phase method was indicated by TLC, routine flash chromatographic workup resulted in a poor recovery off the column. The observed $^1J_{HP}$ = 426 Hz in the ^{1}H NMR spectrum of **7** is that expected for the P(V) oxidation state.

^{1}H NMR Analysis. One must exercise caution in assigning the conformation of heterocycles in solution based solely upon ^{1}H NMR spectral data without supporting ^{13}C NMR studies. However, the observed ^{1}H NMR coupling patterns suggest that compounds **3**, **5**, and **6** have a biased ring conformation in which the proton on phosphorus occupies an axial ring position. This suggestion is consistent with previous studies which have shown that C-substituents assume equatorial ring positions in preference to the substituent on phosphorus, although sterically demanding substituents, e.g., *tert*-butyl, on phosphorus show an increased equatorial preference. Recent studies by Berlin et al. support an axial P–C_6H_5 in **1**.[2]

The ^{1}H NMR is particularly informative as the individual ring protons displayed significant nonequivalence giving an essentially first-order spectrum at 80 MHz (see Table I) from which coupling information is readily extracted. The ^{1}H NMR spectrum of **5** suggests the observation of either a single conformer **5a** (cis isomer) or of a rapid conformational equilibrium **5a** ⇌ **5b** where **5a** is highly favored. That conformer **5b** does not appear to



5a



5b

be present (or is a minor contributor to the equilibrium **5a** ⇌ **5b**) is not surprising in view of the severe 1,3-diaxial interaction which results between an axial C(4)–OH and the C(2,6) axial methyl groups. The GPC and TLC of either the crude or distilled alcohol **5** showed no evidence for the presence of the trans isomer. Supportive of this interpretation, the ^{31}P {^{1}H} NMR spectrum of **5** showed a single resonance at δ −17.1. Barring accidental equivalence, two resonances would be expected in the ^{31}P NMR spectrum for a mixture of cis and trans isomers. That **5a** has the conformation illustrated rests on the following observations.

The ^{1}H NMR spectrum of **5** shows a triplet of triplets at δ 3.68, which was assigned to the H(4) proton. This would be the case if the H(4) proton was axial and it was coupled to both two equivalent H(3,5) axial and H(3,5) equatorial protons with $^3J_{HCCH}$ = 11 Hz and $^3J_{HCCH}$ = 3.7 Hz, respectively. The magnitude of the observed vicinal coupling is in accord with the usual Karplus relationship if **5** is in a biased chair conformation. This suggestion is consistent with the known ability of a sterically small C(4)–OH substituent to assume an equatorial position and force a *P*-methyl (and phenyl) group into an axial position in phosphorininan-4-ols studied by Quin et al.[10] The axial

(7) Grim, S. O.; Molenda, R. P. *Phosphorus* **1974**, *4*, 189–193.
(8) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper & Row: New York, 1976; pp 78–106.
(9) During preparation of this manuscript, Quin and co-workers reported a similar two-phase system using benzene and aqueous hydrogen peroxide. Quin, L. D.; Rao, N. S. *J. Org. Chem.* **1983**, *48*, 3754–3759.
(10) (a) Shook, H. E., Jr.; Quin, L. D. *J. Am. Chem. Soc.* **1967**, *89*, 1841. (b) Quin, L. D.; Somers, J. H. *J. Org. Chem.* **1972**, *37*, 1217.

H(3,5) protons of **5** are observed at δ 1.27 as a doublet of doublets. This would be the case if the H(3,5) axial protons are coupled both geminally to the H(3,5) equatorial and vicinally to the H(4) axial protons with $^2J_{HCH} = {}^3J_{HCCH}$ = 11 Hz. The H(3,5) equatorial protons are observed at δ 1.87 as a doublet of doublets of doublets. A reasonable explanation for this observation is that the H(3,5) equatorial protons are coupled not only to both the H(4) axial and H(3,5) axial protons, but also to the phosphorus atom with $^3J_{HCCH}$ = 3.7 Hz, $^2J_{HCH}$ = 11 Hz, and $^3J_{HCCP}$ = 3.7 Hz, respectively. That the H(3,5) equatorial protons and *not* the H(3,5) axial protons are coupled to phosphorus suggests that the lone electron pair on phosphorus occupies an equatorial position. The examination of a molecular model of **5** shows that when this is the case, the dihedral angle between the lone electron pair on phosphorus and the C(3)–H(3) equatorial bond would be small. Numerous examples in the literature have demonstrated that larger $^3J_{HCCP}$ (and $^2J_{CHP}$) values are associated with small dihedral angles between the phosphorus lone electron pair and the C–H bond in question, with maximum coupling occurring at a dihedral angle of 0°.[1]

Furthermore, the observed coupling of the H(3,5) equatorial protons to phosphorus is also consistent with the known Karplus-type relatonship for the dependence of $^3J(^{31}P,^1H)$ upon the dihedral angle of the P–C–C–H fragment.[11,12] Larger equatorial $^3J_{HCOP}$ than axial $^3J_{HCOP}$ coupling has been observed in conformationally biased 1,3,2-dioxaphosphorinanes.[13]

The assignment of the lone electron pair on phosphorus to an equatorial position is also in accord with the observation of a similar magnitude for the value of the coupling constant of phosphorus to the protons of both equivalent pairs of C(2,5) methyl groups. An equatorial lone electron pair would have an approximately 60° dihedral angle with both pairs of exocyclic axial and equatorial methyl groups,[14] and similar values of $^3J_{HCCP}$ coupling would be expected. This would *not* be the case if the phosphorus lone electron pair was axial.

One pair of exocyclic C(2,5) methyl group protons are further coupled to the proton on phosphorus with $^4J_{HCCPH}$ = 1.5 Hz. The H(1) proton is tentatively suggested to be coupled to the protons on the axial pair of C(2,6) methyl groups as an examination of a molecular model of **5** shows that the involved atoms may assume a "W" relationship, familiar in carbocyclic chemistry.[15] Larger values of ^4J coupling have also been demonstrated in phosphorinanes to be associated with a "W" relationship.[16] However, such a suggestion requires that the axial C(2,6) methyl group protons are deshielded relative to the equatorial C(2,6) methyl group protons unlike that normally observed for ring protons. Examples of this behavior are known in 1,3,5-trimethylcyclohexanes[17] and methyl-substituted phosphorinanes.[2] However, the suggestion that the axial pair of C(2,6) methyl substituent protons are coupled to the H(1) proton should be considered highly tentative until further studies are made. The question as to whether the axial or equatorial pair of exocyclic C(2,6) methyl group protons are coupled to the axial H(1) proton *does not* affect the conformational arguments presented for the H(4), H(3,5), or H(1) protons. Indeed, only when the H(1) proton is in an axial position would unequal coupling to the exocyclic C(2) methyl group protons be expected, since an axial H(1) proton would have significantly different dihedral angles with the methyl group protons involved.

The H(1) proton in the ^{1}H NMR spectrum of **5** is observed at δ 2.53 as a doublet of septets with J_{HP} = 195 Hz and $^4J_{HPCCH}$ = 1.5 Hz. The peak intensities of each septet follows the 1:6:15:20:15:6:1 relationship expected for the coupling of the H(1) proton to six equivalent protons of one equivalent pair of exocyclic C(2,6) methyl groups.

The ^{1}H NMR data presented clearly suggests the observation of conformer **5a** in solution. Similar coupling patterns were observed in the ^{1}H NMR spectra of **3** and **6**. A constant geometrical relationship is evident. These observations strongly suggest that **3** and **6** have similar conformations in solution with an axial H(1) proton. However, one must clearly exercise caution in the conformational assignment of **3** since the spirocyclic structure might be expected to perturb the ring conformation. Particularly interesting, both pairs of methylene protons of the ketal protecting group appear to be equivalent in the ^{1}H NMR spectrum of **3**. Further study is needed to determine whether this observation is due to accidental equivalence or not. The observed ^{1}H NMR spectra of both **2** and the ketone **4** indicate further studies are warranted to determine the conformation of these compounds, as the observed coupling constants are distinctly different from those observed for **5**.

The axial preference for phosphorus substituents has been previously discussed elsewhere in terms of both 1,3-diaxial van der Waals attraction[4] (in the case of a proton on phosphorus) and on thermodynamic arguments[17] and will not be considered further here.

In summary, the ^{1}H NMR spectra of the alkylated 1*H*-phosphorinanes **3**, **5**, and **6** strongly suggest a highly biased conformation in solution with the proton on phosphorus occupying an axial ring position. Methodology for the preparation of alkylated 1*H*-phosphorinanes has been presented. It is hoped that this work will provide encouragement for further conformational studies of C-alkylated 1*H*-phosphorinanes including the ^{13}C NMR spectra of the compounds of this study.

Experimental Section

All melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra (1% solution in potassium bromide cells) were recorded on a Perkin-Elmer 710 spectrophotometer. ^{1}H NMR spectra were taken on Varian Model XL-100 or CFT-20 spectrometers. ^{31}P NMR spectra were taken on a Varian Model XL-200 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{31}P NMR spectra were acquired by using a 35° flip angle, a 1.4-s repetition rate with 0.6-s pulse delay and with full proton decoupling. Mass spectra were obtained on a AEI (KRATOS) MS 902 spectrometer. MERCK 9385 silica gel-60 (230–400 mesh) was used for flash chromatography.[18] Unless otherwise indicated, all reagents were purchased from Aldrich Chemical Company. All solvents were dried and purged with nitrogen prior to use. Reactions were carried out

(11) Reference 1, p 327.
(12) Harris, R. K.; Mann, B. E. "NMR and the Periodic Table"; Academic Press: New York, 1978; p 74–75 and references therein.
(13) Bentrude, W. G.; Hargis, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 7136–7144.
(14) These angles are approximate as energy minimization is known to be accompanied by a flattening of the ring about the P–C bonds for axial P-substituents: McPhail, A. T.; Steele, J. C. H., Jr. *J. Chem. Soc., Dalton Trans.* **1972**, 2680.
(15) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: New York, 1969; pp 339–341 and references therein.
(16) Reference 1, pp 329–330.
(17) Segre, A.; Musher, J. I. *J. Am. Chem. Soc.* **1967**, *89*, 706–708.
(18) Featherman, S. I.; Quin, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 4349–4355.
(19) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

in a flame-dried apparatus under a dry argon atmosphere. All spectral data were obtained on analytical samples. Elemental analysis were performed by Analytical Research Services, CIBA-GEIGY Corporation.

4,4-(Ethylenedioxy)-2,2,6,6-tetramethyl-1-phenylphosphorinane (2). A mixture of 10.00 g (40 mmol) of 1, 0.73 g (4.0 mmol) of *p*-toluenesulfonic acid, 150 mL of ethylene glycol, and 800 mL of toluene was heated at reflux and 26 mL of a water–ethylene glycol azeotrope was collected (Dean–Stark trap) during a 20-h period. The reaction mixture was washed sequentially with saturated sodium bicarbonate and water. The organic phase was dried over anhydrous potassium carbonate. The solvent was removed in vacuo and the residue was distilled to give 9.20 g (78%) of 2 as a colorless liquid: bp 134–140 °C (0.3 mm); ^{1}H NMR (benzene-d_6): δ 0.85 (d, CH_3, $^3J_{HCCP}$ = 8.8 Hz, 6 H), 1.46 (d, CH_3, $^3J_{HCCP}$ = 18 Hz, 6 H), 1.71 (d of d, C3–H, $^2J_{HCH}$ = 15.2 Hz, $^3J_{HCCP}$ = 6 Hz, 2 H), 2.05 (d of d, C3-H, $^2J_{HCH}$ = 15.2 Hz, $^3J_{HCCP}$ = 2.4 Hz, 2 H), 3.61 (s, OCH_2, 4 H), 7.68 (c, Ar H, 5 H). Anal. Calcd for $C_{17}H_{25}O_2P$: P, 10.6. Found: P, 10.6.

4,4-(Ethylenedioxy)-2,2,6,6-tetramethylphosphorinane (3). A mixture of 8.00 g (27 mmol) of 2, 0.80 g (115 mmol) of lithium metal, and 40 mL of anhydrous THF was heated to reflux and then the reaction mixture was stirred at room temperature for 48 h. The deep red reaction mixture was cooled to −10 °C and to it was added, with stirring, 100 mL of water. The mixture was extracted three times with diethyl ether and the combined ether extracts were dried over anhydrous potassium carbonate. The solvent was removed in vacuo and the residue was distilled to give 1.60 g (27%) of 3 as a colorless liquid: bp 65–69 °C (0.05 mm); IR (film): ν 2280 cm^{-1} (PH); ^{1}H NMR benzene-d_6): δ 1.03 (d, CH_3, $^3J_{HCCP}$ = 14.0 Hz, 6 H), 1.39 (d of d, CH_3, $^3J_{HCCP}$ = 15.2 Hz, $^4J_{HCCPH}$ = 1.8 Hz, 6 H), 1.51 (d, C3–H, $^2J_{HCH}$ = 13.8 Hz, 2 H), 1.85 (d of d, C3-H, $^2J_{HCH}$ = 13.8 Hz, $^3J_{HCCP}$ = 4 Hz, 2 H), 2.80 (d of sept, PH, $^1J_{HP}$ = 167 Hz, $^4J_{HPCCH}$ = 1.8 Hz, 1 H), 3.49 (s, OCH_2, 4 H); high-resolution MS, calcd for $C_{11}H_{21}O_2P$ 216.1278, found 216.1278.

2,2,6,6-Tetramethylphosphorinan-4-one (4). A mixture of 43.2 g (200 mmol) of 3, 250 mL of 3 M aqueous hydrochloric acid, and 250 mL of THF was stirred at room temperature for 20 h. To the reaction mixture was added 100 mL of water and then it was extracted three times with diethyl ether. The combined ether extracts were washed with saturated sodium chloride solution and then they were dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was distilled to give 14.4 g (42%) of 4 as a colorless liquid: bp 53–56 °C (0.9 mm); IR (film): ν 2280 (PH), 1705 cm^{-1} (C=O); ^{1}H NMR (benzene-d_6): δ 0.93 (d, CH_3, $^3J_{HCCP}$ = 13.9 Hz, 6 H), 0.99 (d of d, CH_3, $^3J_{HCCP}$ = 14.9 Hz, $^4J_{HPCCH}$ = 1.5 Hz, 6 H), 2.17 (c, CH_2, 4 H), 2.93 (d of sept, PH, $^1J_{HP}$ = 195 Hz, $^4J_{HCCPH}$ = 1.5 Hz, 1 H); high-resolution MS, calcd for $C_9H_{17}OP$ 172.1013, found 172.1015.

2,2,6,6-Tetramethylphosphorinan-4-ol (5). To a suspension of 9.4 g (250 mmol) of lithium tetrahydroaluminate in 1 L of anhydrous THF was added dropwise a solution of 20 g (120 mmol) of 4 in 140 mL of THF. The reaction mixture was heated to 50 °C and it was stirred at this temperature for 3 h. The reaction mixture was cooled to −15 °C and then to it was added carefully 175 mL of water. To the resultant white suspension was added 100 g of anhydrous magnesium sulfate to remove excess water. The precipitate was removed by filtration and the filter cake was washed with diethyl ether. The filtrate was concentrated in vacuo and the residue was distilled to give 11.1 g (53%) of 5 as a white solid: bp 60–64 °C (0.3 mm); mp 47–50 °C; IR (CCl_4) ν 3375 (OH), 2280 cm^{-1} (PH); ^{1}H NMR (benzene-d_6): δ 1.00 (d, $CH_{3(e)}$, $^3J_{HCCP}$ = 13.8 Hz, 6 H), 1.03 (d of d, $CH_{3(a)}$, $^3J_{HCCP}$ = 15.0 Hz, $^4J_{HCCPH}$ = 1.5 Hz, 6 H), 1.27 (d of d, C3–Ha, $^2J_{H(3)aH(3)e}$ = $^3J_{H(3)aH(4)a}$ = 11 Hz, 2 H), 1.62 (exch. s, OH, 1 H), 1.87 (d of d of d, C3–He, $^2J_{H(3)eH(3)a}$ = 11 Hz, $^3J_{H(3)eH(4)a}$ = $^3J_{H(3)eP}$ = 3.7 Hz, 2 H), 2.53 (d of sept, PH, $^1J_{HP}$ = 195 Hz, $^4J_{HCCPH}$ = 1.5 Hz, 1 H), 3.68 (t of t, C4–Ha, $^3J_{H(4)aH(3)a}$ = 11 Hz, $^3J_{H(4)aH(3)e}$ = 3.7 Hz, 1 H); MS, m/z 174 (M·$^+$).

Bis(2,2,6,6-tetramethylphosphorinan-4-yl) Sebacate (6). A mixture of 2.75 g (15 mmol) of 5, 1.65 g (7.2 mmol) of dimethyl sebacate, and 6 mg of lithium hydride was heated to 70 °C and the evolved methyl alcohol was collected in an acetone:dry ice cooled Dean–Stark trap equipped with a Dewar condenser. The pressure was slowly reduced to 11 mm during which time the temperature of the reaction mixture was increased to 170 °C (8 h). The reaction mixture was cooled and the residue was purified by flash chromatography on silica gel (heptane/EtOAc) to give 1.7 g (47%) of 6 as a white solid: mp 58–63 °C; IR (CCl_4): ν 2260 (PH); 1735 cm^{-1} (C=O); ^{1}H NMR (benzene-d_6): δ 0.98 (d, $CH_{3(e)}$, $^3J_{HCCP}$ = 13.6 Hz, 12 H), 1.13 (d of d, $CH_{3(a)}$, $^3J_{HCCP}$ = 14.6 Hz, $^4J_{HCCPH}$ = 1.8 Hz, 12 H), 1.14–1.86 (c, $(CH_2)_6$, 12 H), 1.33 (d of d, C3–Ha, $^2J_{H(C)aH(3)e}$ = $^3J_{(H(3)aH(4)a}$ = 12 Hz, 4 H), 2.06 (d of d of d, C3–He, $^2J_{H(3)eH(3)a}$ = 12 Hz, $^3J_{H(3)eH(4)a}$ = $^3J_{H(3)eP}$ = 4 Hz, 4 H), 2.23 (t, $CH_2C(=O)O$, 4 H), 2.62 (d of sept, PH, $^1J_{HP}$ = 197 Hz, $^4J_{HPCCH}$ = 1.8 Hz, 2 H), 5.25 (t of t, C4–Ha, $^3J_{H(4)aH(3)a}$ = 12 Hz, $^3J_{(H(4)aH(3)e}$ = 4 Hz, 2 H). Anal. Calcd for $C_{28}H_{52}O_4P_2$: C, 65.3; H, 10.2. Found: C, 65.6; H, 9.9.

2,2,6,6-Tetramethyl-1-oxophosphorinan-4-ol (8). From the reaction residue of compound 6 was isolated by flash chromatography on silica gel (heptane/ethyl acetate) 0.8 g of 8 as a white solid: mp 185–190 °C; IR ($CHCl_3$) ν 3600, 3350 (OH), 2450, 2310 cm^{-1} (PH); ^{31}P NMR (benzene-d_6): δ 56.0; ^{1}H NMR ($CDCl_3$) δ 1.30 (overlapping d, CH_3, 12 H), 1.80 (c, CH_2, 4 H), 3.40 (exchangeable s, OH, 1 H), 3.90 (m, OCH, 1 H), 6.20 (d, PH, $^1J_{HP}$ = 440 Hz, 1 H); MS, m/z 190 (M·$^+$).

Bis(2,2,6,6-tetramethyl-1-oxophosphorinan-4-yl) Sebacate (7). A two-phase mixture of 4.0 g (7.8 mmol) of 6 in 40 mL of toluene and 1.8 g (15.5 mmol) of 30% aqueous hydrogen peroxide in 40 mL of water was stirred until completion of the reaction as determined by the disappearance of 6 by TLC. The organic phase was separated and the aqueous phase was extracted three times with diethyl ether. The combined organic fractions were washed with water and were dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (97.5:2.5 dichloromethane:methyl alcohol) to give 1.2 g (29%) of 7 as a white hygroscopic solid: mp 27–30 %C; IR (CCl_4) ν 2310 (PH), 1740 cm^{-1} (C=O); ^{1}H NMR (benzene-d_6) δ 0.8–2.0 (c, 44 H), 2.16 (t, $CH_2C(=O)$, 4 H), 5.04 (m, C4–H, 2 H), 5.97 (d, PH, $^1J_{HP}$ = 426 Hz, 2 H); MS, m/z 546 (M·$^+$).

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