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Conformational Preferences of Monocyclic Pentaoxyphosphoranes Varying in Ring Size[1,2]

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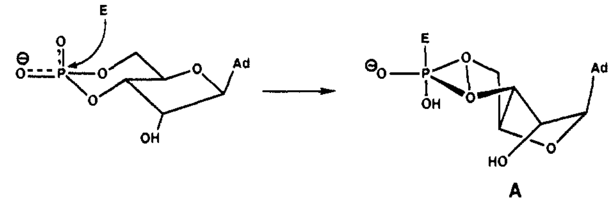
Abstract: New monocyclic pentaoxyphosphoranes **1–4**, **6** and the furanosyl derivative, **7**, were synthesized from the reaction of tris(2,6-dimethylphenyl) phosphite (**5**) with a diol or a quinone. The pentacoordinated derivatives **1–4** were studied by X-ray analysis and represent the first structurally chartacterized monocyclic oxyphosphoranes that have six-, seven-, and eight-membered rings. All possess trigonal-bipyramidal geometries with the rings spanning apical–equatorial positions. Retention of these structures in solution is indicated by ^{1}H, ^{13}C, and ^{31}P NMR. Twist-boat, rowboat, and distorted-tub conformations are found for the six- (**1**), seven- (**2**), and eight- (**4**) membered ring derivatives, respectively. Phosphorane **3** has a more planar phosphorinane ring, a consequence of ring unsaturation. Variable-temperature ^{1}H and ^{13}C NMR establish nonrigid behavior supporting a simple Berry pseudorotation in which the rings exchange apical–equatorial positions. It is concluded that six-membered rings of pentaoxyphosphoranes prefer apical–equatorial sites of a TBP. The preferred conformation of saturated six-membered rings is generally that of a boat. Phosphorane **1** crystallizes in the monoclinic space group C_2/c with a = 29.392 (8), b = 11.420 (5), c = 16.379 (2) Å, β = 92.22 (1)°, and Z = 8. Compound **2** crystallizes in the monoclinic space group $P2_1$ with a = 12.268 (2), b = 9.916 (3), c = 12.625 (2) Å, β = 91.79 (1)°, and Z = 2. The monocyclic derivative **3** crystallizes in the monoclinic space group $P2_1/c$ with a = 20.114 (6), b = 9.554 (2), c = 17.178 (3) Å, β = 114.24 (2)°, and Z = 4. Phosphorane **4** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.690 (2), b = 15.414 (4), c = 21.350 (5) Å, α = 93.07 (2)°, β = 90.17 (2)°, γ = 99.97 (2)°, and Z = 4. The final conventional unweighted residuals are 0.056 (**1**), 0.039 (**2**), 0.038 (**3**), and 0.076 (**4**).

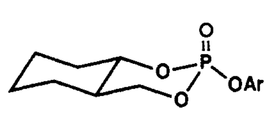
Introduction

As the preceding paper has shown,[1b] a series of bicyclic oxyphosphoranes subjected to X-ray analysis exhibited boat conformations for the six-membered rings comprising one of the cyclic components. The same result was found for a bicyclic pentaoxyphosphorane by Schomburg and co-workers[4] and for a bicyclic oxythiophosphorane containing a six-membered phosphorus–sulfur bonded ring.[5] The rings in these compounds which varied from five to seven membered were located apically–equatorially in trigonal-bipyramidal geometries. The uniformity in conformation and orientation of the six-membered rings might possibly be associated with the presence of the bicyclic system. However, related structural studies on monocyclic oxyphosphoranes with six-membered rings which could assist in deciding this issue appear nonexistent.

Previous work both of an experimental and theoretical nature indicates conflicting views concerning placement of six-membered rings. For example, on the basis of NMR and molecular model considerations, Ramirez et al.[6-8] conclude that diequatorial ring placement in a trigonal bipyramid is lower in energy compared to an apical-equatorial orientation. van Ool and Buck find support for this conclusion from semiempirical molecular orbital calculations[9,10] (CNDO/2) performed on possible pentacoordinated intermediates for the hydrolysis of cAMP. The results indicate a lower energy for diequatorial ring placement of the six-membered ring in a trigonal bipyramid, about 28 kcal/mol, compared to an apical–equatorial ring position. In the activation of protein kinases by cAMP,[11-13] these calculations[9,10] support diequatorial placement of the cyclophosphate ring which is proposed to result from attack by a functional group of the enzyme yielding a covalent complex, A. Also consistent with the above are proposed diequatorial ring orientations in trigonal-bipyramidal transition states for the hydrolysis of epimeric phosphorinanes,[14,15] e.g.,



A



Ar = 2,4(NO$_2$)$_2$Ph

By way of contrast, a low-temperature ^{13}C NMR study[16] indicates the occupancy of apical–equatorial sites for the dioxa-

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[1] (a) Pentacoordinated Molecules 82. (b) Part 81: Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.*, preceding paper in this issue.

[2] Kumara Swamy, K. C.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. Presented in part at the XI International Conference on Phosphorus Chemistry, Tallinn, Estonia, SSR/USSR, July 1989; Abstract 2-22.

[3] This work represents in part a portion of the Ph.D. Thesis of Sarah D. Burton, University of Massachusetts, Amherst, MA.

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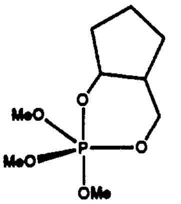
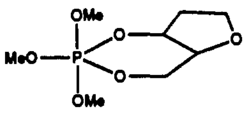
phosphorinane ring in the trans-annelated phosphorane, B, whereas diequatorial ring occupancy in the closely related cyclic derivative, C, is suggested[16] on the basis of semiempirical MO calculations referred to above.[9,10] In continuation of their work van Ool and

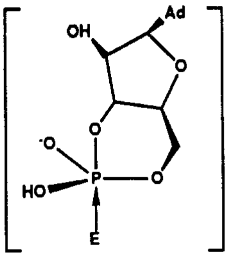


B



C

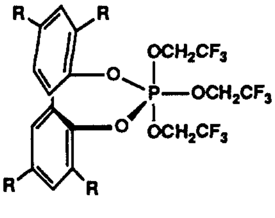
Buck[9] conclude that hydrolysis of cAMP with phosphodiesterase proceeds by way of a trigonal-bipyramidal intermediate with an apical–equatorial ring orientation and the 3′-oxygen atom positioned at the apical site, D.



D

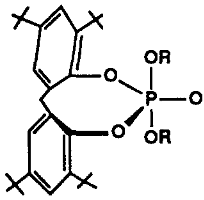
It may be that the conclusions from each of these studies are correct[17] and that the appearance of one or the other ring orientation is governed by reaction media and composition of the phosphorus derivative taking part therein.

With regard to phophoranes having ring systems larger than six-membered, little information is available. On the basis of an NMR study, Denney and co-workers[18] concluded that seven- and eight-membered rings of monocyclic pentaoxyphosphoranes containing OCH_2CF_3 groups, E and F, respectively, are situated in diequatorial positions of a trigonal bipyramid.



R = *t*-Bu
R = H

E

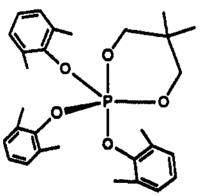


R = R' = CH_2CF_3
R = CH_2CF_3; R' = C_2H_5

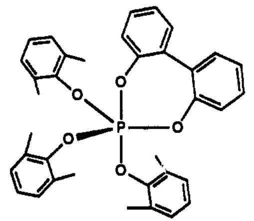
F

To address the absence of a firm structural basis in this area, we have undertaken an X-ray and variable-temperature NMR study of a series of new monocyclic pentaoxyphosphoranes containing ring sizes from six to eight membered and which have a constant acyclic component, **1**–**4**. As a result of the latter feature, interpretation of changes in ring conformations should be facilitated. In addition, the NMR behavior of the related oxyphosphoranes **6**–**7** also was studied. All of these derivatives represent new compounds in Chart I. It is expected that the results will address ring-site preferences and solution-state exchange processes, the knowledge of which should have immediate application in aiding an understanding of mechanistic consequences encountered in nucleophilic substitutions at cyclic tetracoordinated phosphorus containing such rings.[19-22]

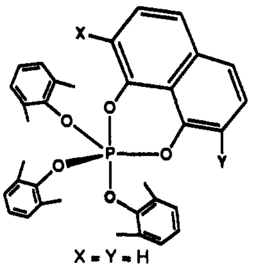
Chart I



1

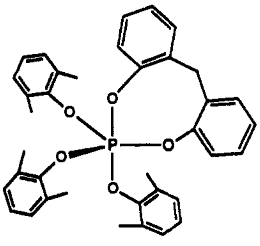


2

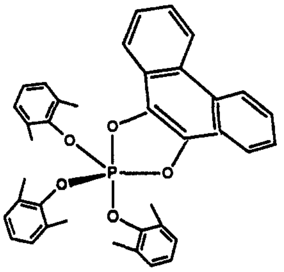


X = Y = H
X = Y = Cl
X = H, Y = Cl

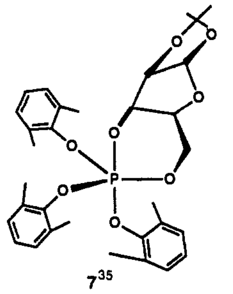
3



4



6



7[35]

Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, or Fluka and used without further purification. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[23]

^1H and ^{13}C NMR spectra were recorded on a Varian XL 300 FT-NMR or a Varian Associates XL 200 FT-NMR. ^{31}P NMR spectra were recorded on the Varian Associates XL 300 FT-NMR spectrometer. Chemical shifts for ^{31}P NMR spectra were obtained by setting triphenyl phosphate ($CDCl_3$) at −18.0 ppm[24] and are referenced to 85% H_3PO_4 with negative shifts upfield. Temperature calibration was accomplished by using an ethylene glycol sample with a calibration error of ±0.5 °C.

Synthesis. Tris(2,6-dimethylphenyl) phosphite (**5**) was prepared in 70% yield by the reaction of phosphorus trichloride with 2,6-dimethylphenol in the presence of triethylamine with diethyl ether as the solvent: mp 92–94.5 °C (lit.[25] mp 92–94.5 °C). ^{31}P NMR ($CDCl_3$, ppm): 147.5.

The synthesis of **1**–**4** and **7** follows the same general procedure. The method is illustrated for **1**.

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(2,2-Dimethylpropanediyl-1,3-dioxy)tris(2,6-dimethylphenoxy)phosphorane, (Xyl-O)$_3$P(O$_2$C$_3$H$_4$Me$_2$) (1). To a solution of tris(2,6-dimethylphenyl) phosphite (**5**) (3.80 g, 9.63 mmol) and 2,2-dimethyl-1,3-propanediol (1.00 g, 9.60 mmol) in diethyl ether (60 mL) maintained at −60 °C was added dropwise a solution of *N*-chlorodiisopropylamine (1.45 mL, 1.334 g, 9.85 mmol) in diethyl ether (20 mL) over a period of 20 min with continuous stirring under a nitrogen atmosphere. The reaction was brought to 20 °C and stirred at this temperature for 10 h. The precipitate was filtered using standard Schlenk techniques[26] and the filtrate concentrated to ca. 25 mL by passing a stream of nitrogen. Crystallization occurred after standing about 8 h to afford **1**, mp 105–107 °C (yield 3.00 g, 62%). The product was separated from the mother liquor with use of a frit in the presence of a nitrogen atmosphere. Compound **1** becomes a liquid if exposed to air after a few minutes. ^{1}H NMR ($C_6D_5CD_3$, ppm) at 20 °C: 0.50 (s, 6 H, $CH_2C(C\mathit{H}_3)_2$), 2.40 (s, 18 H, $OC_6H_3(C\mathit{H}_3)_2$), 3.60 (d, $^3J(P\text{–}\mathit{H})$ = 18.3 Hz, 4 H, $OC\mathit{H}_2$), 6.60–7.20 (m, 9 H, H (Ar)); at −70 °C 0.31 (s, 3 H, $CH_2C(C\mathit{H}_3)$), 0.53 (s, 3 H, $CH_2C(C\mathit{H}_3)$), 2.38 (s, 12 H, $OC_6H_3(C\mathit{H}_3)$) (eq), 2.70 (s, 6 H, $OC_6H_3(C\mathit{H}_3)$ (ax), 3.32 (br, 2 H, $OC\mathit{H}_2$), 3.68 (br, 2 H, $OC\mathit{H}_2$), 6.73–7.23 (m, 9 H, H (Ar)). ^{31}P NMR (C_6D_6, ppm): −77.45. Anal. Calcd for $C_{29}H_{37}O_5P$: C, 70.16; H, 7.41. Found: C, 69.41; H, 8.03.

(Biphenylene-2,2′-dioxy)tris(2,6-dimethylphenoxy)phosphorane, (Xyl-O)$_3$P(O$_2$C$_{12}$H$_8$) (2). Quantities used were as follows: tris(2,6-dimethylphenyl) phosphite (**5**) (0.819 g, 2.02 mmol), *o,o′*-biphenol (0.377 g, 2.02 mmol), *N*-chlorodiisopropylamine (0.46 mL, 2.88 mmol), and diethyl ether (100 mL). After the precipitate was filtered, clear crystals of **2** formed from the mother liquor on standing, mp 257 °C (yield 1.07 g, 92%). ^{1}H NMR ($C_6D_5CD_3$, ppm) at −70 °C consists of a set of six signals of equal intensity,[27] at 1.59, 1.83, 2.09, 2.51, 2.85, and 2.95 assignable to the xylyloxy $C\mathit{H}_3$ protons, and a multiplet in the range 6.5–7.2 assignable to the 17 aromatic protons. Variable-temperature spectra for the $C\mathit{H}_3$ proton region is shown in Figure 9. ^{31}P NMR ($CDCl_3$, ppm): −68.34. Anal. Calcd for $C_{36}H_{35}O_3P$: C, 74.73; H, 6.10. Found: C, 74.45; H, 6.36.

(2-Chloro- or 2,7-dichloronaphthalenediyl-1,8-dioxy)tris(2,6-dimethylphenoxy)phosphorane, (Xyl-O)$_3$P(O$_2$C$_{10}$H$_4$XY), X = H$_{0.14}$Cl$_{0.86}$, Y = H$_{0.68}$Cl$_{0.32}$ (3). Quantities used were as follows: tris(2,6-dimethylphenyl) phosphite (**5**) (2.03 g, 5.14 mmol), 1,8-dihydroxynaphthalene (Fluka, 0.82 g, 5.12 mmol), *N*-chlorodiisopropylamine (0.70 g, 5.17 mmol) and diethyl ether (100 mL). During the workup after the precipitate was filtered, the solvent from the filtrate was evaporated slowly (ca. 24 h) to afford **3**, mp 195–198 °C (yield 0.80 g, 26%). The residue turned black over a period of time. Compound **3** is sufficiently stable in air (2–3 h) and stable in sealed ampules for several months. ^{1}H NMR ($C_6D_5CD_3$, ppm) (see text) at 20 °C: 2.31–2.36 (m (closely spaced), 18 H, $C\mathit{H}_3$), 6.60–7.20 (m, ca. 14 H). At −89 °C, the $C\mathit{H}_3$ protons appear as a set of six major signals at 1.77, 1.87, 2.38, 2.45, 2.79, and 3.12 ppm along with some minor (not well-resolved, 15–20%) peaks. ^{31}P NMR ($CDCl_3$, ppm): −88.17, −88.32, −88.55 (approximate intensity ratio 1:2:3). Anal. Calcd for $C_{34}H_{31.8}Cl_{1.2}O_5P$ (see X-ray discussion for explanation): C, 68.76; H, 5.36; Cl, 7.17; P, 5.22. Found: C, 68.74; H, 5.23; Cl, 7.50; P, 4.78.

[Methylenebis(*o*-phenyleneoxy)]tris(2,6-dimethylphenoxy)phosphorane, (Xyl-O)$_3$P(O$_2$C$_{13}$H$_{10}$) (4). Quantities used were as follows: tris(2,6-dimethylphenyl) phosphite (**5**) (0.942 g, 2.33 mmol), bis(2-hydroxyphenyl)methane (0.466 g, 2.33 mmol), *N*-chlorodiisopropylamine (0.418 g, 2.62 mmol), and diethyl ether (80 mL). After filtration, evaporation of the mother liquor yielded **4**, mp 170–199 °C dec (yield 0.58 g, 42%). Crystals were obtained by slow evaporation (24 h) from an ether solution maintained at 25 °C. ^{1}H NMR ($C_6D_5CD_3$, ppm) at 40 °C: 2.37 (s, 18 H, $C\mathit{H}_3$), 4.00 (br, 2 H, $C\mathit{H}_2$), 6.70–7.10 (m, 17 H, Ar); at −44 °C (upfield from the aromatic region) 2.45 (br, 18 H, $C\mathit{H}_3$), 3.12 (d, $^2J(\mathit{H}_A\text{–}\mathit{H}_B)$ = 25 Hz, 1 H, $CH_A\mathit{H}_B$), 4.81 (d, $^2J(\mathit{H}_A\text{–}\mathit{H}_B)$ = 25 Hz, 1H, $C\mathit{H}_AH_B$); at −88 °C (upfield from the aromatic region) five signals assigned to the xyloxy $C\mathit{H}_3$ protons appear at 2.0, 2.2, 2.7, 2.8, and 2.9 all of equal intensity except the signal at 2.2 which is twice as intense as each of the others, 3.2 (br, 1 H, $CH_AC\mathit{H}_B$), 4.8 (br, 1 H, $C\mathit{H}_AH_B$). ^{13}C NMR (CH_2Cl_2, ppm) at −88 °C: six signals of equal intensity appear at 17.32, 18.15, 19.26, 19.84, 20.62, and 20.99 corresponding to the xyloxy $\mathit{C}H_3$ carbons, 36.2 (s, 1 C, $\mathit{C}H_2$), 120–131 (m, 30 C, Ar); at 30 °C (upfield from the aromatic region) 18.9 (s, 6 C, $\mathit{C}H_3$), 19.5 (s, $\mathit{C}H_3$ from $(i\text{-}Pr)_2H_2NCl$ impurity), 36.7 (s, 1 C, $\mathit{C}H_2$).

(Phenanthrenediyl-9,10-dioxy)tris(2,6-dimethylphenoxy)phosphorane, (Xyl-O)$_3$P(O$_2$C$_{14}$H$_8$) (6). Tris(2,6-dimethyl phenyl) phosphite (**5**) (0.55 g, 1.39 mmol) and phenanthrenequinone (0.2 g, 1.39 mmol) were heated together at 210–220 °C for 15 min. The mixture, after cooling, was powdered and washed with 3 × 5 mL of hexane. The residue was washed with diethyl ether (20 mL) to obtain a crystalline solid **6**, mp 213–216 °C (yield 0.4 g, 48%). ^{1}H NMR ($C_6D_5CD_3$, ppm) at 18 °C: 2.36 (s, 18 H, $C\mathit{H}_3$), 6.97 (s, 9 H, $C_6\mathit{H}_3(CH_3)_2$, 7.10–8.20 (m, 8 H, 11 (phen)). All the peaks broadened significantly at −95 °C but the low-temperature limit for Berry pseudorotation could not be reached. ^{31}P NMR ($CDCl_3$, ppm): −57.02. The ^{1}H NMR spectrum at higher temperatures (to 99 °C) was also recorded. Although the pattern observed at 18 °C was discerned, significant decomposition/hydrolysis was inferred from the presence of additional signals. Anal. Calcd for $C_{38}H_{35}O_5P$: C, 75.74; H, 5.81. Found: C, 75.64; H, 5.74.

(1,2-*O*-Isopropylidene-D-xylofuranose-3,4-diyl)tris(2,6-dimethylphenoxy)phosphorane, (Xyl-O)$_3$P(O$_2$CH$_2$(C$_4$H$_4$O)O$_2$CMe$_2$) (7). The procedure was similar to that for 1 reported above. Quantities used were as follows: tris(2,6-dimethylphenyl) phosphite (5) (2.086 g, 5.28 mmol), 1,2-*O*-isopropylidene-D-xylofuranose (1.00 g, 5.26 mmol), *N*-chlorodiisopropylamine (0.72 g, 5.32 mmol), and diethyl ether (60 mL). Addition time was 15 min at −60 °C; reaction time was 4 h at 20 °C. The solvent was removed in vacuo after filtering the precipitate. The residue was redissolved in diethyl ether (40 mL) and filtered. The filtrate was concentrated and *n*-pentane was added. On keeping this turbid solution at 0 °C, **7** slowly precipitated as a white solid. This was separated by filtration and washed with more pentane (2 × 20 mL), mp 98–102 °C (yield 0.6 g, 20%). Although ^{31}P NMR showed it to be essentially pure, ^{1}H NMR and elemental analyses showed it to contain small amounts of impurities (7% determined from the relative intensities of additional signals at 0.98 and 1.26 ppm in the $OC(C\mathit{H}_3)$ region. Attempts to purify this material by sublimation/distillation in vacuum were unsuccessful. ^{1}H NMR ($C_6D_5CD_3$, ppm) at 30 °C: 1.07 (s, 3 H, $OCC\mathit{H}_3$), 1.33 (s, 3 H, $OCC\mathit{H}_3$), 2.32 (s, 18 H, $OC_6H_3(C\mathit{H}_3)_2$), 3.80–4.45 (m, 4 H, $OC\mathit{H}_2$, $OC\mathit{H}$), 4.83 (m, 1 H, $OC\mathit{H}$), 5.35 (d, 1 H, $^3J(\mathit{H}\text{–}\mathit{H})$ = 2.7 Hz, $O_2C\mathit{H}$), 6.60–7.20 (m, 9 H, H (Ar)). Minor peaks (impurity, 5–8%): 0.97, 1.26, 1.97. The spectrum at −77 °C showed more than six peaks for $OC_6H_3(C\mathit{H}_3)_2$ protons (2.73, 2.63, 2.40, 2.34, 2.33, 2.25, and 1.74 ppm) indicating the freezing of C–O bond rotation and possibly the presence of more than one isomer. ^{31}P NMR (C_6D_6): −80.00 ppm. Anal. Calcd for $C_{32}H_{39}O_8P$: C, 65.98; H, 6.70. Found: C, 64.66; H, 6.93 (see above).

X-ray Studies. All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation ($\lambda K\bar{\alpha}$ = 0.71073 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental procedures have been described previously.[28]

Crystals were mounted in thin-walled glass capillaries which were sealed as a precaution against moisture sensitivity. Data was collected with use of the $\theta - 2\theta$ scan mode. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least squares.[29]

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

X-ray Study for (Xyl-O)$_3$P(O$_2$C$_3$H$_4$Me$_2$) (1). Colorless crystals of **1** cut from polycrystalline masses of lath-like crystals are very air/moisture sensitive and diffract poorly. Crystals glued with epoxy into capillaries which are then sealed appear to melt overnight. The crystal used for data collection was wedged wet with mother liquor inside of a capillary which was flame sealed. It was irregular with approximate dimensions of 0.25 × 0.50 × 0.50 mm.

Crystal Data. 1: $C_{29}H_{35}O_5P$, monoclinic space group $C2/c[C^6_{2h}$ – no. 15],[30] $a = 29.392\ (8)$, $b = 11.420\ (5)$, $c = 16.379\ (2)$ Å, $\beta = 92.22\ (1)°$, $Z = 8$, and $\mu_{MoK\bar{\alpha}} = 1.3\ \text{cm}^{-1}$. A total of 2942 independent reflections ($+h, +k, \pm l$) was measured with $3° \le 2\theta_{MoK\bar{\alpha}} \le 42°$. No corrections were made for absorption. Large isotropic thermal parameters for C2, C4, and C5 during solution of the structure suggested disorder in the conformation of the six-membered ring, but attempts to resolve two sets of positions for these atoms were unsuccessful. The 35 independent non-hydrogen atoms were refined anisotropically. The 37 independent hydrogen atoms were included in the refinement as fixed isotropic scatterers (ideal positions or regularized difference Fourier positions for methyl hydrogen atoms). The final agreement factors[31] were $R = 0.056$

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(26) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(27) The extra intensity of the signal at ~2.09 ppm in the spectrum at −70 °C is due to a multiplet for toluene-d_8. This is apparent in Figure 9 where the methyl signals undergo small shifts at higher temperatures (cf. at −30 °C) and the peak at 2.09 ppm splits into separate signals, one for the $C\mathit{H}_3$ protons and one for toluene-d_8. The latter is present due to incomplete substitution, $C_6D_5CD_2H$.

(28) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(29) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_1$.

(30) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. 1, p 101.

(31) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$. For **2**, these values are for the configuration having the lowest R_w.

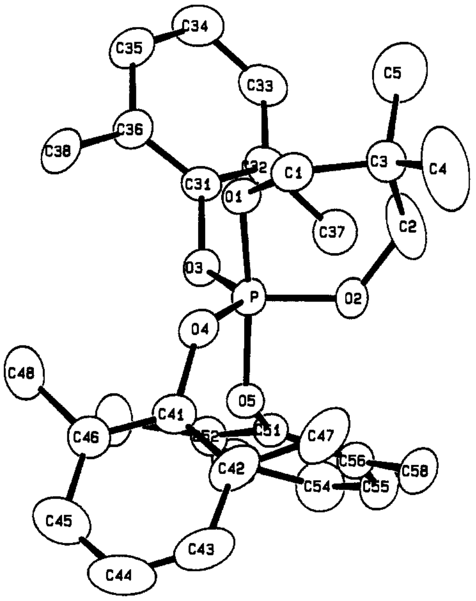

Figure 1. ORTEP plot of $(Xyl\text{-}O)_3P(O_2C_3H_4Me_2)$ (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

and $R_w = 0.066$ for the 1721 reflections having $I > 3\sigma_I$.

X-ray Study for $(Xyl\text{-}O)_3P(O_2C_{12}H_8)$ (2). Crystals of **2** are colorless laths and thick plates. The crystal used for the study was cut to dimensions of 0.33 × 0.45 × 0.45 mm.

Crystal Data, 2: $C_{36}H_{35}O_5P$, monoclinic space group $P2_1$ [C_2^2 – no. 4],[32] $a = 12.268$ (2), $b = 9.916$ (3), $c = 12.625$ (2) Å, $\beta = 91.79$ (1)°, $Z = 2$, and $\mu_{MoK\bar{\alpha}} = 1.26$ cm^{-1}. A total of 2853 independent reflections ($+h$, $+k$, $\pm l$) was measured with $3° \le 2\theta_{MoK\bar{\alpha}} \le 50°$. No corrections were made for absorption.

The 42 independent non-hydrogen atoms were refined anisotropically. The 35 independent hydrogen atoms were treated as described for **1**. The final agreement factors[31] were $R = 0.039$ and $R_w = 0.054$ for the 2302 reflections having $I > 3\sigma_I$.

X-ray Study for $(Xyl\text{-}O)_3P(O_2C_{10}H_4XY)$, X = $H_{0.14}Cl_{0.86}$, Y = $H_{0.68}Cl_{0.32}$ (3). The colorless, polyfaceted, irregular crystal used for the X-ray study had approximate dimensions of 0.30 × 0.38 × 0.50 mm.

Crystal Data, 3: $C_{34}H_{31.82}O_5PCl_{1.18}$, monoclinic space group $P2_1/c$ [C_{2h}^5 – no. 14],[33] $a = 20.114$ (6), $b = 9.554$ (2), $c = 17.178$ (3) Å, $\beta = 114.24$ (2)°, $Z = 4$ and $\mu_{MoK\bar{\alpha}} = 2.2$ cm^{-1}. A total of 3426 independent reflections ($+h$, $+k$, $\pm l$) was measured for $3° \le 2\theta_{MoK\bar{\alpha}} \le 43°$. An empirical absorption correction based on ψ scans was applied (0.919 to 1.00 on I).

During solution of the structure, a difference Fourier map phased on the 40 independent non-hydrogen atoms (isotropic) of the non-chlorinated species showed two prominent peaks (8.56 e/Å^3 and 3.10 e/Å^3) in bonding proximity of C2 and C7 of the naphthalene group. Refinement including Cl atoms in these positions as isotropic scatterers with variable multiplicity resulted in occupancy factors of 0.86 (Cl1) and 0.32 (Cl2) with reasonable thermal parameters (6.3 and 6.5 Å^3, respectively). These multiplicites were held fixed during subsequent anisotropic refinement of the 42 independent non-hydrogen atoms. The 31 independent hydrogen atoms in full occupancy were treated as described for **1**. No attempt was made to include contributions from the partial hydrogen atoms coresiding with Cl1 and Cl2. The final agreement factors[31] were $R = 0.038$ and $R_w = 0.049$ for the 2374 reflections having $I > 3\sigma_I$.

X-ray Study for $(Xyl\text{-}O)_3P(O_2C_{13}H_{10})$ (4). Colorless crystals of **4** are badly striated laths and plates. A single crystal (0.08 × 0.30 × 0.45 mm) for the X-ray study was difficult to obtain, diffracted poorly, and suffered severe degradation in the X-ray beam.

Crystal Data, 4: $C_{37}H_{37}O_5P$, triclinic space group $P\bar{1}$ [C_i^1 – no. 2],[34] $a = 9.690$ (2), $b = 15.414$ (4), $c = 21.350$ (5) Å, $\alpha = 93.07$ (2)°, $\beta = 90.17$ (2)°, $\gamma = 99.97$ (2)°, $Z = 4$ and $\mu_{MoK\bar{\alpha}} = 1.244$ cm^{-1}. A total of 4319 independent reflections ($+h$, $\pm k$, $\pm l$) was measured with $3° < 2\theta_{MoK\bar{\alpha}} < 36°$. No corrections were made for absorption. Isotropic decay corrections (correction factors from 1.000 to 1.686) were applied. Due to the paucity of observed data, of the 86 independent non-hydrogen atoms in the asymmetric unit only the phosphorus and oxygen atoms were refined anisotropically. The 34 independent aromatic hydrogen atoms were included as described for **1**. The remaining hydrogen atoms were omitted from the refinement. The final agreement factors[31] were $R = 0.076$ and $R_w = 0.085$ for the 1783 reflections having $I \ge 3\sigma_I$.

Table 1. Selected Distances (Å) and Angles (deg) for $(Xyl\text{-}O)_3P(O_2C_3H_4Me_2)$ (**1**)[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
P	O1	1.644 (4)	O1	C1	1.419 (7)
P	O2	1.585 (4)	O2	C2	1.396 (9)
P	O3	1.619 (4)	O3	C31	1.416 (7)
P	O4	1.611 (4)	O4	C41	1.408 (7)
P	O5	1.677 (4)	O5	C51	1.387 (6)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	P	O2	94.6 (2)	O3	P	O5	88.1 (2)
O1	P	O3	89.7 (2)	O4	P	O5	88.5 (2)
O1	P	O4	88.0 (2)	P	O1	C1	118.6 (3)
O1	P	O5	173.8 (2)	P	O2	C2	126.2 (5)
O2	P	O3	117.1 (2)	P	O3	C31	127.8 (3)
O2	P	O4	118.6 (2)	P	O4	C41	129.1 (3)
O2	P	O5	91.6 (2)	P	O5	C51	126.3 (3)
O3	P	O4	124.2 (2)				

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

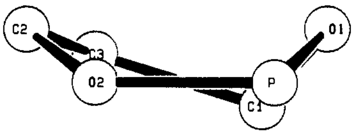

Figure 2. ORTEP plot showing the conformation of the six-membered ring in **1**. Atoms are represented as spheres of arbitrary radius.

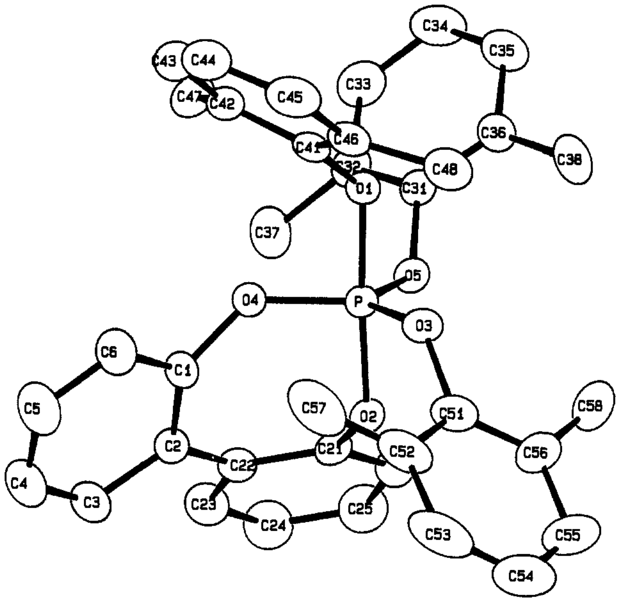

Figure 3. ORTEP plot of $(Xyl\text{-}O)_3P(O_2C_{12}H_8)$ (**2**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

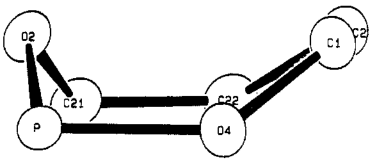

Figure 4. ORTEP plot showing the conformation of the seven-membered ring in **2**.

Results

The atom labeling scheme for **1** is shown in the ORTEP plot of Figure 1. Selected bond lengths and angles are given in Table 1. The corresponding information for **2**, **3**, and **4** is given in

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(32) Reference 30, p 79.
(33) Reference 30, p 99.
(34) Reference 30, p 75.

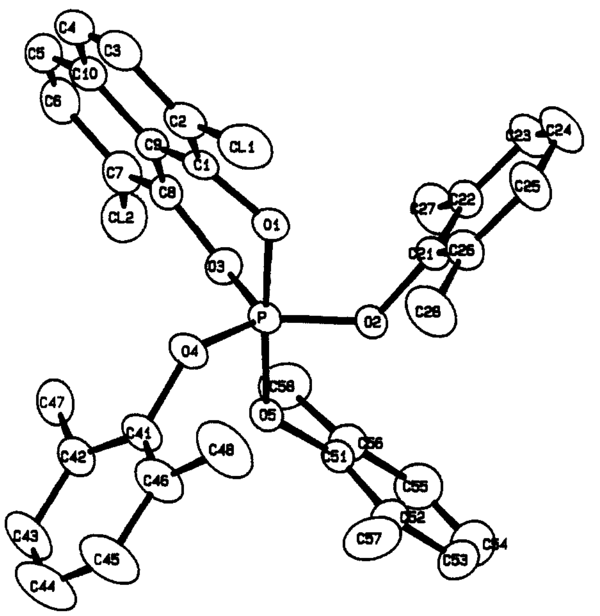


Figure 5. ORTEP plot of $(Xyl\text{-}O)_3P(O_2C_{10}H_4XY)$ (3) with thermal ellipsoids at the 30% probability level. X = Cl1 = $H_{0.14}Cl_{0.86}$; Y = Cl2 = $H_{0.68}Cl_{0.32}$. Hydrogen atoms are omitted for clarity.

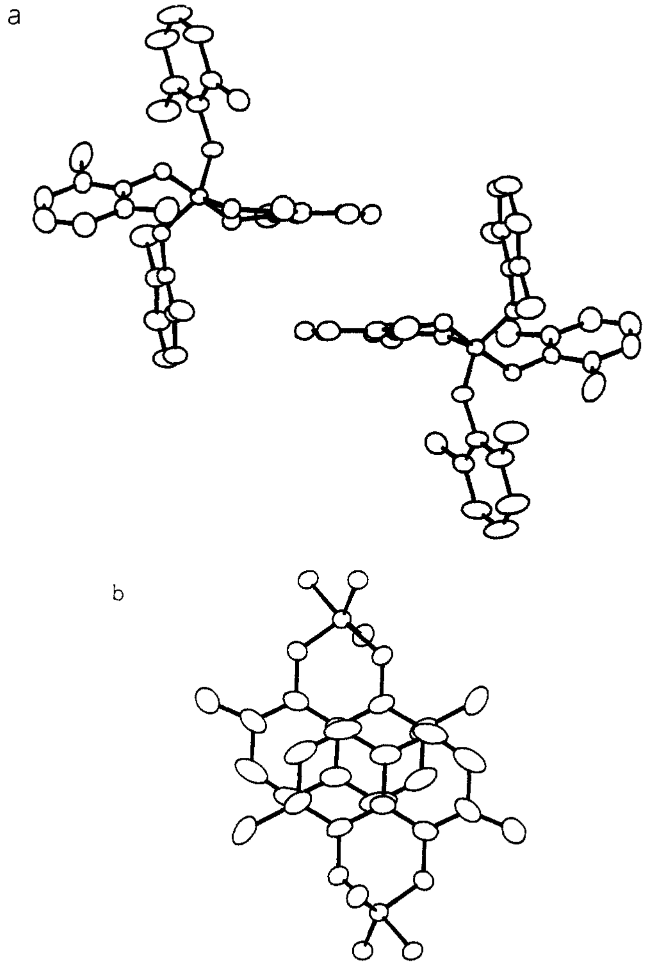


Figure 6. ORTEP plots showing the stacking interaction in 3: (a) viewed roughly parallel to the stacked planes and (b) viewed roughly perpendicular to the stacked planes with xylyl groups omitted for clarity.

Figures 3, 5, and 7 and in Tables II–IV. Atomic coordinates, anisotropic thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for all four compounds are provided as supplementary material.

Table II. Selected Distances (Å) and Angles (deg) for $(Xyl\text{-}O)_3P(O_2C_{12}H_8)$ (2)[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
P	O1	1.679 (2)	O1	C41	1.385 (4)
P	O2	1.678 (2)	O2	C21	1.383 (4)
P	O3	1.603 (2)	O3	C51	1.407 (4)
P	O4	1.601 (3)	O4	C1	1.393 (4)
P	O5	1.606 (2)	O5	C31	1.414 (4)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	P	O2	176.4 (1)	O3	P	O5	120.7 (1)
O1	P	O3	89.2 (1)	O4	P	O5	118.2 (1)
O1	P	O4	89.6 (1)	P	O1	C41	125.8 (2)
O1	P	O5	89.6 (1)	P	O2	C21	122.3 (2)
O2	P	O3	88.9 (1)	P	O3	C51	130.4 (2)
O2	P	O4	94.0 (1)	P	O4	C1	133.3 (2)
O2	P	O5	88.7 (1)	P	O5	C31	129.2 (2)
O3	P	O4	121.1 (1)				

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

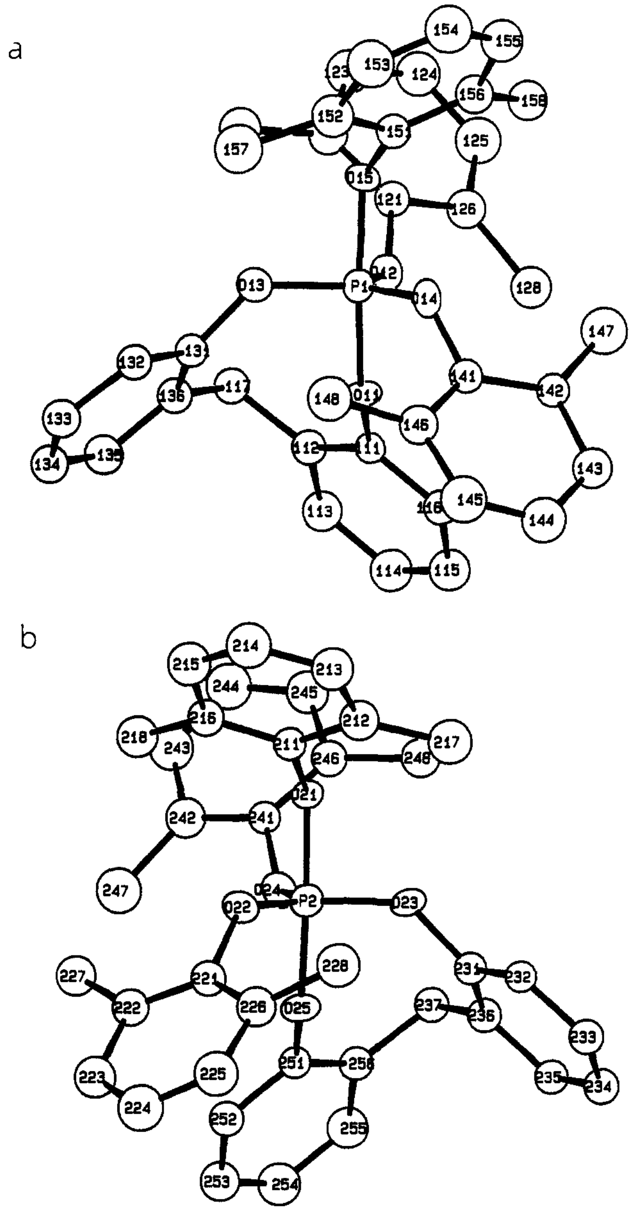


Figure 7. ORTEP plots showing the two independent molecules of $(Xyl\text{-}O)_3P(O_2C_{13}H_{10})$ (4) with thermal ellipsoids at the 30% probability level, (a) molecule A and (b) molecule B. Carbon atoms are identified by number only. Hydrogen atoms are omitted for clarity.

Discussion

Synthesis and Basic Structures. The monocyclic pentaoxyphosphoranes, **1–4** and **7**, resulted from the common reaction of

Table III. Selected Distances (Å) and Angles (deg) for $(Xyl\text{-}O)_3P(O_2C_{10}H_4XY)$, X = $H_{0.14}Cl_{0.86}$, Y = $H_{0.68}Cl_{0.32}$ (**3**)[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
P	O1	1.696 (2)	O1	C1	1.366 (3)
P	O2	1.601 (2)	O2	C21	1.415 (4)
P	O3	1.610 (2)	O3	C8	1.403 (3)
P	O4	1.596 (2)	O4	C41	1.412 (3)
P	O5	1.649 (2)	O5	C51	1.401 (4)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	P	O2	87.3 (1)	O3	P	O5	92.1 (1)
O1	P	O3	95.3 (1)	O4	P	O5	91.7 (1)
O1	P	O4	86.1 (1)	P	O1	C1	122.4 (2)
O1	P	O5	172.6 (1)	P	O2	C21	129.6 (2)
O2	P	O3	116.1 (1)	P	O3	C8	126.4 (2)
O2	P	O4	131.7 (1)	P	O4	C41	133.1 (2)
O2	P	O5	88.9 (1)	P	O5	C51	128.3 (2)
O3	P	O4	112.1 (1)				

[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 5.

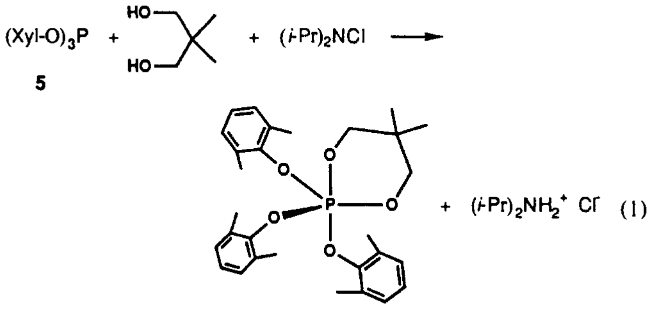
Table IV. Selected Distances (Å) and Angles (deg) for $(Xyl\text{-}O)_3P(O_2C_{13}H_{10})$ (**4**)[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
P1	O11	1.65 (1)	O11	C111	1.37 (2)
P1	O12	1.63 (1)	O12	C121	1.42 (2)
P1	O13	1.60 (1)	O13	C131	1.40 (2)
P1	O14	1.65 (1)	O14	C141	1.41 (2)
P1	O15	1.66 (1)	O15	C151	1.40 (2)
P2	O21	1.66 (1)	O21	C211	1.41 (2)
P2	O22	1.61 (1)	O22	C221	1.43 (2)
P2	O23	1.61 (1)	O23	C231	1.42 (2)
P2	O24	1.60 (1)	O24	C241	1.44 (2)
P2	O25	1.68 (1)	O25	C251	1.39 (2)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O11	P1	O12	90.0 (6)	O22	P2	O24	124.8 (6)
O11	P1	O13	93.0 (6)	O22	P2	O25	88.6 (6)
O11	P1	O14	88.7 (6)	O23	P2	O24	115.4 (6)
O11	P1	O15	175.7 (7)	O23	P2	O25	93.6 (6)
O12	P1	O13	115.1 (7)	O24	P2	O25	89.7 (6)
O12	P1	O14	125.5 (6)	P1	O11	C111	133 (1)
O12	P1	O15	91.6 (7)	P1	O12	C121	135 (1)
O13	P1	O14	119.4 (6)	P1	O13	C131	130 (1)
O13	P1	O15	90.0 (6)	P1	O14	C141	130 (1)
O14	P1	O15	87.1 (6)	P1	O15	C151	130 (1)
O21	P2	O22	88.7 (5)	P2	O21	C211	130 (1)
O21	P2	O23	89.2 (5)	P2	O22	C221	132 (1)
O21	P2	O24	90.5 (7)	P2	O23	C231	132 (1)
O21	P2	O25	176.8 (5)	P2	O24	C241	135 (1)
O22	P2	O23	119.8 (7)	P2	O25	C251	133 (1)

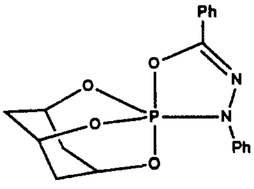
[a] Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 7.

tris(2,6-dimethylphenyl) phosphite (**5**) with a diol in diethyl ether solvent in the presence of *N*-chlorodiisopropylamine. The reaction, which was conducted at −60 °C for **1–3** and **7**[35] and at 25 °C for **4**, is illustrated for **1** in eq 1. For the formation of **6**, an oxidative

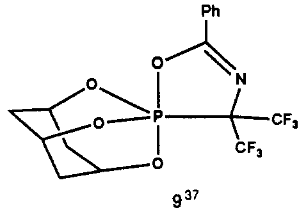


addition reaction of phenanthrenequinone with phosphite **5** conducted at elevated temperatures (210–220 °C) was employed. Overall yields varied from 25 to 65%. All represent new cyclic oxyphosphorane compounds and are the first structurally characterized monocyclic oxyphosphoranes (**1–4**) containing six-, seven-, and eight-membered rings.

The structures of **1–4** resulting from X-ray analysis were uniformly found to be trigonal bipyramidal (TBP) with the ring residing in apical–equatorial positions similar to that reported for a series of bicyclic oxyphosphoranes in the preceding article.[1b] Thus, the inclusion of one ring varying in size from six- to eight-membered into the five-coordinated framework and the introduction of ring unsaturation in **2–4** as an additional constraint are not sufficient criteria to induce diequatorial ring placement, at least with the range of substituents that were chosen for investigation. The only example where a ring is found to be located diequatorially arises from X-ray analysis of the adamantyl derivatives, **8**[36] and **9**,[37] which, under the special ring constraints associated with the tridendate character of the adamantyl group require it to occupy equatorial positions.



8[36]



9[37]

However, the lack of equatorial occupancy of the rings in the present monocyclic phosphoranes, **1–4**, suggests that diequatorial ring occupancy represents a higher energy arrangement. The NMR support[18] for diequatorial ring placement for the seven- and eight-membered pentaoxyphosphoranes cited in the Introduction (E and F, respectively) remain as isolated examples of this configurational arrangement.

Most interesting is the ring conformations themselves. Although the precise conformation of the six-membered ring in **1** is somewhat unclear due to apparent unresolved disorder in the positions of atoms C2, C4, and C5, the ring can be viewed as having a twist-boat conformation (Figure 2) with the axial oxygen atom, O1, at the prow of the boat. This conformation is similar to the preferred conformation of this same ring system in related bicyclic compounds discussed in the preceding paper[1b] where a near-perfect boat with the ring spanning axial–equatorial sites and the axial oxygen atom at the prow of the boat is usually observed. This is in accord with Trippett's[17a] earlier conclusion that a boat conformation occupying apical–equatorial sites of a TBP is the most stable for a saturated six-membered ring in that it is the only conformation that allows the equatorial oxygen atom lone pair to be located near the equatorial plane. Presumably this feature enhances $P-O_{eq}$ back-bonding. However, the six-membered ring system in **3**, which has the five ring atoms of the chelating ligand constrained to be nearly coplanar ±0.076 (3) Å, is not in a boat conformation yet it still assumes apical–equatorial sites of a TBP. The phosphorus atom is displaced 0.579 (1) Å out of this plane. Alternatively, the dihedral angle between the plane defined by atoms P, O1, and O3 and the aforementioned plane is 31.5 (1)°.

In **3** there is a stacking interaction between inversion-related pairs of molecules (Figure 6). The planes through inversion-related pairs of naphthalene moieties, required by symmetry to be parallel, are separated by a distance of 3.413 (4) Å. The phosphorus atoms are displaced 0.459 (1) Å out of these planes in a direction away from the inversion-related molecule. Even in the presence of this out of plane distortion, there is van der Waals' contact between the hydrogen bonded to C4 of the naphthalene ligand and a xylyl ligand of the inversion-related molecule (H4–C22 = 2.951 and H4–C27 = 3.030 Å compared to the van der Waals' sums of 2.9 and 3.2, respectively).

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[35] The CH_2OH and OH groups in the diol used to synthesize **7** were cis to each other.

[36] Hamilton, W. C.; Ricci, J. S., Jr.; Ramirez, F.; Kramer, L.; Stern, P. *J. Am. Chem. Soc.* **1973**, *95*, 6335.

[37] Carrell, H. L.; Berman, H. M.; Ricci, J. S., Jr.; Hamilton, W. C.; Ramirez, F.; Maracek, J. F.; Kramer, L.; Ugi, I. *J. Am. Chem. Soc.* **1975**, *97*, 38.

Table V. Internal Ring Angles in Oxyphosphoranes **1–4** and **10–12** (deg)[a]

	ring size no. atoms	O_{eq}–P–O_{eq}	P–O_{ap}–C	P–O_{eq}–C
10	5	88.60 (8)	113.7 (1)	115.8 (1)
11	5	90.3 (4)	113.2 (7)	114.5 (8)
10	6	95.98 (9)	118.3 (2)	120.4 (2)
11	6	96.7 (5)	122.4 (8)	121.6 (8)
1	6	94.6 (2)	118.6 (3)	126.2 (5)
3	6	95.3 (1)	122.4 (2)	126.4 (2)
12	6	95.2 (2)	119.3 (3)	122.3 (3)
12	7	92.9 (2)	119.8 (3)	130.9 (3)
2	7	94.0 (1)	122.3 (2)	133.3 (2)
4A	8	93.0 (6)	133 (1)	130 (1)
4B	8	93.6 (6)	133 (1)	132 (1)

[a] Angles for **1–4** are from this study while those for **10–12** are reported in ref 1b.

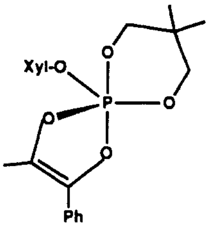
Examination of the conformation of the seven-membered ring system in **2** reveals a "rowboat" conformation with the axial oxygen atom, O2, at the prow of the boat (Figure 4). Atoms P, O4, C21, and C22 are coplanar to within ±0.003 (4) Å. The dihedral angle between this plane and the plane defined by P, O2, and C21 is 66.1 (2)°, while the dihedral angle formed with the plane defined by O4, C1, C2, and C22 (coplanar to within ±0.027 (4) Å) is 35.2 (2)°. The conformation of this ring is dictated, at least in part, by the rigidity of the ortho-substituted aromatic systems: O4, C1, C2, and C22 coplanar as previously described and O2, C21, C22, and C2 coplanar to within ±0.008 (4) Å. The dihedral angle between these last two planes is 40.2 (1)° which reflects, in part, a rotation out of coplanarity about the C2–C22 bond, as measured by the torsion angle C21–C22–C2–C1 of 35.6 (5)°.

The X-ray structure of **4**, containing an eight-membered ring system formed from the methylenebis(*o*-phenyleneoxy) ligand, shows two independent molecules. Each has a very similar ring conformation which can best be described as a very distorted "tub" (Figure 8). For molecule A, the atoms O11, C111, C131, and C136 are coplanar to within ±0.023 Å while atoms C117, C112, O13, and P1 are displaced in the same direction from this plane by distances of 0.972, 0.385, 0.845, and 1.253 Å, respectively. The corresponding values for the eight-membered ring in molecule B are atoms O25, C251, C231, and C236 coplanar to within ±0.026 Å and atoms C237, C256, O23, and P2 displaced by distances of 0.988, 0.391, 0.885, and 1.275 Å, respectively.

As in the case of **2**, the conformation of the eight-membered ring is most likely dictated by the required near coplanarity of ortho substituents with an aromatic moiety. For molecule A, atoms O11, C117, and the bonded aromatic ring, C111–C116 are coplanar to within ±0.040 Å, while atoms O13, C117, and C131–C136 are also coplanar to within ±0.040 Å. For molecule B, the corresponding values are ±0.047 Å for atoms O25, C237, and C251–C256; and ±0.029 Å for atoms O23, C237, and C231–C236.

As the discussion in a subsequent section on NMR behavior indicates, the solid-state structures are indicated to be retained in solution, thus diminishing any argument about apical–equatorial ring placement in a TBP based on packing effects. As already discussed, dihedral angles between the plane of the P–O_{eq}–C ring bond and the equatorial plane for **1–4** shows that the six-membered ring of **1**, having a twist-boat conformation, has the value closest to 90°, i.e., 83.6°. The 90° angle presumably is the one that maximizes the equatorial oxygen lone pair effect.[17a,38] The most constrained ring system, that of the six-membered ring of **3**, has the lowest dihedral angle, 56.1° while this angle for the more flexible seven- and eight-membered ring systems, i.e., in **2** and **4**, is 69.3° and 76.9°, respectively. This compares to a range of dihedral angles from 66.2° to 88.1° associated with the P–O_{eq}–C planes of the xylyloxy groups which lack ring constraints. Thus, the contribution of the lone pair effect is implied to vary somewhat across this series of monocyclic derivatives.

Further insight into the observance that ring conformations of pentaoxyphosphoranes adopt apical–equatorial instead of diequatorial positions of a TBP is realized by examining internal ring angles in the series studied here as well as **10–12** studied earlier[1b] (Table V).



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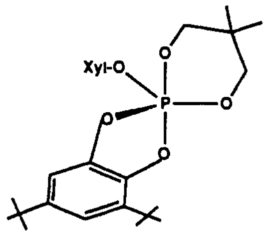

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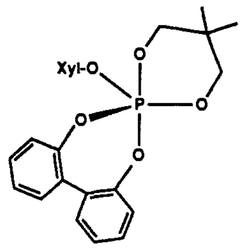

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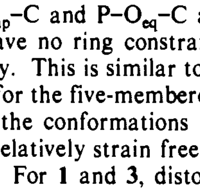
There is a general increase in ring angles paralleling an increase in ring size, although the range of angles at the phosphorus atom is smaller (88.6–95.3°) than either the range of ring angles at apical or equatorial oxygen atoms (113.2–133° and 114.5–132°, respectively). The internal angles at oxygen atoms for the six-membered rings are close to the 120° suggesting sp^2 hybridization which in simplistic terms may be most favorable for lone pair (p_x) back-bonding to the phosphorus atom.



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The range of P–O_{ap}–C and P–O_{eq}–C angles for the acyclic substituents which have no ring constraints is 126–130° and 128–135°, respectively. This is similar to the ranges found for the ring if the angles for the five-membered rings are excluded, thus suggesting that the conformations for the six- to eight-membered rings are relatively strain free.

Structural Details. For **1** and **3**, distortions from the ideal trigonal-bipyramidal geometry are found to lie on the Berry[39] pseudorotational coordinate connecting this trigonal bipyramid with a rectangular pyramid (RP) having the equatorial ring oxygen atom in the apical position and the ring system spanning apical–basal sites. With use of the dihedral angle method[40] to assess displacement, **1** is displaced 15.4% (14.8% using unit vectors) from the TBP towards the RP, while **3** is displaced 29.9% (30.2% using unit vectors).

Compound **2** is more nearly trigonal bipyramidal than **1** or **3**. When the dihedral angle method is applied to this compound the best fit to the coordinate, again with the equatorial ring oxygen atom pivotal, is not perfect and an average percent displacement of 6.7 (5.9% with unit vectors) results. The deviation from the ideal local C_{2v} symmetry in this case may be due to crowding in the molecule. The angle O4–P–O3 is opened up to 121.1 (1)° rather than closed down to less than 120°. Even in the presence

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[38] Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

[39] Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

[40] Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

of this distortion, there is van der Waals' contact between a xylyl methyl group (C57) and atoms C1 and C6 of the biphenylene system (C1–H573 = 2.806 Å; C6–H573 = 2.774 Å compared to the van der Waals' sum of 2.9 Å).

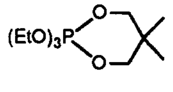
The two independent molecules of **4** have very similar geometry. As in the case of **2**, application of the dihedral angle method with the equatorial ring oxygen atom pivotal gives the best fit to the pseudorotation coordinate. The average percent displacements from the TBP towards the RP are 14.2% (13.4% with unit vectors) for the molecule containing P1 (molecule A) and 12.3% (11.8% with unit vectors) for the molecule containing P2 (molecule B). Again, intramolecular contacts suggest that crowding has an effect on the geometry. For molecule A, the larger of the "closed down" equatorial angles (O13–P1–O14 = 119.4 (6)°) is accompanied by van der Waals' contact[41] between C148 and C132 (3.61 (3) Å), while the "opened up" equatorial angle (O12–P1–O14 = 125.5 (6)°) accommodates van der Waals' contact between C128 and C147 (3.81 (3) Å). For molecule B, the corresponding angles are O22–P2–O23 = 119.8 (7)° with contact between C228 and C232 (3.56 (3) Å) and O22–P2–O24 = 124.8 (6)° with contact between C227 and C247 (3.47 (3) Å.

As noted in the Experimental Section, the formula for phosphorane **3** included noninteger numbers. During solution of the structure of **3** it became apparent that the crystalline substance did not consist of a molecule containing a simple, unsubstituted-naphthalene diol. Electron density in bonding proximity to both C2 and C7 of the naphthalene moiety was interpreted as two chlorine atoms in partial occupancy. The refined site multiplicites were 0.86 and 0.32 for Cl1 (bonded to C2) and Cl2 (bonded to C7), respectively. This corresponds to 1.18 chlorine atoms per molecule which is in agreement with the chemical analysis.

^{31}P NMR of crystals of **3** dissolved in $CDCl_3$ shows three phosphorus signals in the ratio of 8:19:30.8, which corresponds to 14%, 33%, and 53%. While in the solid state two monochloro isomers are possible, these would be expected to be equivalent in solution. Therefore, the three signals must correspond to three different compounds: a dichloro compound, a monochloro compound, and a non-chlorinated species. The X-ray data are consistent with the cocrystallization of these three species: The maximum amount of the dichloro compound consistent with the refined site multiplicites is 32% (Cl2, multiplicity = 0.32). Consistent with this is the presence of 54% of the monochloro isomer (Cl1, multiplicity = 0.86 = 0.32 + 0.54). The remaining 14% must then be assigned to the non-chlorinated species. The assigned percentages from the X-ray data (32% dichloro, 54% monochloro, and 14% non-chlorinated) match the observed ratios from the ^{31}P NMR within the uncertainty of the data.

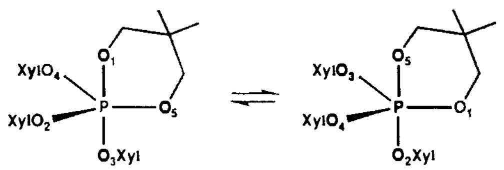
NMR and Intramolecular Ligand Exchange

Analysis of the variable-temperature ^{1}H NMR spectra of the cyclic pentaoxyphosphoranes indicates that the solid state structures are retained in solution. For example, the partial ^{1}H NMR spectrum of the monocyclic phosphorinane derivative, **1**, given in Figure 11 shows at 19 °C a single resonance at 0.50 ppm, a singlet at 2.40 ppm and a doublet at 3.60 ppm. On the basis of relative intensities, chemical shifts and assignments for related phosphorinanes,[43] e.g.,

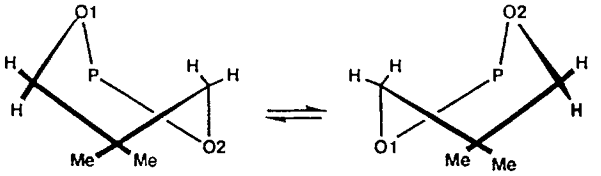


the peaks observed here are assignable to the methyl protons of the phosphorinane ring, the methyl protons of the xylyl groups, and the methylene protons of the phosphorinane ring, respectively. The doublet for the methylene protons results from phosphorus coupling, ^3J P–H = 18.3 Hz. The ^{31}P shift at −77.5 ppm confirms that the compound is pentacoordinated.

The equivalence of the phosphorinane ring methyls, the xylyl methyls, and methylene protons indicated at 19 °C, changes to a more complex pattern at −68 °C. As an approximation, two types of each of these units are indicated. The integrated intensity of the xylyl methyl groups of 2:1 supports the presence of two equatorial and one apical 2,6-dimethylphenoxy groups. The spectral changes are consistent with the presence of an apical–equatorial ring placement at −68 °C, as found for the solid-state structure, and the onset of pseudorotation to give the higher-temperature spectrum at 19 °C. The more complex character

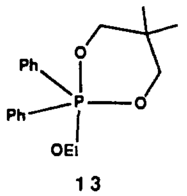


shown by the low-temperature spectrum (−68 °C) in the xylyl methyl group region may indicate a slowing of the C–O bond rotation which causes the appearance of two phosphorinane ring methyl signals. Also, under the assumption that the boat form is retained in solution for the six-membered ring, rapid interchange of boat forms which is required to accompany pseudorotation, may be incompletely stopped at low temperatures for phosphorane **1**.



Evidence that this ring interchange may still be occurring at the reduced temperature reached is the presence of unresolved signals for OCH_2 protons and the somewhat broad signals for the methyl protons of the ring observed at −68 °C. Also, the disorder shown in the X-ray structure by the high thermal motion associated with the phosphorinane ring atoms C2, C4, and C5 (Figure 1) may be indicative of the extent of the nonrigid character associated with this ring for **1**.

Further evidence that the ring puckering is occurring at −68 °C for **1** is found in the ^{1}H NMR spectrum at −65 °C for the analogous monocyclic phosphorane **13** studied by Denney and co-workers[42] where the spectrum indicated one type of ring methyl group and two types of methylene protons instead of two ring methyls and four methylene protons expected for a static structure. At higher temperatures, only one type of methylene hydrogen was present, a doublet, showing the presence of a pseudorotational process.



13

In the oxyphosphoranes **2**–**4** and the furanosyl derivative **7**, separate resonances assigned to the xylyl methyl groups appear at low temperature compared to the presence of one resonance or closley spaced multiplet at higher temperatures. All of these derivatives have more complex ring systems compared to that for **1** and are expected to reveal greater crowding which may be conducive to "stopping" C–O bond rotation for the xylyl groups. This suggests then that Berry pseudorotation and C–O bond rotation of the xylyl groups are "stopped" at reduced temperatures in these compounds. The ^{1}H NMR spectrum of the seven-membered ring phosphorane **2** obtained in toluene-d_8 at −70 °C, illustrates this feature (Figure 9). The resonance at 2.07 ppm is

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[41] The van der Waals' sum for an aromatic ring and a methyl group is 1.7 + 2.0 = 3.7 Å. The van der Waals' sum for two methyl groups is 2.0 + 2.0 = 4.0.

[42] Change, B. C.; Conrad, W. E.; Denney, D. B.; Denney, D. Z.; Edelman, R.; Powell, R. L.; White, D. W. *J. Am. Chem. Soc.* **1971**, *93*, 4004.

[43] Holmes, R. R. *Pentacoordinated Phosphorus—Structure and Spectroscopy*, ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol. I, Chapter 3 and references cited therein.

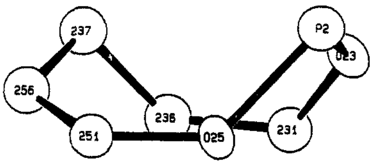


Figure 8. ORTEP plot showing the distorted tub conformation for the eight-membered ring in molecule B of compound **4**. Carbon atoms are identified by number only.

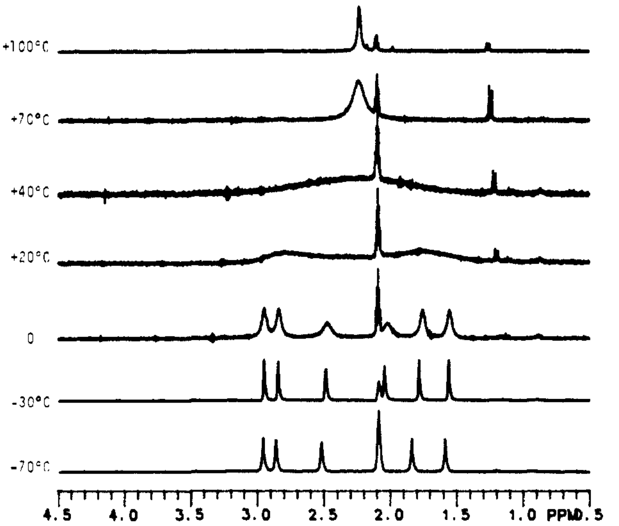


Figure 9. Partial ^1H NMR spectra of **2** in toluene-d_8 as a function of temperature showing coalescence of the xylyloxy methyl proton signals. The peak at 2.1 ppm is due to toluene-d_8. The doublet, which is at 1.2 ppm at 20 °C, is due to a small amount of *N*-chlorodiisopropylamine impurity.

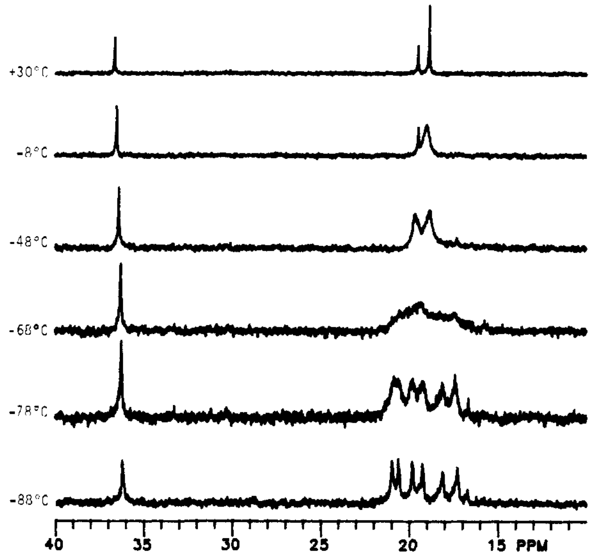


Figure 10. Partial ^{13}C NMR spectra of **4** in CH_2Cl_2 as a function of temperature showing coalescence of the xylyloxy methyl carbon signals. The signal at 19.5 ppm at 30 °C is due to a small amount of *N*-chlorodiisopropylamine impurity.

enhanced due to toluene-d_8. Similar behavior is seen at reduced temperatures in the ^{13}C NMR spectrum illustrated for **4** in Figure 10.

In the case of the monocyclic phosphorane **6** which is the only derivative possessing a five-membered ring, the ^1H NMR spectrum shows singlets at 18 °C for the xylyl methyl protons and xylyl ring protons. These signals remain as such down to −95 °C with only some broadening occurring. This spectral invariance implies that Berry pseudorotation (a–e $\rightleftharpoons$ e–a) is not stopped on lowering the temperature. The latter is consistent with earlier studies, e.g., on the $(EtO)_3\overline{P(OCH_2CH_2O)}$ ring derivative.[42] In comparison, six- (**3**, **1**, **7**) and seven-membered (**2**) ring compounds reveal progressively higher coalescence temperatures for slowing the exchange process, Table VI. Thus, a static structure exists near 0 °C for the seven-membered ring derivative, **2**. However, exchange for the eight-membered ring derivative **4** is not stopped until temperatures below −65 °C are reached, similar to that for the six-membered ring derivative **3**.

Table VI. Activation Parameters of Ligand Exchange Determined from Variable-Temperature NMR

compd	no. of atoms per ring	T_c, °C	$\Delta\nu$, Hz	$\Delta G^{\ddagger}_c$,[a] kcal/mol	NMR behavior
6	5				exchange down to −95 °C
3	6				exchange and C–O bond rotation stopped <−60 °C
1	6	−43[b]	97.3	10.9	exchange stopped <−50 °C
		−57[c]	35.6	10.6	
		−47[d]	105.0	10.6	
		−52[e]	59.5	10.6	
7	6	−30[b]	300	≥11.0	exchange and C–O bond rotation stopped <−20 °C
2	7	15[b]	30.1	14.2	exchange and C–O bond rotation stopped <40 °C
		40[b]	314.4	14.0	
4	8	−4[f,h]	352.2	12.1	exchange and C–O bond rotation stopped <−65 °C
		−68[g,h]	118.0	9.6	

[a] All $\Delta G^{\ddagger}$ values are calculated from ^1H NMR spectra except for **4** (footnote g). Values are estimated to be accurate to within ±0.5 kcal/mol. See ref 49b. [b] $\Delta G^{\ddagger}$ calculated from coalescence of $C_6H_3(C\mathit{H}_3)_2$ signals. [c] $\Delta G^{\ddagger}$ calculated from coalescence of $C_6\mathit{H}_3(CH_3)_2$ signals. [d] $\Delta G^{\ddagger}$ calculated from coalescence of $OC\mathit{H}_2$ signals. [e] $\Delta G^{\ddagger}$ calculated from coalescence of $OCH_2C(C\mathit{H}_3)_2$ signals. [f] $\Delta G^{\ddagger}$ calculated from coalescence of the ring methylene signals. [g] $\Delta G^{\ddagger}$ calculated from coalescence of $C_6H_3(\mathit{C}H_3)_2$ signals. [h] Decomposition begins above 40 °C.

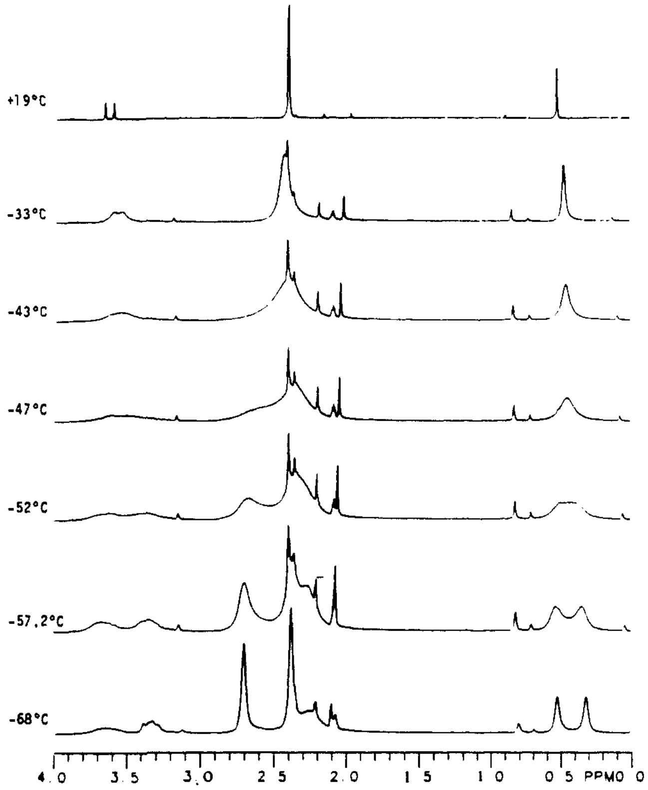
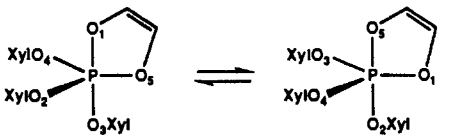


Figure 11. Partial ^1H NMR spectra of **1** in toluene-d_8 as a function of temperature. The signal at 2.1 ppm is due to toluene-d_8.

The Exchange Process

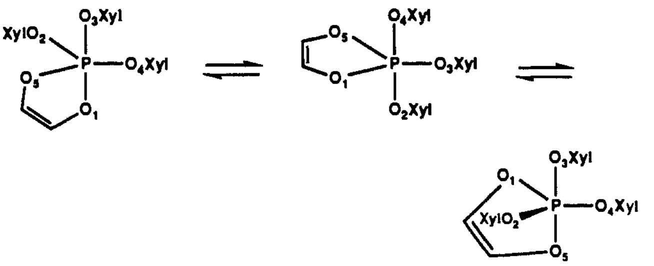
Although it is established that the monocyclic pentaoxyphosphoranes under study here undergo intramolecular ligand exchange, it is not clear what the exchange mechanisms is for the derivatives containing six-, seven-, and eight-membered rings. For **6** containing a five-membered ring, the generally accepted mechanism[43,44] involves Berry pseudorotation[39] which maintains the ring in an apical–equatorial position (a–e ⇌ e–a). The other

Process I

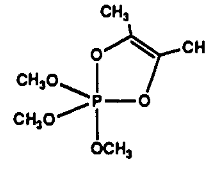


possibility is to have the ring traverse a trigonal-bipyramidal intermediate where it locates diequatorially.

Process II



Within this mechanistic framework, as Tripett[17] and others[42–46] have shown, the latter represents a considerably higher energy process. For example, exchange for the dioxaphospholene **14**,[47] like that for **6**, is not stopped even at −100 °C, indicative of a low barrier, whereas the activation energy for exchange of **15** via a TBP intermediate with a diequatorial ring is 17.4 kcal/mol.[17a]



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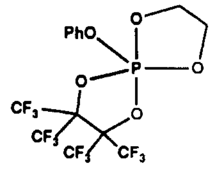

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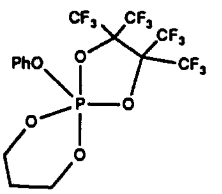
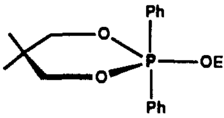
The unsubstituted ring in **15** is the one postulated to be positioned diequatorially for the exchange intermediate. This accounts for the observed equivalence of the CF_3 groups in the ^{19}F spectrum. Hence there is little question that the exchange mechanism for **6** is similar to that for **14** and is conventionally represented by process I.

Available evidence suggests that similar exchange processes for oxyphosphoranes involving six-membered ring systems provide much smaller activation energies. For example, the activation energy required to equilibrate CF_3 groups in **16** via process II which places the phosphorinane ring in diequatorial sites is 6.1 kcal/mol.[17a] Such information is nonexistent for larger ring derivatives.

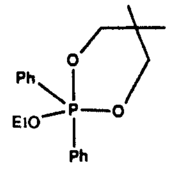


16

The variable-temperature NMR spectra for **1–4** and **7** presented here are consistent with either process I or II. The principal evidence that we can cite favoring a–e ⇌ e–a exchange for six-membered rings is that it should be a lower energy process compared to a–e ⇌ e–e exchange. The boat conformation in process I most likely exchanges via a chair conformation in process II. In the TBP intermediate for the latter process, the stabilizing feature associated with the boat conformation[17a] which places the lone pair of the equatorial ring oxygen atom in the equatorial plane when the ring is in an apical–equatorial orientation is lost for the ring located diequatorially. Further, if the exchange mechanism for Denney's compound **13**[42] follows the diequatorial ring route, an intermediate G which places both phenyl groups apically must be traversed compared to intermediate H that would form by the simpler exchange process I. Trippett[17] estimates the loss due to



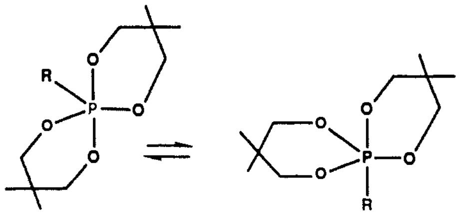
G



H

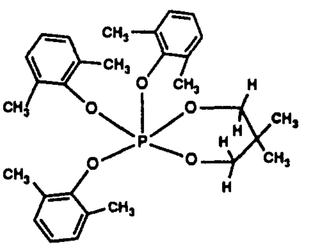
the unfavorable oxygen lone pair orientation at ~5 kcal/mol. This coupled with an estimate of the apicophilicity difference between Ph and the more electronegative $O-CH_2$ group of about 4 kcal/mol[48] suggests a stabilization energy near 9 kcal/mol for H relative to G.

If preference is given to e–a ⇌ a–e exchange for these monocyclic phosphoranes, one is left with rationalizing the value of the exchange barrier obtained for **1**, 10.6 kcal/mol, compared to that for the related spirocyclic phosphorinane derivative **17**, 11.8 kcal/mol, and **18**, 12 kcal/mol.[1b] The latter values are for exchange via process II. Phosphorane **17** and **18** also undergo a–e ⇌ e–a exchange which is not stopped down to −65 °C. The exchange barriers via diequatorial ring formation for these spirocyclics are appropriate when compared to Trippett's[17a] results for **16** for e–e ring placement, 6.1 kcal/mol if the apicophilicity difference between Ph and OPh is accounted for, i.e., ~5 kcal/mol.[17a,48]



17 (R = Ph); **18** (R = Me)

In the context outlined here, then it must be assumed that the presence of three xylyloxy groups exerts an appreciable steric effect in the e–a ⇌ a–e exchange process relative to this facile process for the related spirocyclic derivatives, e.g., **1** relative to **17**,[17b] and **2** relative to **12**.[1b] This rationale appears reasonable. In the spirocyclics **10–12**[1b] with their single xylyloxy group, the transition-state geometry for process I is closely approximated by a square pyramid of the type shown



In the square pyramid with ideal angles of 88°, cis basal, and 105°, axial–basal, the xylyloxy groups are in closer proximity than in the ideal trigonal bipyramidal 90°, apical–equatorial, and 120°, diequatorial.

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(44) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119 and references cited therein.

(45) Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *Phosphorus* **1974**, *4*, 213.

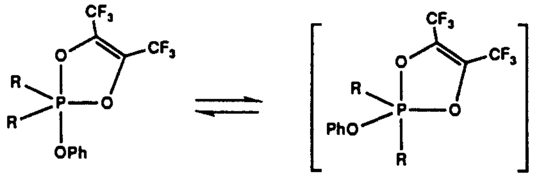
(46) Houalla, D.; Wolf, R.; Gagnaire, D.; Robert, J. B. *J. Chem. Soc., Chem. Commun.* **1969**, 443.

(47) (a) Ramirez, F.; Desai, N. B. *J. Am. Chem. Soc.* **1963**, *85*, 3252. (b) Ramirez, F.; Desai, N. B.; Ramanathan, N. *Tetrahedron Lett.* **1963**, 323.

(48) Reference 22, p 35.

There are two relevant studies suggesting the magnitude of the steric effects that we may be encountering. In contrast to the usual observation of rapid exchange down to low temperatures for tetraoxyphosphoranes of the type, $RP(OR)_4$, Westheimer and co-workers[25] found from a ^1H NMR study that pseudorotation in $MeP(OXyl)_4$ was inhibited at −65 °C. Signals of equivalent intensity were observed from two types of xylyloxy methyl groups compared to one at room temperature. This implied the presence of a TBP structure possessing severe steric crowding due to the xylyloxy groups which continue to rotate "freely" at −65 °C. The activation energy for Berry pseudorotation in this molecule is 7.7 kcal/mol. The degree of steric interaction may be somewhat similar in the monocyclic phosphoranes **1**–**7** containing three xylyloxy groups and one ring system.

The other study of interest arises from an NMR investigation yielding activation energies for pseudorotation for a series of perfluorobiacetyl adducts **19**. The activation energy, $\Delta G^{\ddagger}$, which increased from 10 kcal/mol for R = Me to 15 kcal/mol for R = *t*-Bu, was associated with a steric crowding due to the increasing size of the R group.[17a]



19

Thus, it is apparent that steric effects can appreciably influence pseudorotational exchange behavior in phosphoranes. In this connection, van Ool and Buck[16] expressed surprise that their ^{13}C NMR study of the trans-annelated dioxaphosphorinane B gave a relatively high exchange barrier of 10.0 kcal/mol. They attributed the result to a hindering of pseudorotation via a square pyramidal transition state due to the trans-fusion of the six- and five-membered rings. In the context of the data presented here, this may very well be the case.

In summary, the above discussion indicates that the preferred exchange process for the monocyclic phosphoranes is a–e ⇌ e–a. As noted, the interplay of steric and relatively small conformational energy effects between the two sets of TBP positions for these ring systems must still be worked out in greater detail before a definitive choice is made.

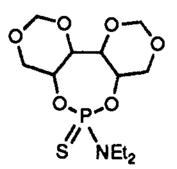
Activation Energies

Activation energies for pseudorotation in the monocyclic phosphoranes are listed in Table VI. $\Delta G^{\ddagger}$ calculated from eq 2[49] with the insertion of line separations ($\Delta\nu$) and coalescence temperatures (T_c) for temperature-dependent spectra of resonances of **1** assigned to both the ring protons and the methyl substituents of the xylyl groups, and both the methylene protons and methyl groups of the six-membered ring, give the same value within experimental deviations. The respective values are 10.6, 10.9,

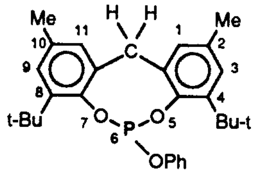
$$\Delta G^{\ddagger} = 4.57 \times 10^{-3} T_c\left(10.32 + \log\left(T_c\sqrt{2}/\pi\Delta\nu\right)\right) \quad (2)$$

10.6, and 10.6 kcal/mol. Consistent with the increasing temperature for the onset of a–e exchange from five- to seven-membered rings is the larger activation energy of 14.3 kcal/mol found for the seven-membered ring derivative **2** compared to 10.6 kcal/mol for the six-membered ring phosphorane **1**. For the five-membered ring derivative **6** exchange is not stopped at all even at low temperature.

Since the rings are indicated to be undergoing a–e to e–a exchange, presumably positional reorientation of the rings themselves occurring during this process plays a role. In reaching the square-pyramidal transition state, little ring angle change at phosphorus is required. In an ideal TBP this angle is 90° and in the SP, it is 88°.[44] A six-membered ring stabilized in a boat conformation in the ground state TBP, e.g., **1**, most likely reorients to a chair conformation as the special stabilization effect associated with the boat orientation in the TBP is lost in this transition. For this exchange process to take place for a TBP containing apically–equatorially positioned five-membered rings, as in **6**, ring energy changes in reaching the square pyramid should be relatively more modest since ring constraints due to unsaturation are maintained and little ring conformational reorientation is required. This may account for the ease with which Berry pseudorotation occurs for **6**.



13



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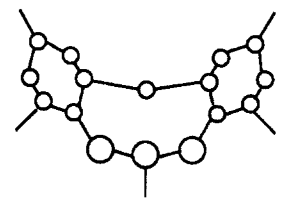

C_S symmetry

As the structure (Figure 3) of the seven- and eight-membered ring phosphoranes **2** and **4** show, rearrangement of a "rowboat" form and "tub" form, respectively, must accompany apical–equatorial bond interchange. The conformations assumed in the transition state are not known but by analogy with X-ray structures of related ring compounds of tetracoordinate phosphorus which have equivalent phosphorus ring bonds, similar to the equivalency encountered with the cis positions of the square pyramid, rearrangement to a distorted chair of the type found for the seven-membered ring derivative **13**[50] and a boat-chair conformation of the type found for the eight-membered ring compound **14**[51] may prevail. If they do form, the relative energies would be required to assess their importance in accounting for the more facile exchange for the eight-membered ring phosphorane **4** compared to that for the seven-membered ring derivative **2**. Lacking these quantities, construction of molecular models proves instructive. They reveal that the seven-membered ring conformation present in phosphorane **2** rearranges with difficulty because of the ring constraints imposed by unsaturation associated with the biphenyl moiety compared to the relative ease of conformational rearrangement of the eight-membered ring in **4** that is required to accompany apical–equatorial Berry pseudorotation. The latter ring flexibility is attributed to the presence of the methylene group bridging the two benzo groups. The greater ring flexibility in **4** is made somewhat apparent in that C–O bond rotation of the xylyl groups exhibits a lower activation energy, 9.6 kcal/mol, compared to 12.1 kcal/mol for the activation energy of the pseudorotational process (Table VI). In this regard, the ease of xylyl group rotation follows the order, $MeP(OXyl)_4$[49] > **1** ≈ **4** > **2**, which may be used to support a reasoned order of increasing steric crowding along this series.[52] Thus, in contrast to the five-membered (**6**) and six-membered (**1**, **3**, and **7**) ring containing phosphoranes, it appears that both **2** and **4** require considerable ring rearrangement

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(49) (a) Kessler, H. *Angew. Chem.* **1970**, *82*, 237. (b) See also Buono, G.; Llinas, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 4532. Errors in $\Delta G^{\ddagger}$ using this method are indicated to be less than ±0.5 kcal/mol when compared to line-shape analysis. See ref 36 in the paper by Buono and Llinas cited here.

(50) Litvinov, I. A.; Yufit, D. S.; Struchkov, Y. T.; Arbuzov, B. A.; Gurrarii, L. I.; Mukmenev, E. T. *Dokl. Akad. Nauk SSSR* **1982**, *265*, 884.

(51) Litvinov, I. A.; Struckhov, Y. T.; Arbuzov, B. A.; Arshinova, R. P.; Ovodova, O. V. *Zh. Strukt. Khim.* **1984**, *25*, 118.

(52) Reference 18 discusses NMR behavior of E and F, depicted in the Introduction, and concludes that steric inhibition of pseudorotation exists due to the presence of the ring *tert*-butyl groups. However, activation energies for E (R = *t*-Bu) of 14.6 kcal/mol and for F (R = R′ = CH_2CF_3) of 15.4 and (R = CH_2CF_3, R′ = Et) 15.7 kcal/mol refer to ground-state TBP's with diequatorial rings which are postulated to exchange via a–e sites.

during Berry pseudorotation, but due to the more rigid ring system for **2**, a higher barrier exists in executing this process compared to **4**.

Conclusion

The principal conclusion of the work presented here is that six-membered rings of oxyphosphoranes, like that previously known for five-membered ring derivatives, have an apical–equatorial site preference in a trigonal bipyramid. The preferred ring conformation of saturated six-membered rings is that of a boat. The apical–equatorial site preference also seems to apply to phosphoranes with seven-membered and eight-membered rings. These results support the recent NMR studies of Yu and Bentrude[53] indicating that nonchair (boat and/or twist) conformations are the normal conformations for six-membered rings in oxyphosphoranes and that these conformations for intermediates in enzymatic reactions of nucleoside 3′,5′-monophosphates should receive serious consideration. Our study also lends credence to the theoretical investigation by van Ool and Buck[9] who conclude that hydrolysis of cAMP with phosphodiesterase proceeding by way of trigonal-bipyramidal intermediate D (see Introduction) must have the intermediate with an apical–equatorial ring orientation.

The solution state structure of phosphorinane C, closely related to the cis-annelated furanose ring system in **7**, has been suggested[16] to be trigonal bipyramidal with a diequatorially oriented ring. This conclusion bears further scrutiny in view of the uniform apical–equatorial disposition of phosphorinane rings found in the present study.[54]

We may anticipate that additional studies focusing on six-membered ring systems in oxyphosphoranes and related analogues will yield further insight that should prove useful in constructing mechanistic pathways for enzymatic and nonenzymatic nucleophilic displacement reactions of phosphorus.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE88-19152 and the Army Research Office is gratefully acknowledged.

Supplementary Material Available: Tables of thermal parameters, additional bond lengths and angles, hydrogen atom parameters (Tables S1–S3 for **1**, Tables S4–S6 for **2**, Tables S7–S9 for **3**, and Tables S10–S12 for **4**), and atomic coordinates (Tables S13–S16 for **1–4**, respectively) (39 pages). Ordering information is given on any current masthead page.

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[53] Yu, J. H.; Bentrude, W. G. *J. Am. Chem. Soc.* **1988**, *110*, 7897. Ibid. *Tetrahedron Lett.* **1989**, *30*, 2195.

[54] Holmes, R. R.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O., submitted for publication.

Communications to the Editor

Molecular Recognition of Ethers with Modified Organoaluminum Reagents

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The chemistry of molecular recognition is a subject of current interest, and a number of recognition systems capable of reversible binding interactions have been developed for this purpose.[1-4] Most of these artificial enzymes utilize effective hydrogen-bonding interactions between substrate and receptor as also seen in natural enzymes. With organic substrates of weak hydrogen-bonding capability such as ethers, however, such tight binding behavior cannot be expected. Here we introduce exceptionally bulky, oxygenophilic methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) featuring a Lewis acidic molecular cleft for recognition of structurally or electronically similar ether substrates based on selective Lewis acid–base complex formation.[5]

Table I. Recognition Ability of Various Lewis Acids with Two Different Ethers[a]

Lewis acid	complexatn ratio:[b] $Ph(CH_2)_3OMe + Ph(CH_2)_3OEt$
MAD	100:0
methylaluminum bis(2,6-diisopropylphenoxide)	*c*
i-Bu_3Al	4:1
$SnCl_4$	*d*
BEt_3	*c*
$BF_3{\cdot}OEt_2$	5:3

Lewis acid	complexatn ratio:[b] $CH_3CH_2CH_2OMe + EtOEt$
MAD	96:4
$BF_3{\cdot}OEt_2$	3:2

[a] Two different ethers (1 mmol each) were mixed with 1 equiv of Lewis acid in $CDCl_3$ or CD_2Cl_2 (2 M solution) in a 5-mm NMR tube at 20–25 °C, and the 125-MHz ^{13}C NMR spectra were taken at −50 to −100 °C. [b] The complexation ratio was determined by low-temperature ^{13}C NMR analysis of ethereal α-carbons. [c] No complexation was observed. See also text. [d] Two equivalents of ethers coordinated to $SnCl_4$ to give a 2:1 complex.

1

Lewis acid-base complex

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(1) Polyethers as host: (a) Cram, D. J. *Science (Washington, D.C.)* **1983**, *219*, 1177. (b) Lehn, J.-M. *Ibid.* **1985**, *227*, 849. (c) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (d) Cram, D. J. *Ibid.* **1988**, *27*, 1009.

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(3) Cyclophanes as host: (a) Stetter, H.; Roos, E.-E. *Chem. Ber.* **1955**, *88*, 1390, 1395. (b) Odashima, K.; Itai, A.; Iitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504. (c) Miller, S. P.; Whitlock, H. W., Jr. *Ibid.* **1984**, *106*, 1492. (d) Winkler, J.; Coutouli-Argyropoulou, E.; Leppkes, R.; Breslow, R. *Ibid.* **1983**, *105*, 7198. (e) Diederich, F.; Griebel, D. *Ibid.* **1984**, *106*, 8037. (f) Schneider, H.-J.; Blatter, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1163. (g) Collet, A. *Tetrahedron* **1987**, *43*, 5725.

(4) Molecular clefts as receptors: (a) Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476. (b) Rebek, J., Jr.; Askew, B.; Islam, N.; Killoran, M.; Nemeth, D.; Wolak, R. *Ibid.* **1985**, *107*, 6736. (c) Rebek, J., Jr. *Chemtracts: Org. Chem.* **1989**, *2*, 337. (d) Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245.

(5) For synthetic applications of MAD, see: Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588.

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