Pseudorotation in a Sterically Hindered Phosphorane

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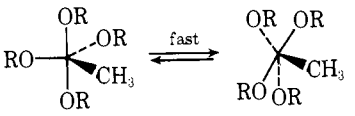
Abstract: Methyltetrakis(2,6-dimethylphenoxy)phosphorane has been synthesized and shows a temperature-dependent NMR spectrum, indicating ligand reorganization between room temperature and −65 °C. Comparison of the NMR spectra with those for methyltetrakis(*o*-cresoxy)phosphorane and for dimethyltris(*o*-cresoxy)phosphorane suggests that all the compounds exist as trigonal bipyramids. Since phosphoranes with four phosphorus to oxygen bonds generally undergo pseudorotation rapidly on an NMR time scale even at low temperature, the slow ligand reorganization of methyltetrakis(2,6-dimethylphenoxy)-phosphorane is unexpected and is here ascribed to the intense steric crowding of the molecule. Additionally, the phosphorane differs from others in showing hydrogen–deuterium exchange at a measurable rate between the P-CH_3 group and deuteriochloroform.

The ligand reorganization (pseudorotation) of oxyphosphoranes is of special interest because it may, and in some cases must, intervene in the hydrolysis of phosphate esters.[2] The rules for the reorganization[2,3] arose in part from kinetic studies and were confirmed by NMR spectroscopy;[4] the field has been extensively investigated[5] and thoroughly reviewed.[6] Methyltetrakisaryloxyphosphoranes are expected to show trigonal-bipyramidal structures, with the methyl group in an equatorial position and with rapid—almost unhindered—pseudorotation about this methyl group as pivot to exchange the positions of the aryloxy groups.



Methyltetrakis(2,6-dimethylphenoxy)phosphorane, however, shows unusual properties: its NMR spectrum is temperature dependent, and ligand reorganization can be observed on the NMR time scale between room temperature and −65 °C; furthermore, the protons of the *P*-methyl group exchange with the deuterium atoms of deuteriochloroform at a measurable rate at room temperature. These unusual properties are here ascribed to steric effects. A space-filling model for the molecule cannot be constructed at all, although the synthesis proceeds smoothly, and there can be no doubt as to the topology of its structure. The question naturally arose, however, as to its geometry and in particular as to whether the compound exists as a trigonal bipyramid or a tetragonal pyramid; investigation of analogous compounds suggests that the former is the case. The chemistry of methyltetrakis(2,6-dimethylphenoxy)phosphorane is outlined below.

Experimental Section

General. Glassware was vacuum dried and filled with dry argon; reaction vessels were connected to a modified Ace-Burlitch inert atmosphere system (Ace Glass 7818), connected through a drying tower to a tank of argon (Med-tech). Solids were handled in a nitrogen-filled Labconco drybox. Reactions were carried out in Schlenck reaction vessels (Ace Glass 7756), filtrations performed with a Schlenck filter tube (Ace Glass 7759), and recrystallizations in a double-tube recrystallizer (Ace Glass 7772). All solvents were carefully dried.

Materials. Tris(2,6-dimethylphenyl) Phosphite. This compound was prepared in 65% yield from PCl_3 and 2,6-dimethylphenol: mp 92–94.5 °C (lit.[7] 83–84 °C); ^{1}H NMR ($CDCl_3$) δ 2.25 (C-CH_3) 6.96 (aromatic).

Methyltris(2,6-dimethylphenoxy)phosphonium Trifluoromethanesulfonate. A solution of tris(2,6-dimethylphenyl) phosphite (4.10 g) and methyl trifluoromethanesulfonate (methyl triflate) (2.56 g) in 50 ml of methylene chloride was refluxed under argon for 20 h. The solvent was removed by trap-to-trap distillation. Recrystallization of the off-white solid residue from methylene chloride/ether yielded 3.87 g (67% of theory) of colorless rectangular crystals, mp 193.0–194.0 °C. Anal. Calcd for $C_{26}H_{30}F_3O_6PS$: C, 55.91; H, 5.41; P, 5.55; S, 5.74; F, 10.20. Found: C, 55.87; H, 5.63; P, 5.60; S, 6.41; F, 10.65. The structure was confirmed by ir, NMR, and mass spectroscopy. ^{1}H NMR ($CDCl_3$) δ 2.30 (C-CH_3), 2.69 (d, J = 14 Hz, P-CH_3, 7.16 (aromatic); ^{31}P NMR ($CDCl_3$) δ −41.71.

Methyltetrakis(2,6-dimethylphenoxy)phosphorane. A suspension of methyltris(2,6-dimethylphenoxy)phosphonium triflate (2.60 g) and sodium 2,6-dimethylphenoxide (0.61 g), prepared from 2,6-dimethylphenol and sodium hydride,[8] was stirred in 60 ml of methylene chloride under argon at room temperature for ca. 20 h. The precipitate was removed by filtration under argon and the solvent partially evaporated from the filtrate by trap-to-trap distillation. When the solvent was cooled to −20 °C, the phosphorane crystallized from the residual methylene chloride to yield 1.35 g (55% yield) of phosphorane, mp 197–199 °C. An analytically pure sample was obtained by recrystallization from toluene. Anal. Calcd for $C_{33}H_{39}O_4P$: C, 74.69; H, 7.41; P, 5.84. Found: C, 74.69; H, 7.67; P, 5.71. ^{1}H NMR (CCl_4) δ 2.00 (d, J = 16 Hz, P-CH_3), 2.15 (C-CH_3), 6.78 (m, aromatic); ^{31}P NMR ($CDCl_3$) δ +48.77.

Products of Hydrolysis of the Phosphorane. A sample of methyltetrakis(2,6-dimethylphenyl)phosphorane was dissolved in $CDCl_3$ in an NMR tube, and a few drops of water were added. The ^{1}H NMR spectrum was that of a 2:1 mixture of 2,6-dimethylphenol and bis(2,6-dimethylphenyl) methylphosphonate. The phosphonate was isolated and shown identical with an authentic sample by ir, ^{1}H, and ^{31}P NMR spectroscopy.

Bis(2,6-dimethylphenyl) Methylphosphonate. The compound was prepared from methylphosphonic dichloride (Specialty Organics) and 2,6-dimethylphenol essentially by the procedure of Hovanec and Lieske.[9] After recrystallization from hexane, the compound melted at 75–76 °C. Anal. Calcd for $C_{17}H_{21}O_3P$: C, 67.09; H, 6.96; P, 10.18. Found: C, 67.12; H, 7.05; P, 10.33. ^{1}H NMR ($CDCl_3$) δ 1.80 (d, J = 17 Hz, P-CH_3), 2.30 (C-CH_3), 7.00 (aromatic); ^{31}P NMR ($CDCl_3$) δ −22.86; principal ir bands below 1500 cm^{-1}: 1475, 1316, 1264, 1190, 1166, 1091, 943–928 (b), 806, 775, 770 (sh) cm^{-1}.

Dimethyltris(*o*-cresoxy)phosphorane. A solution of methylphosphonous dichloride (21.46 g; Ethyl Corporation) in 60 ml of anhydrous ether was added drop by drop at 0 °C to a stirred solution of *o*-cresol (39.7 g) and pyridine (29.1 g) in 200 ml of ether. The thick reaction mixture was stirred at room temperature for 26 h. The pyridinium hydrochloride that had formed was removed by filtration under nitrogen and the ether evaporated from the filtrate at reduced pressure. The yellow oily residue was distilled in vacuo, bp 110–120 °C (0.1 mm), to yield 40.8 g of phosphonite: ^{1}H NMR ($CDCl_3$) δ 1.55 (d, J = 10 Hz, P-CH_3), 2.20 (C-CH_3), 6.98 (aromatic). Then the phosphonite (5.20 g) was stirred under nitrogen at 0 °C, and methyl triflate (3.28 g) was introduced slowly from a syringe through a serum cap. The reaction was rapid and exothermic, but the phosphonium triflate was obtained only as a thick syrup, which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 2.35 (C-CH_3), 2.55 (d, J = 14 Hz, P-CH_3), 7.25 (m, aromatic).

A mixture of the syrupy phosphonium triflate (8.4 g) and barium *o*-cresoxide[10] (3.48 g) in 100 ml of methylene chloride was stirred under nitrogen at room temperature for 18 h. The precipitated salt was removed by filtration under nitrogen, and methylene chloride was

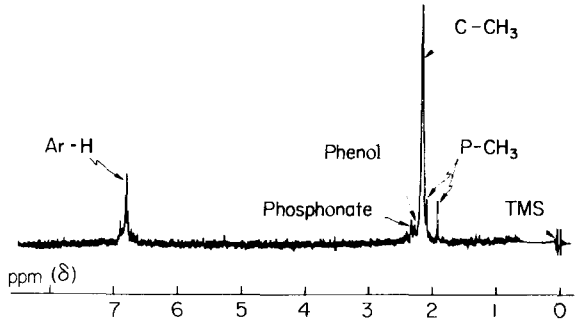


Figure 1. The 100-MHz NMR spectrum of methyltetrakis(2,6-dimethylphenoxy)phosphorane in carbon tetrachloride at room temperature. The signal from the aromatic methyl groups appear as a singlet, while that from the P-CH_3 group appears as a doublet, with J = 16 Hz. The signals from the aromatic *C*-methyl groups of a trace of phosphonate and from the *C*-methyl groups of a trace of 2,6-dimethylphenol (formed by hydrolysis with adventitious water) are visible downfield from the signal from the aromatic *C*-methyl groups of the phosphorane.

evaporated from the filtrate at reduced pressure. The brown oily residue was purified by several crystallizations from *n*-hexane to yield 1.42 g (19%) of the phosphorane, mp 95–98 °C. Anal. Calcd for $C_{23}H_{27}O_3P$: C, 72.23; H, 7.12; P, 8.10. Found: C, 71.49; H, 7.28; P, 8.14. ^1H NMR ($CDCl_3$) δ 2.00 (C-CH_3), 2.25 (d, J = 15 Hz, P-CH_3), 6.96 (m, aromatic).

Methyltetrakis(*o*-cresoxy)phosphorane was prepared as reported.[10]

Exchange Reactions. Methyltetrakis(2,6-dimethylphenoxy)phosphorane (40 mg) was transferred in a drybox to a thoroughly dried 5-ml flask containing 1.5 ml of $CDCl_3$. The flask was closed with a serum cap and magnetically stirred overnight in the drybox. The solvent was then vacuum evaporated through a hollow needle in the serum cap. The NMR spectrum in CCl_4 showed no peaks for the P-CH_3 group.

A sample of the methyl-d_3 compound prepared above was then dissolved in $CHCl_3$ using the same care to exclude moisture, and the procedure was repeated. The NMR spectrum in CCl_4 then showed the doublet at δ 2.00 (J = 16 Hz) of the P-CH_3 compound.

Measurement of the Rate of Hydrogen–Deuterium Exchange. A sample of the phosphorane in $CDCl_3$ was prepared in the drybox in a stoppered NMR tube and observed in the probe of a Varian A-60 NMR spectrometer, stabilized at 25 °C. Spectra were taken every 20 min, and the rate of the reaction followed from the increase in the intensity of the $CHCl_3$ peak in the spectrum.

Variable-Temperature NMR Experiments. Variable-temperature NMR experiments were conducted with a Varian A-60 equipped with a V-6040 variable temperature controller and with a Varian HA-100 spectrometer. Temperatures were determined by the method of VanGeet.[11] Calculations for line shape analyses were performed on a PDP 11/45 computer, and spectra were plotted with a Calcomp 6127 plotter.

Analyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside, N.Y. Samples for analysis were prepared in a drybox, with stringent precautions against adventitious moisture.

The 250 MHz spectra were obtained with the Carnegie-Mellon instrument in Pittsburgh, Pa., with the help of Dr. A. A. Bothner-By.

Results

The ^1H NMR spectrum of methyltetrakis(2,6-dimethylphenoxy)phosphorane in CCl_4 is shown in Figure 1. The major peaks are those for the aromatic methyl groups at δ 2.15 and the aromatic protons at δ 6.78, but the doublet from the P-CH_3 group is visible at δ 2.00 (J = 16 Hz). In addition, the weak signal from the aromatic methyl groups of bis(2,6-dimethylphenyl) methylphosphonate, present as a slight impurity from hydrolysis of the phosphorane, is visible at δ 2.33; apparently the precautions to exclude moisture, although extensive, were imperfect. Despite the presence of a little phosphonate in all the samples of the phosphorane that were here examined, the qualitative features of the chemistry of the phosphorane are clear. When the compound is subjected to exchange with

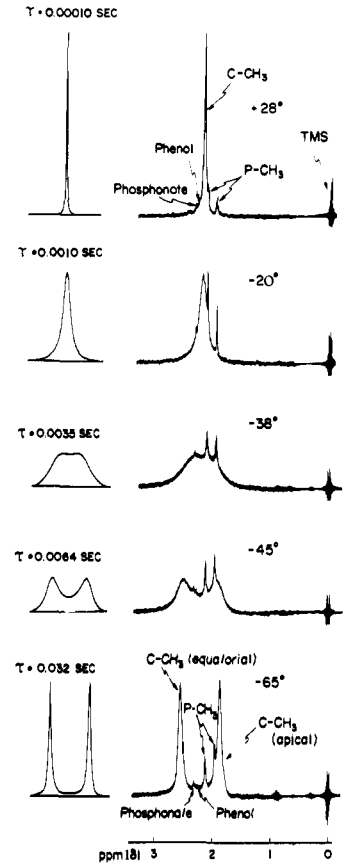
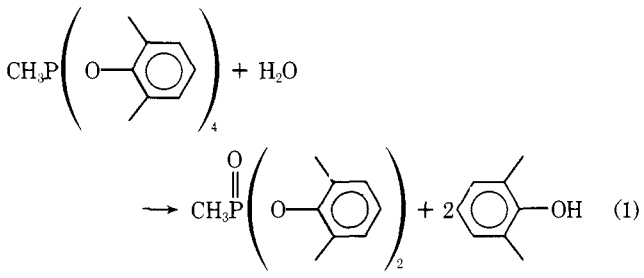


Figure 2. The temperature dependence of the 100 MHz NMR spectrum of methyltetrakis(2,6-dimethylphenoxy)phosphorane in chloroform. In the experimental spectra, the signals from the *C*-methyl groups of the phosphonate and phenol, formed by hydrolysis with adventitious water, are barely visible. The simulated spectra show only the signals for the aromatic *C*-methyl groups; additional peaks from the P-CH_3 doublet are prominent features of the experimental spectra, especially at intermediate temperatures; the minor peaks from the hydrolytic impurity can also be seen. The activation energy for the ligand reorganization is 7.7 kcal/mol.

deuteriochloroform, the signals from the P-CH_3 group disappear, and the signal from the proton in $CHCl_3$ appears at δ 7.22 with a rate constant at 25 °C of 9.3×10^{-5} s^{-1}; the effect can be reversed by equilibration of the CD_3 compound with chloroform, although with each exchange the amount of the phosphonate, produced by hydrolysis by adventitious water, increases.

The temperature dependence of the spectrum of methyltetrakis(2,6-dimethylphenoxy)phosphorane in $CHCl_3$ is shown in Figure 2. (Chloroform, rather than deuteriochloroform, was used so as to avoid the exchange cited above. The signal from the proton in chloroform is so far from the region of interest that, despite its overwhelming size, it does not interfere with the signals from the C-CH_3 and P-CH_3 groups.) At room temperature, a sharp singlet at δ 2.19 is observed for the *C*-methyl groups of the aryl residues in the phosphorane, whereas at −65 °C the signals from the *C*-methyl groups appear as two separate peaks, at δ 1.85 and 2.54 ($\Delta\delta$ 0.69 ppm). The simulated spectra, calculated with the aid of the exchange equations,[12] show only the aromatic methyl groups.

Hydrolysis of the phosphorane by traces of adventitious water produces both 2,6-dimethylphenol and bis(2,6-dimethylphenyl) methylphosphonate (eq 1); the weak signals from the *C*-methyl groups of these compounds are barely visible in all spectra. The stoichiometry of the hydrolysis is such as to produce equal numbers of aryloxy groups from the two products. Since the two signals are therefore of equal intensity, they give the appearance of a doublet, as if they arose from



(1)

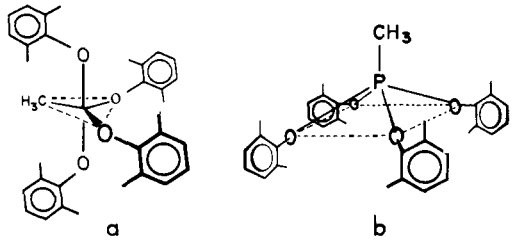
some group that interacts with the spin of one-half of phosphorus. However, spin decoupling does not affect the signal. Furthermore, at 0 °C and 250 MHz, the signals in question emerge from under the major peak of the aromatic methyl groups and are separated by 20 Hz, rather than the 8 Hz observed in the 100 MHz spectrometer. Finally, the positions of the signals correspond to those for the stated impurities. Integration suggests that these impurities are present to the extent of about 1%. The signal from the *P*-methyl group of the trace of phosphonate is too weak to be observed.

The ^1H NMR spectrum of methyltetrakis(*o*-cresoxy)-phosphorane is independent of temperature down to −86 °C. The spectrum of dimethyltris(*o*-cresoxy)phosphorane is shown as a function of temperature in Figure 3. At room temperature only one signal arises from the aromatic methyl groups, and only one sharp signal is observed at −34 °C in CD_2Cl_2. (The small peaks to the high-field side of the major ones arise from the phosphinate produced by hydrolysis with adventitious water.) At −80 °C the signal has obviously broadened and at −95 °C has separated into two peaks, where one of the two peaks has appeared on the low-field side of the signal from the *P*-methyl doublet. The simulated spectra again showed only the aromatic methyl group. The two peaks are separated by 0.66 ppm.

Discussion

The exchange of hydrogen atoms from the P–CH_3 group of methyltetrakis(2,6-dimethylphenyl)phosphorane presumably occurs by way of the ylide and parallels the exchange observed with other methyl phosphoranes.[10] The extraordinary result here, however, is that the exchange occurs in the absence of added phenoxide as catalyst, with such a weak donor as deuteriochloroform (see Scheme I).

The temperature-dependent NMR spectrum of methyltetrakis(2,6-dimethylphenoxy)phosphorane demands that, at low temperature, two different kinds of aromatic methyl groups be present in equal concentration. These could be accounted for in (at least) two ways: (a) If the molecule exists as a trigonal bipyramid and if pseudorotation is inhibited at low temperatures (presumably by the severe crowding of the molecule), then two different types of aryl groups (apical and equatorial) are present. If the aryl groups are free to rotate rapidly about the *O*-aryl bond, then the methyl groups of the 2 and 6 positions of any given ring will be equivalent on the NMR time scale, and the molecule will show signals with equal intensities from just two kinds of aromatic methyl groups. (b) Alternatively, if the molecule exists as a tetragonal pyramid,[13-16] with the *P*-methyl group at the apex, then all four aromatic rings occupy more or less the same position. But if



a b

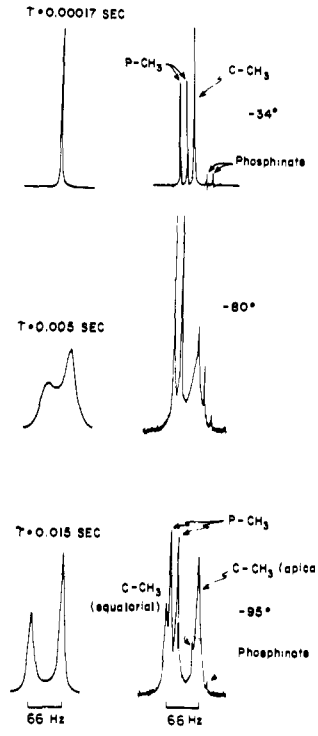
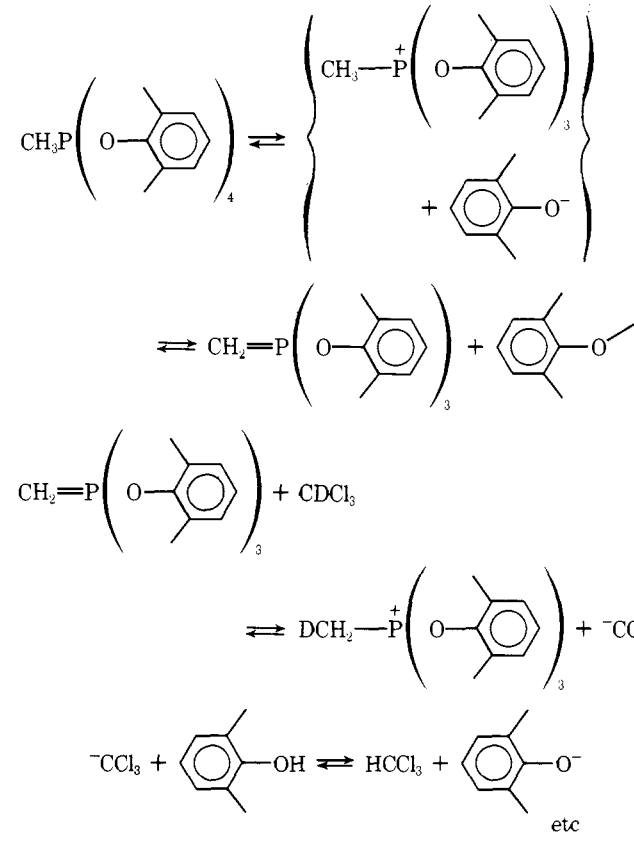


Figure 3. The temperature dependence of the 100 MHz NMR spectrum of dimethyltris(*o*-cresoxy)phosphorane in deuteriochloroform. The simulation is only for the aromatic *C*-methyl groups; the activation energy for the ligand reorganization is 5.8 kcal/mol.

Scheme I



the rotation of the rings is sterically hindered,[17,18] then the methyl group in the 2 position of each ring will lie in a different environment from that in the 6 position; one set of four methyl groups will lie below the base of the square pyramid, and one

set of four will lie above the base. Again, the molecule would be expected to display separate signals, in equal intensities, for two kinds of aromatic methyl groups.

On the other hand, dimethyltris(*o*-cresoxy)phosphorane would be expected to behave normally. Models show that the molecule is not excessively crowded, and furthermore, the ^1H NMR spectrum of the phosphorane is that of the typical trigonal-bipyramidal molecule that undergoes pseudorotation with an activation energy controlled by the barrier to placing a methyl group in the unfavorable apical position.[2-6] This is what would be expected; it is what is observed. First and foremost, only one signal at δ 2.25 (a doublet with J = 15 Hz) is observed for the two P–CH_3 groups, so they must occupy equivalent positions in the structure. This is possible in a trigonal-bipyramidal structure only if they are both equatorial. At low temperatures, the trigonal bipyramidal structure for dimethyltris(*o*-cresoxy)phosphorane would be expected to be "frozen" on the NMR time scale with two apical and only one equatorial aryloxy ring. This should lead to two different kinds of aromatic methyl groups in the ratio of 2:1. The signals obtained at −95 °C in CD_2Cl_2 show chemical shifts of 1.73 and 2.39, separated by 0.66 ppm, in the ratio of 2:1. The high-field signal is therefore that from the apical and the low-field signal that from the equatorial C–CH_3 groups.

Perhaps, however, one should consider the possibility that dimethyltris(*o*-cresoxy)phosphorane itself exists as a tetragonal pyramid; if such were the fact, then the arguments presented above would be without merit. This assignment, however, is most unlikely. Tetragonal-pyramidal structures for phosphoranes are probably restricted to spiro derivatives and other special structures;[15] they have not been found for "ordinary" noncyclic phosphoranes. Further, in order to accommodate the low-temperature NMR spectrum of dimethyltris(*o*-cresoxy)phosphorane on the assumption that it exists as a square pyramid, both methyl groups would have to lie in the basal plane; otherwise the two methyl groups could not be equivalent. But at the same time, in order that methyltetrakis(2,6-dimethylphenoxy)phosphorane exist as a square pyramid, the methyl group would have to be at the apex. Such ad hoc structural assignment, devoid of rule, but specially adapted for each compound, contrast with general precepts of scientific simplicity.

The NMR spectra of the two phosphoranes show similar temperature behavior. The signals from the *C*-methyl group at low temperatures are separated by 0.66 ppm for dimethyltris(*o*-cresoxy)phosphorane and by 0.69 ppm in methyltetrakis(2,6-dimethylphenoxy)phosphorane. The parallel behavior strongly suggests that the two compounds have the same geometry; if so, then the difference in the signals at low temperature from the *C*-methyl groups of the methyltetrakis(2,6-dimethylphenoxy)phosphorane arises, as the similar difference arises in dimethyltris(*o*-cresoxy)phosphorane, from a difference between equatorial and axial position in a trigonal-bipyramidal structure. The alternative explanation, i.e., that the methyltetrakisaryloxyphosphorane is a tetragonal pyramid with the *P*-methyl group at the apex, is of course possible, but requires a considerable coincidence, i.e., that the signals from methyl groups above and below the basal plane of the tetragonal pyramid would be separated by the same amount as those in equatorial and apical positions in a trigonal bipyramid. Coincidence occurs with a large enough frequency in chemistry that it cannot be disregarded, and the geometry of the methyltetrakisaryloxyphosphorane must finally be determined by x-ray crystallography. Coincidence, however, appears an unlikely alternative; methyltetrakis(2,6-dimethylphenoxy)-phosphorane probably exists as a trigonal bipyramid, and ligand reorganization is inhibited sterically.

An extension of these investigations to other compounds is in progress.

Acknowledgments. The work here reported was supported by the National Science Foundation under Grant No. GP-6465X. The XL-100 spectrometer was purchased under NSF Grant No. GP-32317. Dr. Ivanke Szele, while on leave from the Rudjer Bošković Institute of Zagreb, received financial support from the Zlatko and Joyce Balokovic Fund administered by the Yugoslav Academy of Sciences and Harvard University. Steven Kubisen, Jr., was supported by a Graduate Fellowship from E. I. du Pont de Nemours and Co. The authors are indebted to Professor A. A. Bothner-By and Dr. Josef Dadok for 250 MHz spectra, to Mr. Hampar Janijigian and Dr. Wm. Hull for assistance with 100 Mhz spectra, and to Charles Lerman for assistance with the computer programming. Special thanks are due to Dr. S. M. Castallano of the Carnegie-Mellon University, who suggested the possibility of the H/D exchange with chloroform described in this paper.

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(17) Steric crowding can be severe in phosphoranes with direct carbon to phosphorus bonds. In particular in *o*-isopropylphenylbis(*p,p'*-bitolyl)-phosphorane, the rotation[18] of the isopropylphenyl group is fast, on the NMR time scale, only above 100 °C. The phosphorane exhibits trigonal-bipyramidal geometry.[18] Since its behavior contrasts strongly with that of methyltetrakis(2,6-dimethylphenoxy)phosphorane, which shows rapid ligand reorganization even at room temperature, it might be argued that the latter cannot also be a trigonal bipyramid. Steric crowding, however, depends strongly on detailed structure, and a strict parallel between arylphosphoranes and aryloxyphosphoranes is unwarranted.
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