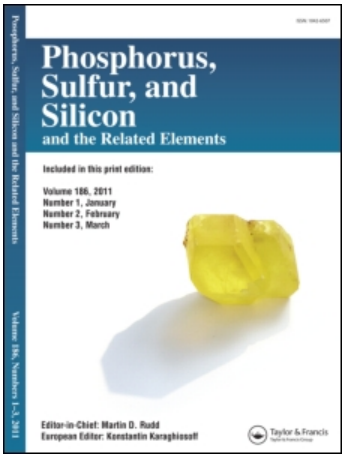

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STUDIES OF THE 1,3,5,2,4,6-TRIOXATRIPHOSPHORINANE RING SYSTEM

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STUDIES OF THE 1,3,5,2,4,6-TRIOXATRIPHOSPHORINANE RING SYSTEM

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Dedicated to Professor Reinhard Schmutzler on his sixtieth birthday

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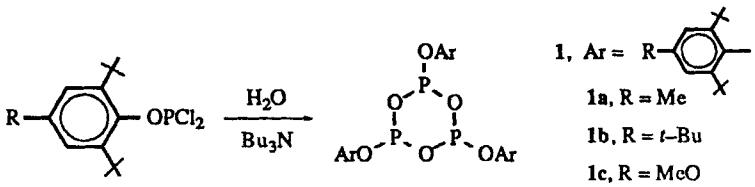
Phosphorodichloridites with sterically demanding O-aryl groups are known to undergo controlled partial hydrolysis to give 1,3,5,2,4,6-trioxatriphosphorinane derivatives, but the O-(1-adamantyl) and O-neopentyl groups failed to provide control of the hydrolysis and the cyclic products could not be obtained. The reaction of the O-aryl phosphorodichloridites or of diisopropylaminodichlorophosphine with silver oxide or lithium oxide was found to be useful for the synthesis of the trioxatriphosphorinanes, but again this reaction failed with the O-alkyl phosphorodichloridites. Some new observations on the reactivity of the ring system included: oxidation by pyridine N-oxide, sodium periodate or ozone, forming a water-sensitive trioxide; addition of sulfur in pyridine; addition of tetrachloro-1,2-quinone to form a phosphorane which with water gave a 1,3,2-dioxaphospholane oxide derivative; attack by ethanol which opened the ring and gave, surprisingly, ArO—PH(O)OH as the product rather than an O-ethyl compound.

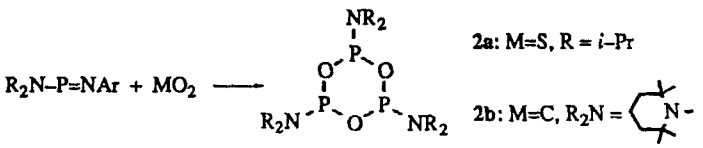
Key words: Phosphorodichloridite reactions, 1,3,5,2,4,6-trioxatriphosphorinane-2,4,6-trioxide, 2,4,6-tris(diisopropyl-amino)-1,3,5,2,4,6-trioxatriphosphorinane.

INTRODUCTION

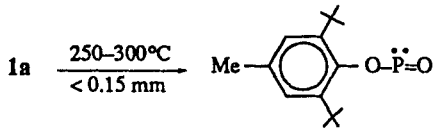
In 1986, it was demonstrated by Chasar and coworkers that the rare 1,3,5,2,4,6-trioxatriphosphorinane ring system with phosphorus in the P(III) state could be easily constructed by the partial hydrolysis of sterically blocked phosphorodichloridites.[1] The steric blocking on phosphorus was provided by various 4-substituted-2,6-di-*tert*-butylphenoxy groups (*e.g.*, **1a–1c**).



Another type of derivative of this ring system possesses a dialkylamino substituent on phosphorus, and results from the reaction of an aminoiminophosphine with sulfur dioxide[2] or carbon dioxide.[3]

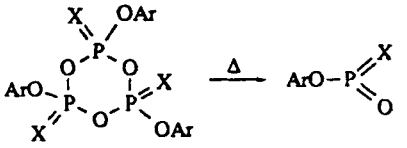


The ring system is of importance since with O- or N-substituents on P it can be viewed as the cyclic trimer of a phosphenous acid (HO—P=O) derivative. Indeed in 1992 the detrimerization of the ring in one of the Chasar compounds (**1a**) was accomplished and provided the first example of an aryl phosphenite (**3**).[4] As is true of all 2-coordinate phosphoryl derivatives,[5] the phosphenite was highly reactive and could not be isolated; it was observed at low temperatures by ^{31}P NMR, infrared, and UV spectroscopy. Some chemical properties of the phosphenite have been recorded in later work and will be reported elsewhere.[6]



3

In principle, other sterically blocked phosphenous acid derivatives could become available from the detrimerization of the trioxatriphosphorinane ring. Also, the trioxide (**4**) and the trisulfide (**5**) derivatives in principle could serve as precursors of sterically stabilized 3-coordinate phosphoryl derivatives, equally rare and reactive.[7]



4a, X = O

4b, X = S

To facilitate studies of detrimerization processes, a broader range of sterically blocked trioxatriphosphorinanes was needed, and we have attempted to extend the Chasar partial hydrolysis method in this direction. During this study, we have observed that this method, at least under the conditions we have used, is not applicable to P-alkoxy derivatives, and this prompted us to explore another method for the construction of the ring system, employing the reaction of anhydrous metallic oxides with phosphorodichloridites. As will be reported here, this method also proved to have limited scope, but is of some value in making readily available a sterically blocked amino derivative.

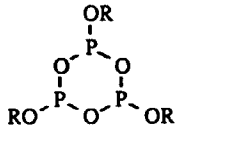
Some new observations on the chemical properties of the 1,3,5,2,4,6-trioxatriphosphorinane system (called "trimer" hereafter) have also been made and are reported here.

Extensions of the Chasar Method

We have successfully repeated Chasar's synthesis[1] of the sterically blocked aryloxy derivatives **1a**, **1b** and **1c**, all in 40–60% yield. These trimers are easily characterized by ^{31}P NMR spectroscopy; as noted by Chasar *et al.*, one P atom is trans-related

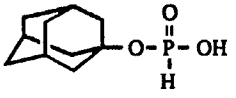
to the other two P atoms, giving rise to a well-resolved AX_2 spectrum in the range of δ 120–130 with the doublet upfield of the triplet.

We then attempted to extend the method to include the synthesis of derivatives with the sterically demanding 1-adamantyl or neopentyl groups replacing the aryl group on oxygen. 1-Adamantyl and neopentyl phosphorodichloridites were formed from the conventional reaction of equimolar amounts of the corresponding alcohol with PCl_3 in the presence of a tertiary amine. Solutions of these chlorides were used directly in the partial hydrolysis procedure. In the case of adamantyl, the hydrolysis did not stop at the desired stage to give the cyclic trimer (**5a**); there were no ^{31}P NMR signals anywhere close to those characteristic of the trioxatriphosphorinane system, and the major product (>90%) had a shift of δ −4.6 that split to a doublet with J = 687.6 Hz when proton-coupled. These properties are consistent with the major product having structure **6** from complete hydrolysis of the phosphorodichloridite (*cf.* to **7**, δ −1.1 $^1J_{P-H}$ = 674 Hz[7a]). The reaction was also conducted in an NMR tube, and progress of the reaction was monitored by ^{31}P NMR spectroscopy. A transient signal was observed at δ 204.7, which could conceivably indicate the presence of a trace of 1-adamantyl-O—P=O (*cf.* to δ 238 for **3**[4]), but there is no confirmation of this suggestion.



5a, R =

5b, R = Me_3CCH_2



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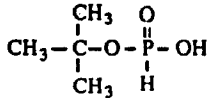
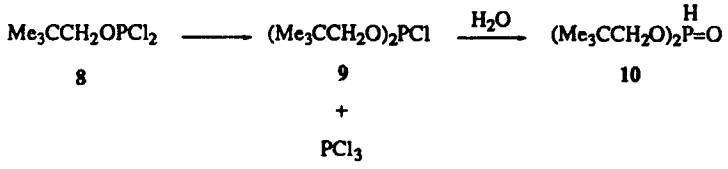


7

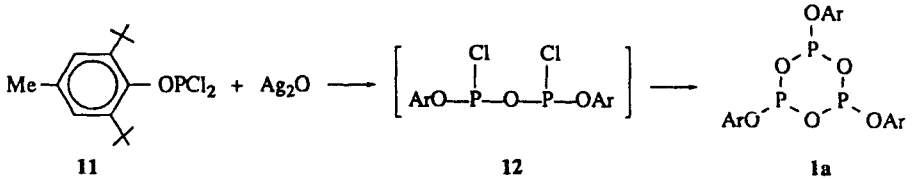
The attempted partial hydrolysis of neopentyl phosphorodichloridite gave more complicated results, but again there were no ^{31}P NMR signals suggesting the formation of the trimer. The major signal occurred at δ 7.75, and showed coupling to ^1H of 700 Hz. This suggested a hydrogen phosphite structure, and distillation provided a sample that had the properties of the known[8] dineopentyl phosphite (**10**; δ ^{31}P 7.7, $^1J_{PH}$ = 695 Hz). This would arise from a disproportionation process, which was found to occur at the phosphorodichloridite stage. Thus, simply adding a tertiary amine to an ether solution of the phosphorodichloridite (**8**, δ 178.0) caused the appearance of a new ^{31} P NMR signal at δ 165.7 attributable to dineopentyl phosphorochloridite (**9**). Some trineopentyl phosphite (δ 138.6; lit.[7b] δ 137–139) was also present. In the partial hydrolysis reaction, monitoring by ^{31}P NMR revealed transient species at δ 202 (possibly C_5H_{11}—O—P=O), δ 111–117, δ 193. The latter two fall in the approximate range expected for the trimeric (*e.g.*, **1a**, δ 120–130) and the dimeric (*e.g.*, the dimer of **3**, δ 176[8]) forms, respectively, of the phosphenite, but were absent in the final product.



No further experiments at utilizing the Chasar method for synthesizing alkoxy derivatives were performed, following these disappointing results.

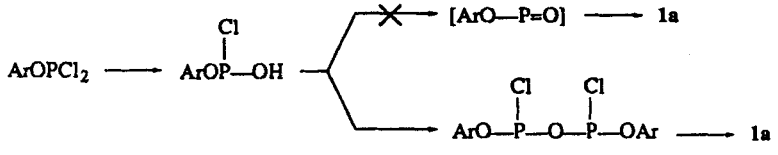
Trioxatriphosphorinanes from Phosphorodichloridites and Metallic Oxides

The literature notes that simple alkyl phosphorodichloridites form polymeric products containing P—O—P bonds when reacted with anhydrous silver oxide.[10] We have explored the consequences of having sterically demanding O-substituents on phosphorus, with the hope that the course of the reaction might be modified so as to give the cyclic trimeric P—O—P system rather than the polymer. The reaction was performed first on the hindered aryloxy phosphorodichloridite **11** since a sample of the trimer (**1a**) was available from the Chasar synthesis. Reaction of **11** with anhydrous silver oxide was performed in methylene chloride at room temperature. After about three weeks, all **11** had been consumed as determined by ^{31}P NMR. The product recovered from the solution after removing the insoluble silver salt was recrystallized from acetone and found to have the same m.p. (185–186°C) and ^{31}P NMR spectrum (δ 127.9 (t) and 120.0 (d), $^2J_{PP}$ = 8.9 Hz) as the trimer from the Chasar partial hydrolysis. The yield was 76%. Transient intermediates were observed in the reaction that had ^{31}P NMR δ 164.8 and 163.9. A reasonable assumption is that these signals arise from the pyrophosphite derivative **12**, which would exist in *meso* and *dl* diastereoisomeric forms. We have noted similar transient signals in the partial hydrolysis of the phosphorodichloridite, as did Chasar *et al.*[9]



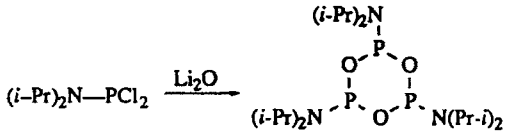
11 **12** **1a**

Lithium oxide was also used in this reaction; a shorter time period (two weeks) was required, and the yield was improved to 81%. Again the transient ^{31}P NMR peaks at δ 164.8 and 163.9 were observed, establishing the fact that the same intermediate from coupling two molecules of the phosphorodichloridite is formed *en route* to the trioxatriphosphorinane by three different procedures. This observation may point to a mechanism for the hydrolysis to the trimer that involves the pyrophosphite as an intermediate, rather than the monomeric phosphenite that proceeds to trimerize.



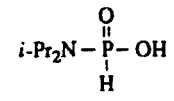
Of greater synthetic significance is the observation that the metal oxide coupling method can be applied to the production of amino derivatives of the trioxatriphosphorinane ring. Diisopropylaminodichlorophosphine was found to give a 53% yield (after recrystallization from hexane) of **2a** when reacted with lithium oxide

for three weeks. The m.p. (107–108°C) and ^{31}P NMR spectrum (δ 140.2 (t) and 131.6 (d), $^2J_{PP}$ = 12.6 Hz) matched closely the values reported for this compound by Niecke *et al.*[2] when prepared from the aminoiminophosphine-SO_2 reaction. The same compound was formed with silver oxide but in the lower yield of 35%.



2a

The partial hydrolysis procedure was also explored as a route to the trimer **2a**. The ^{31}P NMR spectrum of the reaction mixture showed that some (20%) of the trimer was indeed formed, but full hydrolysis (*e.g.*, to **13**) was indicated by signals around δ 5–8. The mixture was unattractive for separation.



13

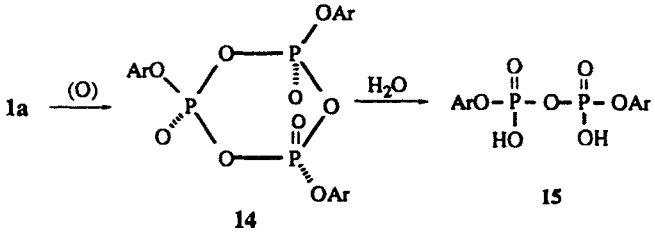
Having succeeded in the synthesis of two different types of trimers by the metal oxide coupling method, we returned to the problem of construction of the P-alkoxy derivatives of the trimer system. However, neither 1-adamantyl- nor neopentyl phosphorodichloridite gave satisfactory results when reacted with silver or lithium oxides. Both dichloridites were slow to react in the usual 2–3 week periods and mainly gave complex ^{31}P NMR signals clustered in the δ −10 to +5 region. The adamantyl compound gave no signals in the downfield region expected for the cyclic structure, but a weak signal at δ 166.9 was suggestive of a pyrophosphite structure (*cf.* to **12**, δ 164.8, 163.9). For the neopentyl compound, there was a hint of the cyclic product from very weak signals around δ 150, but the major signals occurred in the region δ −5 to +10.

The lack of success in the two approaches to the P-alkoxy derivatives of the trioxatriphosphorinane system has discouraged further attempts in this direction. It appears that the steric hindrance supplied by the alkyl substituents is not sufficient to guide the reactions in the desired way.

Reactions of the 1,3,5,2,4,6-Trioxatriphosphorinane System

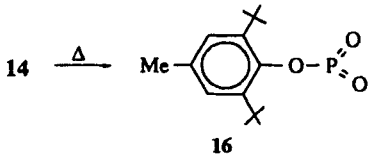
Little is known about the reactivity of the trioxatriphosphorinane ring system. Chasar and coworkers[1] noted that, in general, the hindered O-aryl compounds of their study resisted oxidation on exposure to air, and that one compound (**1a**) was not appreciably oxidized by *tert*-butyl hydrogen peroxide. The compounds were stable to water; **1a** and **1b** were not hydrolyzed after 100 days at pH 7. We have proceeded to extend the study of the reactivity of this family of compounds, using **1a** as the model substance.

Oxidation and sulfuration. Three reagents have been found that can effect the conversion of compound **1a** to its trioxide (**14**), which we considered to be potentially significant as a precursor, on pyrolysis, of a kinetically stabilized metaphosphate ($ArOPO_2$). The oxidation was accomplished by ozone in CH_2Cl_2 at $-76°C$; signals for trimer **1a** vanished, and a product with δ −34.0 was formed. This shift is appropriate for a cyclotriphosphate such as **14** with O-aryl substituents; as is generally true of phosphoric acid derivatives,[7c] the signal is significantly upfield of the value reported for the parent acid (δ −20.7[11a]). The signal showed weak splitting, as might be expected for a trimer oxide with non-equivalent phosphorus atoms as are present in **14**. Water must be rigorously excluded in this reaction, since the product is extremely easily hydrolyzed with opening of the ring to give pyrophosphate **15** with δ −17.9. This signal was almost always present in the reaction product, and when water was intentionally present it became the only product. The oxidation could also be accomplished in pyridine solution by either pyridine N-oxide or sodium periodate, but difficulties in obtaining an anhydrous medium always led to the pyrophosphate **15** as the major product. In this case, the compound was isolated as a pyridine salt and conclusively identified by analysis. The ^{31}P NMR shift of δ −17.0 ($CDCl_3$) is in excellent agreement with that of a model diaryl pyrophosphate (PhO(MeO)P(O)O—P(O)(OMe)OPh, δ −17.3[11b]). Attempts to isolate the trioxide **14** from any of the oxidation products were not successful, always resulting in the formation of the pyrophosphate **15**. This difficulty



14 **15**

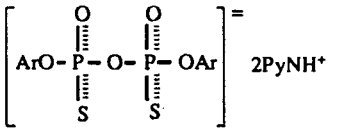
in obtaining the trioxide in pure form has, unfortunately, prevented any attempt to determine if it would act as a precursor of a monomeric metaphosphate **16** on pyrolysis.



16

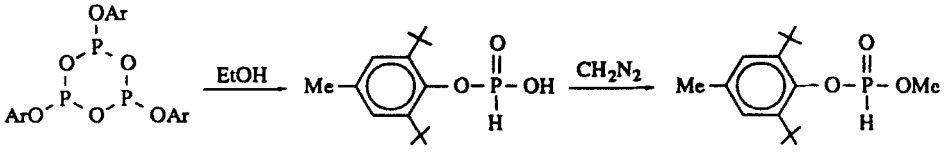
Trimer **1a** also was oxidized by sulfur in pyridine solution at room temperature; the trimer was completely reacted after two weeks, as easily seen by ^{31}P NMR. No appreciable reaction occurred in the solvents benzene, chloroform, and triethylamine, however. The ^{31}P NMR spectrum of the crude product had signals in the region expected for a thiono structure (δ 54.4, 45.7, and 41.7; compare to $(PhO)_3P{=}S$, δ 52.2[7d] as a model, but the pyrophosphate structure can cause additional upfield shifts). Inconsistent results accompanied attempts to isolate a definite product. On one occasion, a crystalline product separated from a chloroform

solution and was examined by X-ray diffraction analysis. The product proved to be a pryidinium salt of a non-cyclic diphosphate of structure **17**. Unfortunately, the crystal quality was poor and precluded a detailed structural analysis. The isolation of such a diphosphate indicates that the ring system of the sulfide is sensitive to water, just as was found for the oxide.

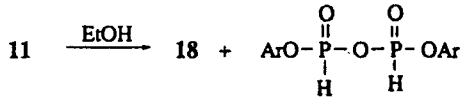


17

With alcohols. In contrast to the reported stability in water,[1] trimer **1a** was decomposed after standing in ethanol for two weeks. Surprisingly, the product had the structure (**18**) that might have been expected from a simple hydrolytic ring-opening, and was clearly not the anticipated ethoxy derivative from a nucleophilic displacement on phosphorus. This product was isolated in 78% yield, and was conclusively identified by elemental analysis, by the ^{31}P spectral features (δ 4.0 ($CDCl_3$), $^1J_{PH}$ = 708 Hz; δ 1.9 in THF—$CDCl_3$ has been reported[9]) and by conversion to its methyl ester (**19**) with diazomethane. It was also observed that a low yield (39%) of **18**[1] was obtained on reaction of phosphorodichloridite **11** with ethanol, which additionally gave the anhydride **20** (1:1). The large aryloxy group has therefore drastically modified the reactivity at the trivalent phosphorus atom in both the cyclic compound and the phosphorodichloridite. Mechanistic details of the unusual behavior of the trimer remain to be examined; it will be of interest in future work to determine the fate of the ethanol partner in the reaction.



1a **18** **19**

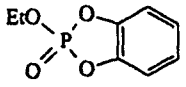


20

The reactivity of the trimer toward a hindered alcohol (neopentyl alcohol) was also examined. In this case, no reaction was observed after 3 weeks at room temperature.

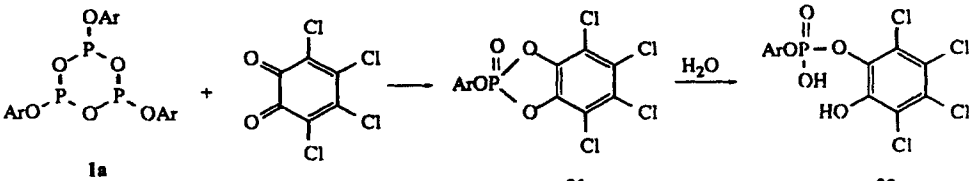
With tetrachloro-1,2-benzoquinone. Trimer **1a** reacted quite readily with three equivalents of tetrachloro-1,2-quinone. After 2 hr at room temperature, **1a** was converted completely to a single product that had δ 5.4. This shift is in the phosphate region, and structure **21** was suggested. The 5-membered cyclic phosphate feature

would normally cause a strong downfield displacement from the usual phosphate region (0 ± 3 ppm), but this is countered by the upfield shifting common for aryloxy groups. The shift compares well with that of a model compound **22** with δ 10.0.[12] Compound **21** was reactive to water and not easily purified, but the



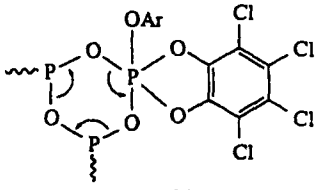
22

hydrolysis product proved to be of value in confirming the structure. This product (**23**) was stable and easily purified. It gave the correct analysis, and a ^{31}P shift at δ −8.1 as expected for a non-cyclic diaryl phosphate (*cf.* to $(PhO)_2PO_2H$, δ −12[7c]).



1a **21** **23**

To account for the formation of the cyclic phosphate, we propose that the 5-coordinate phosphorane structure (as in **24**) is initially formed at one or more P atoms, as is common for phosphites. Cleavage of P—O bonds in the ring would then follow.



24

EXPERIMENTAL

Trimers **1a**, **1b**, and **1c** were prepared as described in the literature.[1] Physical properties matched those reported. ^{31}P NMR spectra were recorded in $CDCl_3$ solutions with a Bruker 80 MHz spectrometer. Methylene chloride was dried by distillation from phosphorus pentoxide, and THF from calcium hydride.

Partial Hydrolysis of 1-Adamantyl Phosphorodichloridite

The phosphorodichloridite was generated in solution by heating at 100°C a mixture of 5.0 g (0.033 mol) of 1-adamantanol, 4.51 g (0.033 mol) of PCl_3, and 24.3 g (0.131 mol) of tributylamine. The product had δ ^{31}P 190.5 (lit.[13] δ 190.9). This reaction mixture was diluted, at room temperature, with 20 mL of acetone, and then treated with a solution of 0.60 g (0.033 mol) of water in 3 mL of acetone over a period of 30 min. The precipitated amine salt was removed by filtration and the residue washed with 100 mL of hexane. The filtrates were evaporated to leave 10.86 of solid, m.p. 106°C, ^{31}P NMR ($CHCl_3$) δ −4.6, $^1J_{PH}$ = 687.6 Hz. The solid is most likely the Bu_3N salt of acid **6**, but satisfactory elemental analysis could not be obtained (*e.g.*, Calc. for $C_{22}H_{44}NO_3P$: C, 65.80; H, 11.05; N, 3.49. Found: C, 65.49; H, 10.23; N, 2.48.)

Partial Hydrolysis of Neopentyl Phosphorodichloridite (**8**)

To a solution of 1.5 g (7.9 mmol) of **8** (δ ^{31}P 178.0; lit.[14] δ 178.3) and 1.87 g (18.5 mmol) of triethylamine in 10 mL of acetone at room temperature was added a solution of 0.14 g (7.9 mmol) of water in 2 mL of acetone over a period of 20 min. The precipitated amine hydrochloride was removed by filtration; the ^{31}P NMR spectrum of the filtrate consisted of a cluster of signals at δ 111 and 117, with the major product (**10**, 80%) at δ 7.75. Product **10** was recovered (0.61 g, 69%) by distillation at 114–115°C (10 mm); lit.[7b] b.p. 116–119°C (13 mm). ^{31}P NMR ($CHCl_3$) δ 7.75, $^1J_{PH}$ = 699.9 Hz, $^3J_{PH}$ = 8.1 Hz (lit.[7b] δ 7.7, $^1J_{PH}$ = 695 Hz); ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 18 H), 3.68 (d, $^3J_{PH}$ = 8.14 Hz, 4 H). Anal. Calcd for $C_{10}H_{23}O_3P$: C, 54.05; H, 10.43. Found: C, 53.78; H, 10.05.

The Reaction of Silver Oxide with 2,6-di-tert-Butyl-4-methylphenylphosphorodichloridite (**11**)

A mixture of 0.49 g (0.0015 mol) of phosphorodichloridite **11**, 0.35 g (0.0015 mol) of silver oxide and 10 mL of methylene chloride was allowed to stand at room temperature for 3 weeks in the dark. Solid was filtered off, and the solvent was stripped from the filtrate. The residue was recrystallized from acetone. The yield of **1a** was 0.31 g (76%), m.p. 185–186°C (lit.[1] 184–186°C); ^{31}P NMR ($CHCl_3$) δ 127.9 (t), 120.0 (d), $^2J_{PP}$ = 8.9 Hz (lit.[1] ^{31}P NMR ($CHCl_3$) 127.9 (t), 120.0 (d), $^2J_{PP}$ = 9.0 Hz).

The Reaction of Lithium Oxide with 2,6-di-tert-Butyl-4-methylphenylphosphorodichloridte (**11**)

A mixture of 2.85 g (0.0088 mol) of phosphorodichloridte **11**, 0.3 g (0.01 mol) of lithium oxide and 15 mL of THF was allowed to stand at room temperature for 2 weeks. Solid was filtered off and the residue was recrystallized from acetone; the yield of **1a** was 1.91 g (81%), m.p. 185–186°C (lit.[1] 184–186°C); ^{31}P NMR ($CHCl_3$) δ 127.9 (t), 120.0 (d), $^2J_{PP}$ = 8.9 Hz (lit.[1] ^{31}P NMR ($CHCl_3$) δ 127.9 (t), 120.0 (d), $^2J_{PP}$ = 9.0 Hz).

The Reaction of Lithium Oxide with Diisopropylaminodichlorophosphine

A mixture of 2.65 g (0.013 mol) of diisopropylaminodichlorophosphine and 0.78 g (0.026 mol) of lithium oxide in 50 mL of THF was stirred for 3 weeks. Solid was filtered off and the filtrate was evaporated. The residue was recrystallized from hexane; the yield of **2a** was 1.02 g (53%), m.p. 107–108°C (lit.[2] m.p. 107°C); ^{31}P NMR ($CHCl_3$) δ 140.23, 131.62, $^2J_{PP}$ = 12.56 Hz (lit.[2] ^{31}P NMR (C_6D_6) 140.3, 131.3, $^2J_{PP}$ = 13.5 Hz). A minor isomer was also observed at δ 133.7 and 130.9.

The Reaction of Silver Oxide with Diisopropylaminodichlorophosphine

A mixture of 0.35 g (0.0017 mol) of diisopropylaminodichlorophosphine and 0.4 g (0.017 mol) of silver oxide in 10 mL of methylene chloride was stirred for 3 weeks. Solid was filtered off and the filtrate evaporated. The residue was recrystallized from hexane; the yield of **2a** was 0.09 g (35%), m.p. 107–108°C (lit.[2] m.p. 107°C); ^{31}P NMR ($CHCl_3$) δ 140.23, 131.62, $^2J_{PP}$ = 12.56 Hz (lit.[2] ^{31}P NMR (C_6D_6) δ 140.3, 131.3, $^2J_{PP}$ = 13.5 Hz). A minor isomer was also observed at δ 133.7 and 130.9.

Oxidation of Trimer **1a** *by Pyridine N-oxide*

A mixture of 1.0 g (0.0013 mol) of **1a** and 0.6 g (0.0063 mol) of pyridine N-oxide in 10 mL of pyridine was stirred overnight. The reaction mixture was evaporated and the residue was recrystallized from pyridine (wet)/hexane (1:1); yield of pyrophosphate **15** as the pyridine salt, 0.46 g (37%), m.p. 233°C, ^{31}P NMR ($CHCl_3$) δ −17.0. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 36 H, Me_3C), 2.23 (s, 6 H, Me-Ar), 7.0 (broad, 5 H, Py), 7.23 (s, 4 H, C_6H_2). Anal. Calcd for $C_{35}H_{53}NO_7P_2$: C, 63.52; H, 8.07; N, 2.12. Found: C, 63.21; H, 7.95; N, 2.14.

Oxidation of Trimer **1a** *by Ozone*

Ozone was generated with a Welsbach ozonator and passed through a solution of 0.8 g (0.0010 mol) of trimer **1a** in 15 mL of CH_2Cl_2 at −75°C. Unreacted ozone was removed from the solution with a stream of nitrogen. The ^{31}P NMR spectrum consisted of a major peak at δ −35 and on occasion a minor peak at δ −20. On standing, or on intentional exposure to moisture, the δ −35 disappeared and δ −20 intensified. Solvent was removed and the residue was recrystallized from wet pyridine-hexane (1:1). The solid had m.p. 233°C, ^{31}P NMR ($CDCl_3$) δ −17, and was identical to the monopyridinium salt of pyrophosphate **15** obtained from the trimer after reaction with pyridine N-oxide in pyridine.

Reaction of Trimer **1a** *with Ethanol*

A solution of 0.8 g (0.0010 mol) of trimer **1a** in 5 mL of chloroform and 3 g of ethanol was stirred for 2 weeks at room temperature. The mixture was evaporated to dryness, and the residue was recrystallized from ethanol.The yield of acid **18** was 0.67 g (78%), m.p. 162–163°C; ^{31}P NMR ($CDCl_3$) δ 4.0 ($^1J_{PH}$ = 708.0 Hz); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 18 H, t-Bu), 2.28 (s, 3 H, Me), 7.09 (s, 2 H, ArH). Anal. Calcd for $C_{15}H_{25}O_3P$: C, 63.38; H, 8.80. Found: C, 63.25; H, 8.86.

Acid **18** was converted to the methyl ester (**19**) with diazomethane, and distilled at 150°C (10^{-6} mm) in a Kugelrohr apparatus; ^{31}P NMR ($CDCl_3$) δ 6.0 ($^1J_{PH}$ = 708.0 Hz, $^3J_{PH}$ = 12.2 Hz); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 18 H, t-Bu), 2.33 (s, 3 H, Me), 3.89 (d, $^3J_{PH}$ = 12.7 Hz, 3 H, OMe), 7.03 (s, 2 H, ArH). Anal. Calcd for $C_{16}H_{27}O_3P$: C, 64.42; H, 9.06. Found: C, 64.71; H, 9.13.

Reaction of Phosphorodichloridite **11** *with Ethanol*

The dichloridite (0.35 g, 0.44 mmol) was added to 5 g of ethanol, whereupon a vigorous reaction occurred. The ^{31}P NMR spectrum showed that acid **18**[1] (δ 4.0, $^1J_{PH}$ = 708 Hz) and its anhydride **20** (diastereoisomers, δ −8.0, $^1J_{PH}$ = 760.1 Hz, and −9.7, $^1J_{PH}$ = 760.9 Hz)) were formed in equal amounts. Water was added to hydrolyze **20** to the acid **18**. The residue from evaporation of the solution was recrystallized from ethanol to yield 0.12 g (39%) of acid **18**, m.p. 162–163°C; ^{31}P and ^{1}H NMR spectra were identical to the product from reaction of trimer **1a** with ethanol.

Reaction of Trimer **1a** *with Tetrachloro-1,2-benzoquinone*

A solution of 0.32 g (0.4 mmol) of **1a** in 10 mL of chloroform was treated with 0.30 g (1.2 mmol) of tetrachlorobenzoquinone at room temperature. After 2 hr the solvent was removed with a rotary evaporator, and the solid residue was recrystallized from acetone to afford 0.57 g (93%) of **21**, m.p. 208–209°C; ^{31}P NMR ($CDCl_3$) δ 5.4.

Compound **21** (0.80 g, 1.6 mmol) was hydrolyzed by wet methanol to give the ring-opened product **23**. Product **23** (0.6 g, 72%) crystallized from the solution, m.p. 185–186°C, ^{31}P NMR ($CHCl_3$) δ −8.1. Anal. Calcd for $C_{21}H_{25}Cl_4O_5P$: C, 47.57; H, 4.75. Found: C, 47.23; H, 4.95.

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