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Synthesis and Melting Behavior of Certain (Aryloxy)cyclotriphosphazene Polymer Precursors

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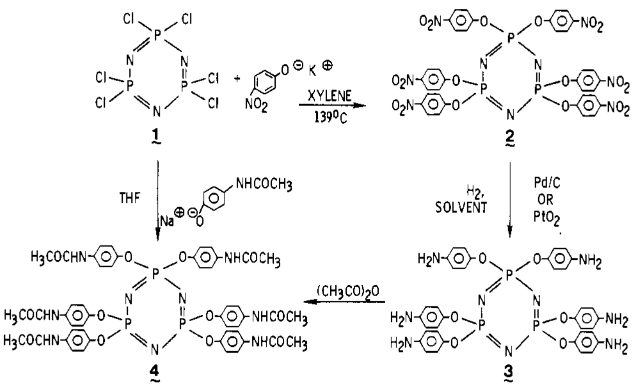
A simple and useful procedure for the preparation of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**) from hexachlorocyclotriphosphazene (**1**) and the readily accessible potassium salt of 4-nitrophenol in refluxing xylene is described. This modification offers advantages over the standard procedure, which employs potassium hydroxide and 4-nitrophenol to prepare **2** in refluxing xylene. The results of a study of the low-pressure hydrogenation of **2** to yield the corresponding amine **3** are discussed. Dimethylformamide and 10% palladium–charcoal are shown to be effective for carrying out this conversion, and in addition, it is demonstrated that this catalyst can be substituted for platinum oxide in aniline, the solvent normally used for carrying out this reduction. It is established that the difference in melting points observed for **2** results from the fact that this compound exists in two crystalline modifications. Differential scanning calorimetry data are supplied to support this conclusion. The melting point reported by previous workers for hexakis(4-aminophenoxy)cyclotriphosphazene (**3**) is questioned. In connection with the melting behavior of **3** the new compound hexakis(4-acetamidophenoxy)cyclotriphosphazene (**4**) was prepared.

As part of a program directed toward the preparation of resins with enhanced fire retardancy we had need for hexakis(4-aminophenoxy)cyclotriphosphazene (**3**). Hexakis(4-aminophenoxy)cyclotriphosphazene (**3**) is an important intermediate for the preparation of resins with enhanced fire retardancy. This amine and a number of its derivatives have been prepared by several groups of investigators[1-4] who have shown these materials to be useful both as polymer precursors and as model compounds in studies of polymeric phosphazene systems. Invariably, amine **3** has been prepared by catalytic reduction of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**). In this present paper, we describe an improved route to nitro compound **2**, the results of a study of its catalytic reduction to **3**, and some interesting observations on the melting behavior of these compounds. (See Scheme I.)

Hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**) was first reported by Yokoyama,[5] who claimed he had prepared it by reaction of hexachlorocyclotriphosphazene (**1**) with the sodium salt of 4-nitrophenol in either toluene or xylene; he recorded a melting point of 212–214 °C. Somewhat later, Kober and co-workers[6] prepared **2** by treatment of **1** with a mixture of 4-nitrophenol and potassium hydroxide in refluxing xylene. Since their product, for which they had obtained a satisfactory elemental analysis and about whose structure there can now be no doubt, melted at 263–264 °C, they not unexpectedly called attention to the lack of agreement between the melting points of the two specimens of compound **2**. In 1969, Allcock and Kugel[7] noted briefly that they had prepared nitro compound **2** by reaction of hexachlorocyclotriphosphazene (**1**) with 4-nitrophenol in the presence of sodium carbonate; no experimental details were given. Their nitro compound was reported to melt at 248 °C, but no mention was made of the discrepancy between the melting point of this preparation and those reported by Yokoyama[5] and by Kober[6] for their products. More recently, Allcock and co-workers[4] prepared hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**) in tetrahydrofuran by reaction of the phosphazene trimer (**1**) with sodium 4-nitrophenoxide, which was obtained by treatment of 4-nitrophenol with sodium hydride in the same solvent; the melting point of **2** was reported to be 261–264 °C—a value that was in good agreement with the one found earlier by Kober.[6] In 1983, Parker and co-workers[2] reported the same melting point for their preparation of **2**, which they carried out by the method of Kober.[6]

Initially, we elected to prepare hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**) by Kober's method,[6] since we envisioned the possible need for larger quantities of **2** and felt this procedure might be safer and somewhat less costly than that of Allcock,[4] which used sodium hydride for generation of the salt of 4-nitrophenol. Unfortunately, in our hands the preparation of nitro compound **2** by Kober's route proved troublesome since we were constantly hampered by unpredictable and unmanageable foaming of the xylene medium during the course of the reaction. Attempts to control the foaming by means of various well-established techniques, including the use of foam breakers, were of no avail. At best, we obtained only small amounts of compound **2** by this procedure. Since it was believed that the foaming stemmed from the in situ formation of water liberated by the neutralization of the phenol by the potassium hydroxide, we decided to modify the procedure by carrying out the reaction of the phosphazene trimer (**1**) with the thoroughly dried preformed potassium salt of 4-nitrophenol.

Scheme I



We chose the potassium salt because Kober and co-workers[6] had indicated that they failed to effect the total replacement of the chlorine atoms of hexachlorocyclotriphosphazene (**1**) by the use of the sodium salt of 4-nitrophenol in refluxing xylene. Among others, Vorländer[9] and Hantzsch[10] had prepared potassium 4-nitrophenoxide; the latter investigator used potassium ethoxide and 4-nitrophenol. We found that the most trouble-free and direct route to this salt consisted of adding an ethanolic solution of potassium hydroxide to a stirred solution of the phenol in the same solvent. Potassium 4-nitrophenoxide precipitated as it formed in

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(1) Ottmann, G.; Lederle, H.; Hooks, H., Jr.; Kober, E. *Inorg. Chem.* **1967**, *6*, 394.

(2) Kumar, D.; Fohlen, G. M.; Parker, J. A. *Macromolecules* **1983**, *16*, 1250.

(3) Allcock, H. R.; Austin, P. E. *Macromolecules* **1981**, *14*, 1616.

(4) Allcock, H. R.; Austin, P. E.; Rakowsky, T. F. *Macromolecules* **1981**, *14*, 1622.

(5) Yokoyama, M. *Nippon Kagaku Zasshi* **1960**, *81*, 481; *Chem. Abstr.* **1962**, *56*, 502*f*.

(6) Kober, E.; Lederle, H.; Ottmann, G. *Inorg. Chem.* **1966**, *5*, 2239.

(7) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 5452. (See ref 26 in this paper.)

(8) Allcock and Austin (ref 3, Table I) also report a value of 263–265 °C for the melting point of **2**.

(9) Vorländer, D. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 3120.

(10) Hantzsch, A. *Justus Liebigs Ann. Chem.* **1932**, *492*, 65.

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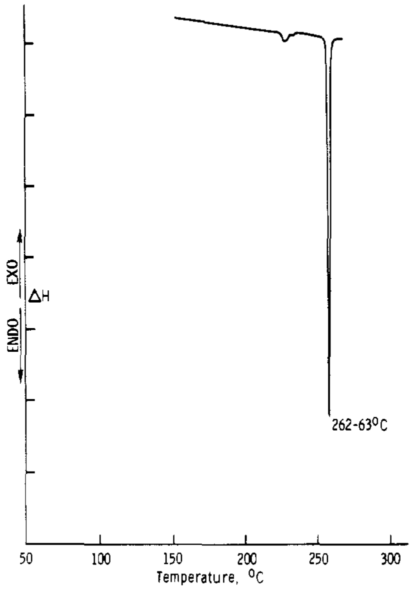


Figure 1. DSC scan of hexakis(4-nitrophenoxy)cyclotriphosphazene (recrystallized from *o*-dichlorobenzene).

almost quantitative yield. In this manner, we were able to prepare even large quantities of the salt with a minimum expenditure of time and effort, and the well-dried material proved eminently satisfactory for the preparation of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**). Thus, reaction of this salt with hexachlorocyclotriphosphazene (**1**) in xylene at reflux temperature gave the desired compound **2** in 60% yield. Improved yields (76%) were realized by use of a phase-transfer catalyst (PTC),[11] and of the two catalysts examined, tricaprylylmethylammonium chloride and tetra-*n*-butylammonium bromide, the latter was found to afford a somewhat cleaner product. Substitution of diglyme or tetrahydrofuran for the xylene did not lead to significantly higher yields of **2**.

The melting behavior of recrystallized specimens of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**) proved rather confusing at first, and for a time it appeared that the displacement reaction was yielding a mixture of two products. Dimethylformamide,[6] cyclohexanone,[6] or *o*-dichlorobenzene[4] have been used for effecting the recrystallization of **2**. Using any one of these solvents for purifying **2**, we obtained a solid that was almost always a mixture of two crystalline forms, one melting at 249–250 °C and the other at 262–263 °C.

On occasion, the recrystallization would afford either one or the other of these components in a high state of purity, with the higher melting modification being observed more frequently. Thin-layer chromatography, elemental analysis, and infrared spectroscopy demonstrated that these substances were actually two modifications of the same compound. Interestingly, crushing of the crystals with a melting point of 249–250 °C raised the melting point to 262–263 °C. Also, it was found that if the melt of the crystals with the lower melting point was allowed to cool, the resulting solid melted at 262–263 °C. These observations were subsequently found to be fully supported by differential scanning calorimetry (DSC). Thus, a recrystallized specimen of compound **2**, which was obtained as a mixture of the two modifications, and also the individual modifications themselves were analyzed by DSC. As can be seen from the scans (Figure 1–3), the endotherms for these substances appear at temperatures that are fully in accord with the values obtained for the corresponding materials by the use of a conventional melting point apparatus. Indeed, the DSC results suggest that a third modification of compound **2** may exist; however, we have been unable to isolate this form. The fact that it was not possible to convert the higher melting form of **2** to the lower melting modification either by crushing of the crystals or by recrystallization of the melt by cooling indicates that the solid with a melting point of 249–250 °C is a metastable modification of **2**. It is interesting to note in connection with the foregoing that the well-characterized compound octaphenoxycyclotetraphosphazene[12] crystallizes in one of three possible modifications, the lower melting form of which displays the same behavior on melting and cooling as that observed by us in the case of the modification of compound **2** having a melting point of 249–250 °C.

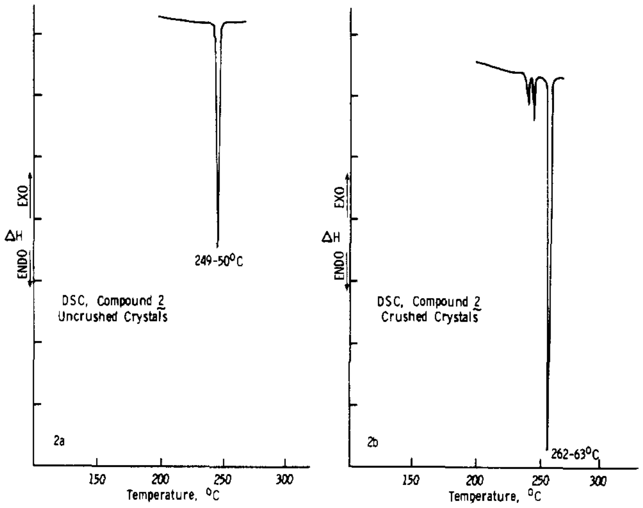
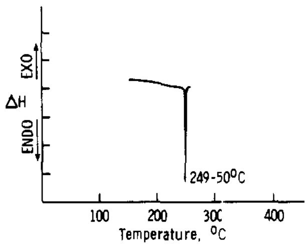
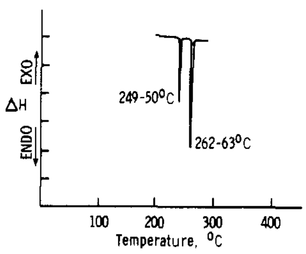


Figure 2. DSC scans of compound **2**.



a. First Melt



b. Remelt

Figure 3. DSC scan of the melt/remelt of compound **2**.

The catalytic reduction of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**) to hexakis(4-aminophenoxy)cyclotriphosphazene (**3**) was first reported by Kober and co-workers,[1] who carried out the hydrogenation in aniline at 1000 psi and 80–90 °C with Raney nickel. Subsequently, Allcock and co-workers[3,4] described a modified procedure in which they used the same solvent at 50 psi and 50 °C in the presence of platinum oxide catalyst. We experienced no difficulty in effecting the conversion of **2** to **3** using the milder conditions of Allcock;[3,4] however, we found that the crude reaction product was invariably contaminated by a small amount of amorphous material. We decided to investigate the low-pressure reduction of **2** under different conditions in the hope of developing a method that would furnish a cleaner product. Using DMF in place of aniline as reaction medium, we

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(11) Similar PTC-mediated displacement reactions have been reported recently. See: Austin, P. E.; Riding, G. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.

(12) Fitzsimmons, B. W.; Shaw, R. A. *Inorg. Synth.* **1966**, *8*, 83.

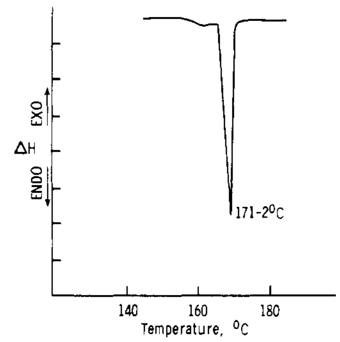

Figure 4. DSC scan of hexakis(4-aminophenoxy)cyclotriphosphazene.

found that uptake of hydrogen did not occur in the presence of platinum oxide, even when the reaction bottle was warmed to 50 °C. In contrast, when the platinum oxide was replaced by 10% palladium–charcoal, the hydrogenation proceeded rapidly with moderate evolution of heat during the early phase of the reaction; toward the end of the reduction, gentle external warming of the reactants was used to ensure completion of the reaction. We also examined glacial acetic acid as a medium for the reduction in the presence of palladium–charcoal catalyst, and it was found to be ineffective; we did not repeat this study with platinum oxide because it appeared that the nitro compound **2** was too insoluble in this solvent. The reduction of **2** to **3** in aniline proceeded smoothly with 10% palladium–charcoal, and it appeared that this catalyst was as effecive as platinum oxide. Unfortunately, none of the methods studied afforded the crude amine **3** free of the amorphous material referred to earlier. It was found, however, that this contaminant could be removed very effectively by dissolving the crude reduction product in dilute acid and adding dilute base, which caused the impurity to precipitate out of solution as a dark intractable material that adhered to the glass walls of the vessel. Removal of the supernatent liquid followed by further treatment of this solution with base then gave hexakis(4-aminophenoxy)cyclotriphosphazene (**3**). In our hands, we found *o*-dichlorobenzene, the solvent normally used to effect the recrystallization of **3**, to be less than ideal. Invariably, we observed that dissolution of the amine in boiling *o*-dichlorobenzene was accompanied by the formation of a small amount of a dark insoluble, viscous oil; this behavior was seen even with highly purified samples of **3**. For this reason, we investigated other solvents for carrying out the recrystallization of amine **3**, and we found the solvent pair 1-butanol–DMF (9:1) to be particularly useful. This solvent mixture not only dissolved the amine cleanly but also afforded the purified crystalline compound in high yield.

The melting point of hexakis(4-aminophenoxy)cyclotriphosphazene (**3**) merits some discussion. Both Kober[1] and Allcock[3,4] have reported a melting point of 189–190 °C for this compound. Parker and co-workers,[2] who have published the most recent account of amine **3**, included a number of physical properties in their description of this substance but failed to report its melting point. Contrary to the observations of Kober and Allcock, we have consistently found compound **3** to melt at 171–172 °C and this value has been confirmed by DSC. The trace (Figure 4) shows an endotherm in this temperature range, and the absence of other thermal events in the scan can be taken as evidence that the compound was pure. We also repeated Kober's[1] method of purification of **3** via its sulfate salt since it was possible that this procedure might yield material with the higher melting point. After regeneration of the amine from this salt and crystallization from *o*-dichlorobenzene, we found the purified compound to melt again at 171–172 °C. Furthermore, recrystallization of **3** from several different solvents including acetonitrile and *n*-amyl alcohol failed to afford a specimen melting at 187–190 °C; in all cases, the recovered compound displayed the lower melting point.

Even though the spectral data for our samples of **3** fully supported its structure, we decided in light of the discrepancy in the melting point of **3** to characterize the amine more fully by converting it to its acetyl derivative **4** and to compare this new compound with a specimen of **4** synthesized by a different route. Thus, acetylation of **3** with acetic anhydride gave without difficulty the expected hexakis(4-acetamidophenoxy)cyclotriphosphazene (**4**); its elemental analysis and infrared and ^{1}H NMR spectra were fully consistent with the expected structure. An authentic specimen of **4** was synthesized in 73% purified yield by treatment in tetrahydrofuran of hexachlorocyclotriphosphazene (**1**) with the sodium salt of 4-acetamidophenol. Both specimens of **4** were shown to be identical by TLC, mixture melting point determination, and comparison of their infrared spectra.

In conclusion, it is interesting to contemplate whether the discrepancy in the melting points of hexakis(4-aminophenoxy)cyclotriphosphazene (**3**) is indicative of the existence of two modifications of this compound, as was observed in the case of the precursor **2**, or is simply the result of an error on the part of the earlier investigators.

Experimental Section

Reagents, Solvents, and Catalysts. Hexachlorocyclotriphosphazene (Inabata and Co., Ltd., Osaka, Japan) was isolated from a trimer–tetramer mixture by repeated recrystallization from hot heptane followed by one or two sublimations at 70–80 °C (0.1 mm); differential scanning calorimetry showed one endotherm at 112.6 °C. 4-Nitrophenol (Aldrich) was sublimed before use. Gold Label *N*,*N*-dimethylformamide (DMF) (Aldrich) was stored over 4A molecular sieves. Tetra-*n*-butylammonium bromide (99%, Aldrich) and tricaprylylmethylammonium chloride (General Mills) were used as received. Acetic anhydride (Aldrich) was redistilled before use. Pyridine, 1-butanol, *n*-amyl alcohol (Fisher), 4-acetamidophenol (Eastman), acetonitrile, *o*-dichlorobenzene (Burdick and Jackson), platinum oxide (Alfa Products), and 10% palladium–charcoal (Matheson Coleman and Bell) were used as received. Xylene (Fisher) was redistilled and stored over 4A molecular sieves. Aniline (Fisher) was distilled from zinc dust. Tetrahydrofuran (Burdick and Jackson) was distilled from sodium benzophenone ketyl. Sodium hydride (55–60% Aldrich) was washed successively with cyclohexane (three times) and pentane (two times).

Analytical Instruments. Infrared (IR) spectra were recorded on a Digilab FTS-10M spectrometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Perkin-Elmer Model R-32 spectrometer; chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as internal standard. Solid-probe mass spectra were obtained on a Finnegan Model 3300 spectrometer at 70 eV and at a source temperature of 130 °C. Differential scanning calorimetry (DSC) data were obtained on a Du Pont 990 thermal analyzer at a heating rate of 5 °C/min in a static-air atmosphere. All melting points were taken on either a Thomas-Hoover or a Fisher-Johns apparatus and are corrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Thin-layer chromatography was carried out with Eastman 6060 silica gel sheets.

Potassium 4-Nitrophenoxide. To a stirred solution of 60.0 g (0.431 mol) of 4-nitrophenol in 200 mL of absolute ethanol was added dropwise over the course of 15 min a solution of 30.0 g of potassium hydroxide in 150 mL of ethanol, during which time a yellow crystalline solid separated. Upon completion of the addition, the mixture was cooled in an ice-water bath and stirred an additional 60 min. The solid was collected by suction filtration and washed twice on a funnel with 50-mL portions of chilled ethanol. Drying of the salt at 125 °C (0.1 mm) for 16 h afforded 76.4 g (99%) of orange crystals, mp >300 °C. When heated on a platinum foil over a free flame, the salt decomposed somewhat violently; 4-nitrophenol did not manifest this behavior. IR (KBr) (cm^{-1}): 3035, 1580, 1550, 1500, 1420, 1360, 1305, 1165, 1115, 1095, 855, 812, 755, 705, 638.

Hexakis(4-nitrophenoxy)cyclotriphosphazene (2). This reaction was carried out in an atmosphere of dry nitrogen. A stirred suspension of 11.6 g (33 mmol) of hexachlorocyclotriphosphazene (**1**), 38.6 g (0.22 mol) of thoroughly dried potassium 4-nitrophenoxide, and 2.0 g of tetra-*n*-butylammonium bromide in 250 mL of dry xylene was heated under reflux for 14 h.[13] The reaction mixture was allowed to cool to room temperature, and the light yellow solid, which was collected by suction filtration, was washed on the funnel with hexane and then with ethanol. The oven-dried product (85 °C for 2 h) was suspended in 200 mL of 5% aqueous potassium hydroxide and stirred at 80–85 °C for 30 min. The

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(13) Some heat is spontaneously evolved when the reagents are mixed. On two occasions we encountered moderate foaming that was readily eliminated by affixing a Dean–Stark trap to the flask and collecting and discarding 10–20 mL of condensate. In both cases, about 1 mL of water was removed.

suspension was filtered by suction, and the filter cake was washed successively with 400 mL of hot water, 200 mL of ethanol, and 100 mL of hexane. The white solid, after being dried at 85 °C for 2 h, weighed 29.6 g (92%) and had a melting point of 262–265 °C with some softening at 235 °C. Recrystallization was effected by dissolving the solid in 100 mL of boiling DMF, adding charcoal and Celite, and filtering to yield a faint yellow solution. After the filtrate had cooled slightly, it was diluted with 50 mL of hot 1-butanol and then set aside at room temperature overnight. Compound **2** was filtered off by suction and washed on the funnel with two 50-mL portions of ethanol and once with 100 mL of hexane. The crystals were dried for 6 h at 125 °C (0.1 mm) and weighed 24.3 g (76%); mp 262–263 °C with some melting at 249–250 °C (uncrushed crystals, capillary tube) (lit.[2] mp 261–264 °C). At times recrystallized samples of **2** were obtained that melted sharply at 262–263 °C without any indication of melting at 249–250 °C. An analytical sample, recrystallized twice from DMF–acetone and then from cyclohexanone, had a melting point of 249–250 °C (uncrushed crystals, capillary tube); the melting point rose to 262–263 °C (capillary tube) when the solid was pulverized. Anal. Calcd for $C_{36}H_{24}N_9O_{18}P_3$: C, 44.87; H, 2.51; N, 13.08; P, 9.65. Found: C, 44.88; H, 2.53; N, 12.90; P, 9.66. A specimen of compound **2**, which had been recrystallized twice from DMF–acetone and melted at 262–263 °C with some melting also being observed at 249–250 °C, was also analyzed. Anal. Found: C, 45.18; H, 2.42; N, 13.04; P, 9.82. The IR (KBr) spectra of all of the above specimens of **2**, in spite of the differences in melting behavior, were identical and displayed the same peaks reported for compound **2** by Parker and coworkers.[2] In addition, the ^1H NMR spectra of our samples corresponded, in all respects, with that reported by these workers for **2**.

Hexakis(4-aminophenoxy)cyclotriphosphazene (3). (a) From 2 by Reduction in Aniline in the Presence of Platinum Oxide. According to the procedure of Allcock and co-workers,[3,4] a suspension of 10.0 g (10.4 mmol) of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**) and 60 mg of platinum oxide in 83 mL of aniline was hydrogenated at 50 psi and 50 °C. The crude product was purified by modification of the reported procedure.[1,3,4] Thus, the solid was dissolved in the minimum amount of 2 N hydrochloric acid, decolorizing charcoal was added, and the resulting suspension was filtered. The stirred filtrate was then slowly treated dropwise with 5% aqueous potassium hydroxide in order to precipitate a dark, tarry material that adhered to the walls of the flask. The supernatant liquid was then transferred to a new flask, and addition of alkali was continued until all of the beige crystals of **3** had deposited. The solid was collected by suction filtration and washed on the funnel successively with water, ethanol, and hexane. Recrystallization from 1-butanol–DMF (9:1) afforded 6.1 g (75%) of amine **3** as off-white plates, mp 171–172 °C (lit.[1,3,4] mp 189–190 °C). The analytical sample was recrystallized from 1-butanol with color and melting point unchanged. Anal. Calcd for $C_{36}H_{36}N_9O_6P_3$: C, 55.17; H, 4.63; N, 16.09; P, 11.86. Found: C, 55.04; H, 4.61; N, 15.95; P, 11.80. Its mass spectrum displayed M^+ at *m/e* 784, and its IR (KBr) and ^1H NMR (dimethyl-d_6 sulfoxide) spectra were in accord with those reported previously.[2]

(b) From 2 by Reduction in DMF with 10% Palladium–Charcoal as Catalyst. A 250-mL Parr bottle was charged with 9.30 g (9.65 mmol) of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**), 75 mL of DMF, and 200 mg of 10% palladium–charcoal. The resulting suspension was shaken at room temperature under a hydrogen pressure of 50 psi; rapid uptake of hydrogen occurred, and within 1 h the temperature of the reaction mixture had risen to 40 °C. Approximately 2 h after the start of the reduction, the temperature began to drop and 60% of the calculated amount of hydrogen had been taken up. External heating was then applied to the reaction bottle so as to bring its temperature to 49–50 °C. This temperature was maintained for 5 h, at the end of which uptake of hydrogen was complete. The cooled reaction mixture was treated with Celite and filtered to give a clear, dark filtrate. This was concentrated in vacuo to a volume of 30 mL, and the concentrate was then added dropwise with stirring to 150 mL of cold water over a period of 20 min. The resulting suspension was filtered by suction, and the gray filter cake was washed on the funnel successively with water, ethanol, and hexane. Purification of the solid by precipitation from acid, followed by recrystallization from *o*-dichlorobenzene or 1-butanol–DMF in accordance with the method described above for amine **3**, yielded 5.60 g (74%) of hexakis(4-aminophenoxy)cyclotriphosphazene (**3**) as off-white plates, mp 171–172 °C. This compound was shown by IR, ^1H NMR, and mass spectrometry to be identical with amine **3** prepared by the procedure described above.

Hexakis(4-acetamidophenoxy)cyclotriphosphazene (4). (a) By Acetylation of Hexakis(4-aminophenoxy)cyclotriphosphazene (3). A solution of 300 mg (0.38 mmol) of amine **3** in 1.0 mL of pyridine was treated with 1.3 mL of acetic anhydride. The solution became warm, and a solid precipitated in about 2 min. The reaction mixture was stirred to break up the solid material, and the resulting suspension was set aside overnight at room temperature. Two milliliters of water was added, and the mixture was stirred for 1 h; a clear solution was obtained. Stirring was continued, and the solution was then heated to 80 °C and maintained at this temperature for 40 min; a solid separated, but it dissolved within 10 min to give a clear light brown solution, which, upon being cooled in an ice bath, afforded a light tan solid. Filtration and washing on the funnel with water followed by two recrystallizations from acetonitrile–methanol (4:1) afforded 350 mg (89%) of **4** as fine needles, mp 257–258 °C. Anal. Calcd for $C_{48}H_{48}N_9O_{12}P_3$: C, 55.65; H, 4.67; N, 12.17; P, 8.97. Found: C, 55.45; H, 4.82; N, 11.83; P, 9.16. IR (KBr) (cm^{-1}): 3280, 3190 (NH stretching); 1660 (amide carbonyl); 1260, 1225, 1193, 1176, 1157 (cyclotriphosphazene ring, P–N stretching).[14] ^1H NMR (dimethyl-d_6 sulfoxide) (δ): 9.91 (s, 6 H, amide); 6.85, 7.45 (each d_{AB}, each 12 H, J_{AB} = 9 Hz, aromatic); 2.07 (s, 18 H, methyl).

(b) By Reaction of Hexachlorocyclotriphosphazene (1) with Sodium 4-Acetamidophenoxide. This reaction was carried out in an atmosphere of dry nitrogen. A solution of 19.61 g (0.130 mol) of 4-acetamidophenol in 125 mL of THF was added dropwise with stirring over a period of 1 h to a suspension of 2.73 g (0.114 mol) of sodium hydride in 75 mL of THF maintained at 55 °C. The reaction mixture gradually turned to a thick slurry, at which point the bath temperature was raised to induce reflux. Stirring and reflux were continued for 120 h, and the suspension was then cooled to room temperature and the solid collected by filtration under nitrogen. Trituration of the solid with THF followed by Schlenk-tube filtration gave 22.7 g of nearly solvent-free sodium 4-acetamidophenoxide sufficiently pure for use in the following step.

A solution of 4.00 g (11.5 mmol) of hexachlorocyclotriphosphazene (**1**) in 100 mL of THF was added dropwise over the course of 1 h to a stirred suspension of 22.7 g of the above sodium salt in 200 mL of THF maintained at 60 °C under an atmosphere of nitrogen. After being heated at reflux for 4 h, the contents of the reaction vessel set to a nearly solid mass. This was broken up, and stirring and reflux were resumed for an additional 24 h. The suspension was cooled, filtered by suction, and the solid triturated, first with THF and then with water. This gave a gelatinous material, which, although resistant to filtration, yielded to centrifugation. The solid thus obtained weighed 10.90 g after having been dried in vacuo at 100 °C for 16 h; mp 242–247 °C. Recrystallization from ethanol–water (1:2.5) yielded 8.72 g (73%) of **4** as a white solid; mp 253.5–255.0 °C. A sample recrystallized from acetonitrile–methanol (4:1) was obtained as fine, white, felted needles, mp 255–256.5 °C. This substance was shown by a mixture melting point determination, TLC (silica gel/CH_3CN–CH_3OH), and IR data to be identical with acetate **4** prepared above by acetylation of amine **3**.

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Registry No. **1**, 940-71-6; **2**, 14711-91-2; **3**, 13441-26-4; **4**, 94732-75-9; potassium 4-nitrophenoxide, 1124-31-8; sodium 4-acetamidophenoxide, 16958-94-4; 4-nitrophenol, 100-02-7; tetra-*n*-butylammonium bromide, 1643-19-2; 4-acetamidophenol, 99-93-4.

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