Phosphonitrilic Compounds. VIII.[1] The Reaction of *o*-Aminophenol with Phosphazenes[2]

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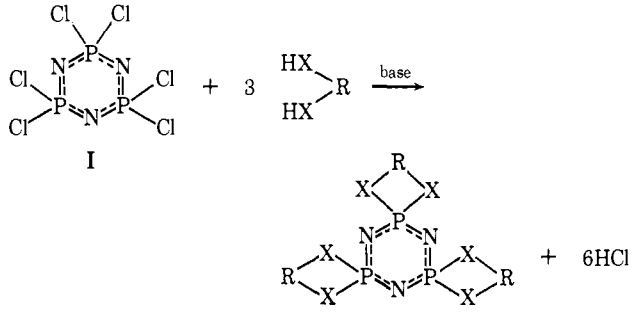
Abstract: *o*-Aminophenol reacts with a number of halo- and organophosphazenes in boiling xylene to yield bis(*o*-phenyleneoxyamino)-2-aminophenoxyphosphorane (III) and ammonium halide or ammonia. This ring cleavage reaction occurs with $(NPCl_2)_3$, $(NPCl_2)_4$, $(NPCl_2)_{15,000}$, $(NPBr_2)_3$, $(NPF_2)_3$, and with certain organocyclotriphosphazenes which contain a five-membered cyclic side unit attached to phosphorus. No reaction was observed with $[NP(OC_6H_5)_2]_3$, $[NP(OC_6H_4NO_2)_2]_3$, $[NP(NHC_6H_5)_2]_3$, or $[NP(O_2C_{12}H_8)]_3$. The structural proof for III is described and the complex reaction mechanism is discussed.

The substitution reactions of halophosphazenes with alcohols, phenols, and amines are well documented in the literature.[1,3-14] Normally, the substitution reaction proceeds stepwise to give partially or fully substituted alkoxy-, aryloxy-, or aminophosphazenes according to the equations

$$(NPCl_2)_n + 2n\text{RONa} \longrightarrow [NP(OR)_2]_n + 2n\text{NaCl}$$

$$(NPCl_2)_n + 4n\text{RNH}_2 \longrightarrow [NP(NHR)_2]_n + 2n\text{RNH}_2\text{HCl}$$

Considerable work has been reported on the reactions of cyclotri- and cyclotetraphosphazenes (n = 3 and 4),[14] but high molecular weight linear chlorophosphazenes ($n \approx 15{,}000$) are now known to react similarly.[1,12] It is also known that difunctional aromatic compounds, such as catechol, 2,3-dihydroxynaphthalene, *o*-phenylenediamine, toluene-3,4-dithiol, and 2,2′-dihydroxybiphenyl react readily with $(NPCl_2)_3$ (I) to form phosphazenes with the appropriate cyclized units at each phosphorus (II).[10,11]



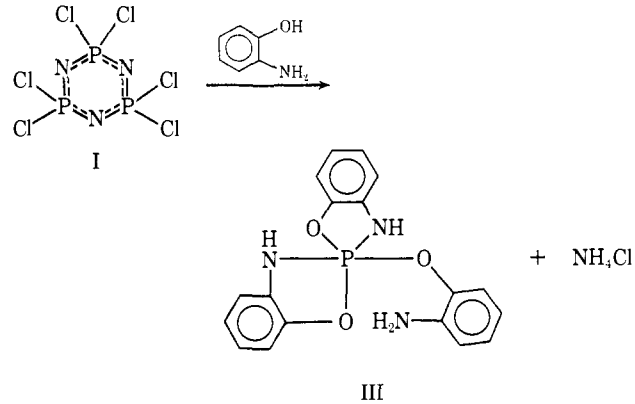
I

II

We now wish to report an alternative substitution process which leads spontaneously to an unusual breakdown of the phosphazene skeleton with formation of a novel phosphorane and ammonium halide or ammonia.

Results and Discussion

Scope of the Reaction. *o*-Aminophenol was found to react rapidly with hexachlorocycloptriphosphazene (I) at 140° in boiling xylene to yield 2-(*o*-aminophenoxy)-2,2′-spirobi[1,3,2-benzooximinophosphole], henceforth referred to as phosphorane III. A similar



I

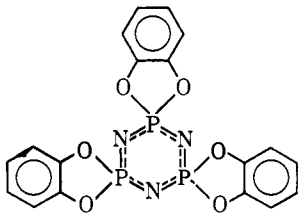
III

reaction occurred when *o*-aminophenol was allowed to interact with $(NPF_2)_3$, $(NPBr_2)_3$, $(NPCl_2)_4$, or $(NPCl_2)_n$ (where $n \approx 15{,}000$). Except in the case of $(NPBr_2)_3$, the ammonium halide sublimed from the reaction mixture, and a solution of III in xylene remained in the reaction mixture.

Phosphorane III was also isolated when tris(*o*-phenylendioxy)cyclotriphosphazene (IV), tris(2,3-dioxynaphthyl)cyclotriphosphazene (V), tris(*o*-phenylenediamino)cyclotriphosphazene (VI), 1,1-*o*-phenylenediamino-3,3,5,5-tetrachlorocyclotriphosphazene (VII), or tris(1-methyl-3,4-dithiophenyl)cyclotriphosphazene (VIII) was treated with a 6:1 excess of *o*-aminophenol under the same conditions. Ammonia and the appropriate diol, dithiol, or diamine were liberated in each case.

However, the interaction of *o*-aminophenol with cyclophosphazenes which contain two independent organic substituents at phosphorus, such as hexa(phen-

(1) Part VII: H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1716 (1966).
(2) A preliminary report of this work was contained in a previous communication: H. R. Allcock and R. L. Kugel, *Chem. Commun.*, 1606 (1968).
(3) H. Bode, K. Bütow, and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).
(4) K. John, T. Moeller, and L. F. Audrieth, *J. Am. Chem. Soc.*, **82**, 5616 (1960).
(5) T. Moeller and S. G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 1397 (1963).
(6) M. Becke-Goehring, K. John, and E. Fluck, *Z. Anorg. Allgem. Chem.*, **302**, 103 (1959).
(7) S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 5032 (1965).
(8) B. W. Fitzsimmons and R. A. Shaw, *ibid.*, 1735 (1964).
(9) R. Rätz, H. Schroeder, H. Ulrich, E. Kober, and C. Grundmann, *J. Am. Chem. Soc.*, **84**, 551 (1962).
(10) H. R. Allcock, *ibid.*, **86**, 2591 (1964).
(11) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).
(12) H. R. Allcock, R. L. Kugel, and K. J. Valan, *ibid.*, **5**, 1709 (1966).
(13) E. T. McBee, K. Okuhara, and C. J. Morton, *ibid.*, **5**, 450 (1966).
(14) For a review of phosphazene substitution reactions, see H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967, Chapter 7.



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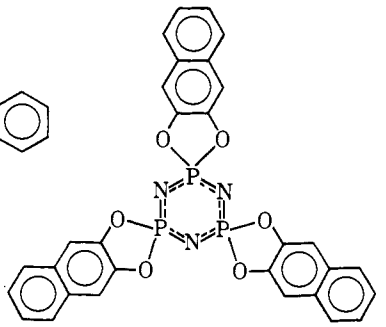
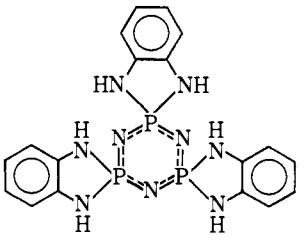


V



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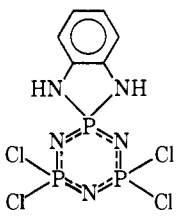
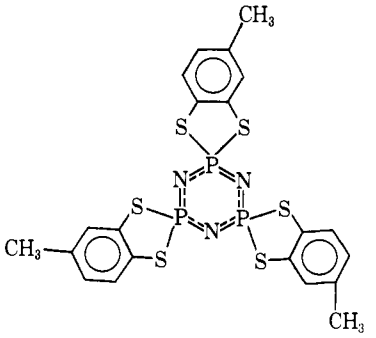
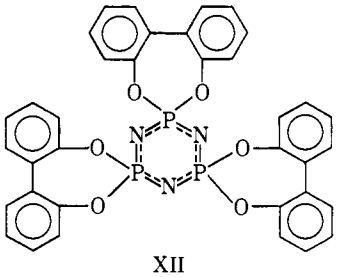


VII



VIII

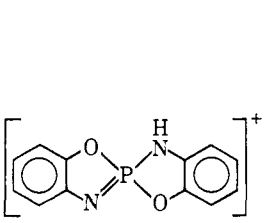


XII

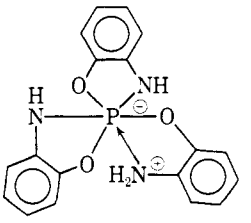
oxy)cyclotriphosphazene, $[NP(OC_6H_5)_2]_3$ (IX), hexa(*p*-nitrophenoxy)cyclotriphosphazene, $[NP(OC_6H_4NO_2\text{-}p)_2]_3$ (X), and hexa(phenylamino)cyclotriphosphazene, $[NP(NHC_6H_5)_2]_3$ (XI), resulted in no detectable reaction even after drastic reaction conditions were employed. Furthermore, no reaction took place between *o*-aminophenol and tris(2,2′-dioxybiphenyl)cyclotriphosphazene (XII) in which a seven-membered cyclic side unit is present at each phosphorus. Similarly, no reaction occurred when hexakis(trifluoroethoxy)cyclotriphosphazene, $[NP(OCH_2CF_3)_2]_3$, was treated with *o*-aminophenol in boiling xylene.

Structural Identification of Phosphorane III. Phosphorane III is a white or pale pink, crystalline solid, mp 232–238° dec. It can be purified readily by recrystallization from xylene or tetrachloroethane, or by vacuum sublimation at 184° (0.03 mm). Thin layer chromatography on a silica gel substrate demonstrated the presence of only one species, and microanalyses (see Experimental Section) were consistent with structure III. A variety of techniques were used to examine the structure of III and these are outlined in turn.

A mass spectrum showed a strong parent peak at mass number 353 (molecular weight for III is 353) and the fragmentation patterns were fully consistent with structure III. For example, a very strong base peak at mass 244 was attributed to cation XIV, formed by loss of one *o*-aminophenoxy group from III. Nearly all the other peaks in the spectrum, including metastable species at



XIV



XV

masses 77.8 and 47.7, could be readily derived from XIV. It is interesting to note the apparent stability of the five-membered rings in these fragmentation species.

Proton nmr spectra (60 Mc) in deuterioacetone provided strong evidence for structure III and argued against an alternative hexacoordinate structure (XV), at least in solution. For example, a strong aromatic multiplet was observed at τ 3.37, together with a broad singlet at τ 6.51 from NH_2 protons, and a doublet at τ 2.53 from NH protons. This doublet presumably arises from coupling with ^{31}P (J = 22 cps), and the absence of ^{31}P splitting of the NH_2 protons is consistent with structure III rather than XV. Integration indicated NH:NH_2:aryl proton ratios of 0.7:1:5.5. The lower ratio of NH protons than expected for III was ascribed to NH exchange with deuterium from the solvent. In tetrahydrofuran solvent the ratio of NH:aryl protons was 1:7. A ^{31}P spectrum of III in acetone showed one peak with a shift of +46.3 ± 1 ppm relative to triethyl phosphate. This value is more consistent with a pentacoordinate[15] than with a hexacoordinate structure where shifts considerably in excess of +100 ppm might be expected.[16]

The ultraviolet spectrum of III in dioxane was consistent with the proposed structure and showed the following maxima and shoulders (wavelengths in mμ, with log ε values in parentheses): 291 sh (4.13), 286 (4.17), 262 sh (3.47), 248 sh (3.95), and 236 (4.34). By comparison, the spectrum of *o*-aminophenol showed two bands at 291 mμ (log ε 3.53) and 240 mμ (log ε 3.65).

Infrared solution spectra in acetone, dioxane, benzene, and dimethyl sulfoxide were also consistent with structure III. Thus the sharp singlet in the 3418–3470 cm^{-1} region provided unambiguous evidence for the presence of NH groups.[17] In benzene solution, weaker aryl–NH_2 bands were also observed in the 3200–3420-cm^{-1} region. Similarly, the remainder of the solution spectrum was also consistent with a pentacoordinate

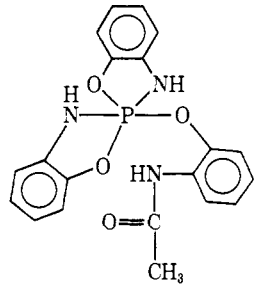
(15) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

(16) V. Mark, C. Dungan, M. Crutchfield, and J. R. Van Wazer in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith Ed., Interscience Publishers, New York, N. Y., 1967, pp 446, 447.

(17) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.

rather than a hexacoordinate form (XV). However, infrared spectra of the *solid* as a Nujol mull showed a very weak, broad band at 3215 cm^{-1} in addition to the sharp, medium intensity NH peak at 3392 cm^{-1}. The former band suggested the presence of the $^{+}NH_2$ group. Further confirmation of this was provided by the presence of a minor $^{+}NH_2$ peak at 1580 cm^{-1} and by the absence of a strong NH_2 deformation band at 1640 cm^{-1}. This would constitute marginal evidence that the hexacoordinate structure, XV, may be present in the crystalline state.[18]

In order to consolidate the general evidence for the structure of III, an acyl derivative (XVI) was prepared by reaction of III with acetyl chloride. This material



XVI

was readily isolated and purified (mp 218–220°). Its identity was confirmed by infrared, nmr, and mass spectrometry. Thus, a Nujol mull of XVI showed peaks at 3200 and 3270 cm^{-1} (sh), which correspond to those normally associated with a monosubstituted amide, and an amidic carbonyl peak at 1670 cm^{-1}. No NH_2 bands were evident in the 3110–2900-cm^{-1} region. Nmr spectra in deuterioacetone showed a multiplet at τ 2.47 from aromatic protons, a doublet at τ 2.34 (J = 22 cps) due to NH protons split by ^{31}P, a singlet at τ 8.22 from the methyl protons, and a doublet at τ 1.85 from the amidic NH group. Integration showed ratios of aryl:NH:CH_3:amidic NH of 12:2:3:1. Noticeably absent was the broad NH_2 singlet at τ 6.51 which was found in III. The ^{31}P spectrum of XVI showed one peak at +46.6 ppm. The mass spectrum showed a parent peak at 395 mass units (mol wt of XVI = 395), and an analysis of the metastable peaks fully confirmed the proposed structure. The very strong base peak at *m/e* 244 confirmed that acylation had occurred at NH_2 rather than at NH, and that the P–O bond to the noncyclized side group is the most readily cleaved of all the bonds to phosphorus.

It must be pointed out that considerable care was taken to prove that the interaction of *o*-aminophenol with IV, V, VI, VII, and VIII did, in fact, yield phosphorane III and that no mixed phosphorane species could be isolated. To this end, a careful examination of the mass spectra, infrared spectra, melting points, and thin layer chromatographic behavior was made, and in no case was evidence found for ligands other than *o*-oxoaminophenyl attached to phosphorus. Thus, remarkably, *o*-aminophenol appears to be capable of displacing all the other five-membered ring systems from phosphorus.

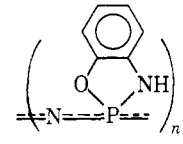
(18) Unfortunately, ^{31}P spectra of the solid have proved to be too weak for confirmation of this structure. We have recently undertaken an X-ray single-crystal examination of III in an attempt to clarify both this problem and the isomer question.

Reaction Mechanism. This is an extremely complex reaction for which no detailed over-all mechanism can be formulated at this time. The yield of III in all these reactions rarely exceeds 30–50% based on the original phosphazene, and apparently minor changes in reaction variables serve to change the reaction path profoundly. For example, lower yields of III were invariably obtained from $(NPBr_2)_3$ than from $(NPCl_2)_3$, apparently because volatilization of ammonium bromide from the reaction mixture is slow and, while present, this product can initiate side reactions or decomposition of III. Even more striking effects were observed when reaction solvents other than hot xylene were employed. No reaction took place between $(NPCl_2)_3$ and *o*-aminophenol after 16 hr in boiling benzene. In dioxane, tetrahydrofuran, or diglyme solvents, phosphazene-containing tars were formed, but no ammonium chloride was evolved and only traces of III were detected. There is, in fact, some evidence that III decomposes in hot ethers or ketones. The principle attributes of xylene as a reaction solvent appear to be its high boiling point and low polarity.

Nevertheless, certain observations do provide an insight into the over-all gross factors involved in this reaction, and these are as follows.

(1) The rate of phosphorane formation increases in the order $(NPCl_2)_3 < (NPCl_2)_4 < (NPCl_2)_n$. This follows the trend of increasing skeletal puckering and flexibility in passing from the trimer to the high polymer, and this result contradicts the supposition that release of *phosphazene* skeletal ring strain is the driving force for this reaction. This order is also consistent with the fact that propylamine and diethylamine react faster with $(NPCl_2)_4$ than with $(NPCl_2)_3$ in substitution reactions.[5,19] Thus, it is tempting to assume that phosphorane formation may be preceded by a normal nucleophilic substitution process.

(2) The formation of phosphorane III during the interaction of halophosphazenes and *o*-aminophenol takes place under conditions which would normally be expected to yield an *o*-aminooxyarylphosphazene of type XVI, or its hydrochloride salt. In the case of the trimer, the structure should be very similar to that of



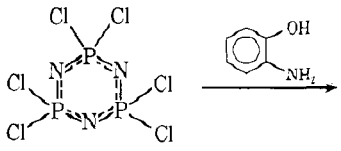
(n = 3, 4, or 15,000)

XVI

IV or VI. However, no product corresponding to XVI or its hydrochloride has yet been isolated from these reactions, although partly substituted phosphazenes have been detected by thin layer chromatography. This suggests that species such as XVI may be formed as unstable intermediates during the early stages of the reaction. Thus, it appears that, when *o*-aminophenol reacts with halophosphazenes, the first step almost certainly is an aminolysis reaction at phosphorus, followed by ring closure (I → XVIII).

Hydrochloride salt formation is assumed to occur at the ring nitrogen atoms because of their known basicity. Geminal diaminolysis at phosphorus is considered to be

(19) B. Capon, K. Hills, and R. A. Shaw, *Proc. Chem. Soc.*, 309 (1962).



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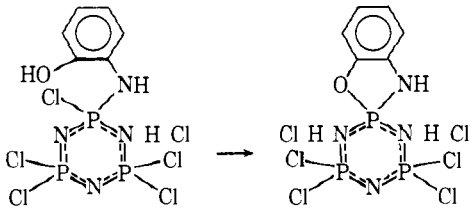
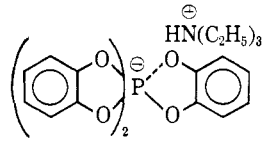


XVIII

unlikely for steric reasons, and labile species, believed to resemble XVIII, have been detected in thin layer chromatography studies. The subsequent reaction steps are largely unknown, but they probably involve degradative attack by *o*-aminophenol on the substituted phosphorus atom of XVIII or its fully substituted derivative. The process then becomes analogous to attack by *o*-aminophenol on derivatives such as IV, V, VI, or VIII.

(3) Although phosphorane III is formed by the interaction of *o*-aminophenol with phosphazenes such as IV, V, VI, or VIII which contain a five-membered ring attached to phosphorus, no reaction occurs with phosphazenes which contain a seven-membered cyclic side unit at phosphorus (XII) or two independent phenoxy or phenylamino groups at phosphorus (IX, X, and XI). Clearly, the presence of a five-membered ring system has a particular destabilizing influence on the phosphazene. This may be due to exocyclic ring strain (the O–P–O angle in IV is known to be 97°[20]), or it could reflect the exposure of the phosphorus atoms to attack by an incoming nucleophile. The former influence appears to be more important since models of XII indicate that exposure of phosphorus to attack is still high, but the O–P–O bond must be widened above 103°. Steric widening of the O–P–O angle above 100° is an expected feature of phosphazenes IX, X, and XI also because of mutual side group repulsions. Thus, the narrow O–P–O, S–P–S, HN–P–NH, or O–P–NH angles appear to be the significant factor for initiation of phosphazene formation.

(4) Phosphoranes which contain five-membered rings are generally stable. This has been shown by the extensive work of Ramirez,[15] by the work of Wolf with aliphatic derivatives,[21] and by our earlier observations with phosphorane XIX.[10] The stability of these compounds is probably connected with the ability of the



XIX

O–P–O angle to approximate to 90° in a trigonal-bipyramidal structure. The facile formation of III from the various phosphazenes almost certainly reflects the greater stability of a five-membered ring in a penta- or hexacoordinate phosphorane than in a phosphazene. In phosphazenes the preferred exocyclic angle at phosphorus is 103–104°,[14] whereas ring strain in IV, V, VI, VIII, or XVI will reduce the angle to 97° or less.[20] Thus, the driving force for the present reaction appears to be the release of *exocyclic* ring strain when a phosphazene is converted to a phosphorane.

(5) Perhaps the most surprising result from a mechanistic point of view is the fact that the same phosphorane (III) is isolated irrespective of the initial side group structure of the phosphorane. No mixed phosphoranes were detected. Furthermore, treatment of phosphazene IV with aniline or with phenol alone (or together) or with aniline hydrochloride did not yield a phosphorane. Furthermore, the formation of XIX from IV occurs with catechol only in the presence of a base such as triethylamine. Thus, it was concluded that the unique characteristics of *o*-aminophenol in this reaction result from the presence of both basic and acidic sites on the molecule and from the zwitterionic character which causes it to react as $o\text{-}H_3N^+\text{–}C_6H_4\text{–}O.^-$ The powerful ability of this reagent to displace catechol, 2,3-dihydroxynaphthalene, *o*-phenylenediamine, and 3,4-toluenedithiol from phosphorus must reflect a rapid scrambling process at phosphorus in which the initial attack by *o*-aminophenol is rate determining (no intermediates are isolated). This initial attack could be by RO^- on phosphorus, or by RN^+H_3 on oxygen or ring nitrogen.

(6) Finally, it should be pointed out that ten isomers of structure III are theoretically possible, but that only one species has been detected in the present work. However, it is reasonable to assume that the free *o*-aminophenoxy ligand occupies an equatorial position, since this would allow both O–P–N bond angles to approach 90°, and this reduces the number of expected isomers to six.

It is anticipated that the above questions will be clarified by work now in progress on the reactions of phosphazenes with other nucleophiles and from a detailed structural examination of phosphorane III.

Experimental Section[22]

Materials. Hexachlorocyclotriphosphazene (I), obtained from Hooker Chemical Co., was recrystallized twice from *n*-heptane to give material of mp 112–112.5°. Hexafluorocyclotriphosphazene, mp 26–27°, was prepared by a modification of the metathetical reaction between hexachlorocyclotriphosphazene and sodium fluoride.[23] Hexabromocyclotriphosphazene, mp 189.5–191°, was synthesized by the reaction of ammonium bromide with phosphorus tribromide and bromine.[24] Octachlorocyclotetraphosphazene (Hooker Chemical Co.) was recrystallized from *n*-heptane before use to give material of mp 121–123°. Poly(dichlorophosphazene) was prepared by the thermal polymerization of I, and low molecular weight homologs were removed by repeated precipitation of a benzene solution of the polymer into *n*-heptane.[12] Hexaphenoxycyclotriphosphazene (IX), mp 111.5–112°, was prepared by the reaction of sodium phenoxide with I.[25] Hexakis(4-nitro-

(20) L. A. Siegel and J. H. van den Hende, *J. Chem. Soc.*, 817 (1967).
(21) M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *Bull. Soc. Chim. France*, 772 (1968).

(22) Mass spectrometric data were obtained with the use of an A.E.I MS 9 spectrometer, infrared spectra were measured on Perkin-Elmer 621 or Beckman IR5A spectrometers, and ultraviolet spectra were recorded on a Cary Model 15 spectrometer. Proton nmr spectra were obtained using a Varian A-60A instrument. ^{31}P measurements were kindly recorded by Dr. J. Lancaster at American Cyanamid Co. on a Varian DP60 instrument at 16.2 Mc. Microanalyses were by Midwest Microlab. Thin layer chromatography work was carried out using chloroform-impregnated D-5 Kiesel-gel with elution by 10% tetrahydrofuran in benzene.
(23) T. Moeller, K. John, and F. Tsang, *Chem. Ind.* (London), 37 (1961).
(24) T. Moeller and K. John, *J. Inorg. Nucl. Chem.*, 22, 199 (1961).

Table I. Reactions of Phosphazenes with *o*-Aminophenol in Boiling Xylene

Phosphazene	Moles of phosphazene ($\times 10^2$)	Moles of *o*-aminophenol ($\times 10^2$)	Xylene, ml	Reaction time, hr	Yield of III based on phosphazene, %
$(NPCl_2)_3$ (I)	4.5	27	1000	16	21.3
$(NPCl_2)_4$	0.25	1.73	65	16[a]	31
$(NPCl_2)_n$	13	2.3	230	16[a]	42
$(NPBr_2)_3$	0.165	0.109	40	1[b]	33
$(NPF_2)_3$	0.4	2.5	85	12	<1
VII	0.29	2	100	16	<10
VI	0.5	6	150	3	<25
IV	1.2	0.22	50	18	67[c]
	0.5	0.5	100	18	23[d]
V	0.164	0.984	50	18	100

[a] Reaction complete in shorter time. [b] Product III not obtained after longer reaction times. [c] Yield quantitative based on *o*-aminophenol. [d] Yield of 41% based on *o*-aminophenol.

phenoxy)cyclotriphosphazene (X), mp 248°, was prepared by reaction of 4-nitrophenol with I, using sodium carbonate as a hydrogen chloride acceptor.[26] Hexa(N-phenylamino)cyclotriphosphazene (XI), mp 270–272°, was prepared by the interaction of aniline with I.[27]

1,1-(*o*-Phenylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene (VII) and 1,1,3,3,5,5-tris(*o*-phenylenediamino)cyclotriphosphazene (VI) were prepared by reaction of *o*-phenylenediamine with I.[11]

Tris(*o*-phenylenedioxy)cyclotriphosphazene (IV), tris(2,3-dioxynaphthyl)cyclotriphosphazene (V), mp 333–335°, and tris(2,2′-dioxybiphenyl)cyclotriphosphazene (XII) were obtained by the interaction of I with catechol, 2,3-dihydroxynaphthalene, or 2,2′-dihydroxybiphenyl.[10,11] Tris(1-methyl-3,4-dithiophenyl)cyclotriphosphazene (VIII), mp 256–263°, was prepared by reaction of toluene-3,4-dithiol with I in the presence of triethylamine.[11]

o-Aminophenol (Aldrich), mp 172–174°, was recrystallized from ethyl acetate; aniline (Eastman) was distilled at 182–183° before use; catechol (Eastman), mp 102–104°, was recrystallized from chloroform; 2,2′-dihydroxybiphenyl (Aldrich), mp 107–109°, was recrystallized from chloroform–pentane; 2,3-dihydroxynaphthalene (Aldrich), mp 163–165°, and toluene-3,4-dithiol (Eastman) were used as received.

Reaction of Hexachlorocyclotriphosphazene (I) with *o*-Aminophenol. A solution of I (15.6 g, 0.045 mole) in dry xylene (200 ml) was added to a boiling solution of *o*-aminophenol (29.4 g, 0.27 mole) in xylene (800 ml). Almost immediately, ammonium chloride began to sublime to the cooler parts of the apparatus and precipitation of III occurred. After 16 hr at reflux temperature the hot solution was filtered, and orange needles of III crystallized out. These were recrystallized three times from hot tetrachloroethylene to yield pale salmon colored needles of **bis(*o*-phenyleneoxyamino)-2-aminophenoxyphosphorane** (III), mp 232–238° dec. *Anal.* Calcd for $C_{18}H_{16}O_3N_3P$: C, 61.19; H, 4.76; N, 11.89; P, 8.77. Found: C, 61.09; H, 4.78; N, 11.48; P, 8.37. The sublimate and hot xylene-insoluble product were identified as ammonium chloride by their infrared spectra and reactions.

Acetylation of Phosphorane III. A slurry of acetyl chloride (1.32 g, 0.017 mole) and pyridine (1.18 g, 0.015 mole) in tetrahydrofuran (50 ml) at 25° was added to a solution of III (1.42 g, 0.004 mole) in tetrahydrofuran (100 ml). After 5 min the mixture was filtered and the solvent was removed at reduced pressure to yield a yellow oil. This solidified when treated with benzene to give a pale yellow material. This was recrystallized from boiling tetrachloroethylene and from boiling xylene to yield **bis(*o*-phenyleneoxyamino)-2-acetylaminophenoxyphosphorane** (XVI), mp 218–220°. Its identity was confirmed as discussed previously by infrared, nmr, and mass spectrometric data.

Reaction of Other Halophosphazenes with *o*-Aminophenol. The procedure was similar to that described above except that, in the case of $(NPBr_2)_3$, minimal sublimation of ammonium bromide occurred and most remained as a precipitate in the reaction mixture. Reaction times, stoichiometries, and yields are listed in Table I.

Reaction of Tris(*o*-phenylenedioxy)cyclotriphosphazene (IV) with *o*-Aminophenol. *o*-Aminophenol (1.32 g, 0.012 mole) was added to a solution of IV (1 g, 0.0022 mole) in boiling xylene (50 ml) and the mixture was heated at reflux for 18 hr. Ammonia was evolved during this time. After filtration of the hot solution, III crystallized from solution. Relevant reaction dat. are recorded in Table I. The phosphorane was identified on the basis of its infrared, mass spectrometric, and thin layer chromatographic behavior.

Reaction of Other Organocyclophosphazenes with *o*-Aminophenol. The general procedure outlined above was used for the reactions of phosphazenes V, VI, VII, VIII, and those which did not react, such as XII, IX, X, and $[NP(OCH_2CF_3)_2]_3$. To confirm the unreactivity of these latter cyclophosphazenes, longer reaction times were used, and quantitative recovery of the cyclophosphazene was carried out at the end of the reaction. Relevant data for reactions which did take place are listed in Table I.

Treatment of IV with Phenol, Aniline, and Catechol. Phenol (4.23 g, 0.045 mole) and IV (2.30 g, 0.005 mole) were allowed to interact in boiling xylene for 18 hr. No phosphorane was formed but small amounts of side group cleavage products were detected. Aniline (2.8 g, 0.03 mole) in xylene (25 ml) was added slowly to IV (2.3 g, 0.005 mole) in xylene (50 ml). After 16 hr at reflux temperature, a 90% recovery of IV was obtained. No phosphorane was detected. Similarly, IV was recovered unchanged from a mixture of IV (2.3 g, 0.005 mole), phenol (2.8 g, 0.03 mole), and aniline (2.8 g, 0.03 mole) after 18 hr in boiling xylene solution. Some evidence was obtained for the formation of oily, weak adducts between IV and phenol in the initial stages of the recovery of IV. No reaction took place when IV (2.3 g, 0.005 mole), aniline (2.8 g, 0.03 mole), and aniline hydrochloride (3.9 g, 0.03 mole) were allowed to interact in xylene (100 ml) for 18 hr. No phosphorane was formed when IV (2.3 g, 0.005 mole) was treated with catechol (3.24 g, 0.03 mole) in boiling xylene (100 ml) for 18 hr.

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