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Substituent Exchange and Carbon–Oxygen Bond Cleavage with Aryloxycyclophosphazenes[1,2]

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Abstract: Aryloxycyclotriphosphazenes, $[NP(OAr)_2]_3$, such as I–IV, undergo substituent exchange reactions with organic nucleophiles. This constitutes a route for the preparation of mixed substituent organophosphazenes, some of which are inaccessible by other methods. The ease of displacement of OAr in $[NP(OAr)_2]_3$ by $CF_3CH_2O^-$ decreased with OAr in the order, $OC_6H_4NO_2$-*o* or -*p* > OC_6H_5Cl-*p* ≫ OC_6H_5. When OAr was $OC_6H_4NO_2$-*o* or -*p*, ligand exchange was either accompanied by or replaced by nucleophilic attack at the α-carbon of the aromatic residue. This effect was significant when the attacking nucleophile was $C_6H_5O^-$ or $C_6H_5S^-$, and it predominated when the nucleophile was $C_6H_5NH^-$ or an uncharged primary or secondary amine. The mechanisms of these reactions are discussed.

The majority of known organocyclo- or organopolyphosphazenes has been prepared by the nucleophilic replacement of halogen in halophosphazenes by alkoxide, aryloxide, or amine reagents,[3] by reactions such as:

$$(NPCl_2)_n \xrightarrow[\text{or } RNH_2]{RO^-} [NP(OR)_2]_n \text{ or } [NP(NHR)_2]_n$$

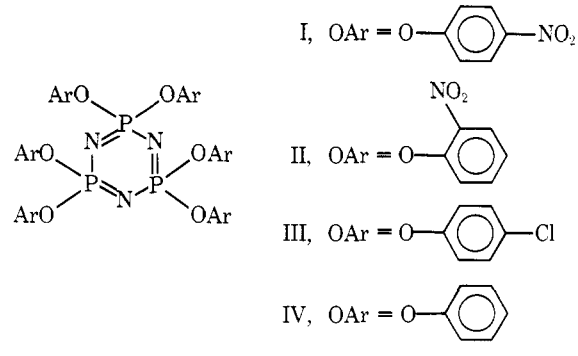
$$(\text{where } n = 3, 4, \text{ or } \sim 15\,000)$$

However, evidence exists from organophosph*ate* chemistry that the replacement of one organic ligand at phosphorus by another can be a facile process.[4] Furthermore, preliminary evidence had been obtained that organic ligand exchange reactions could also occur with cyclophosphazenes.[5] Hence, the prospect existed that the known range of organophosphazene trimers and tetramers might be expanded by the use of organic ligand exchange processes, such as:

$$[NP(OR)_2]_3 + xR'O^- \rightarrow N_3P_3(OR)_{6-x}(OR')_x + xRO^-$$

This work was undertaken with the recognition that ligand exchange data obtained for cyclic trimeric phosphazene systems could ultimately prove valuable for the synthesis of mixed substituent organophosphazene high polymers.[6]

Four aryloxycyclophosphazenes were employed in this investigation. These are depicted as structures I–IV. The solvents



employed varied from dimethylformamide (DMF) or hexamethylphosphoramide (HMPA) to dioxane or tetrahydrofuran (THF). A number of attacking nucleophiles were used, including sodium trifluoroethoxide, sodium phenoxide, sodium thiophenoxide, sodium anilide, and various amines.

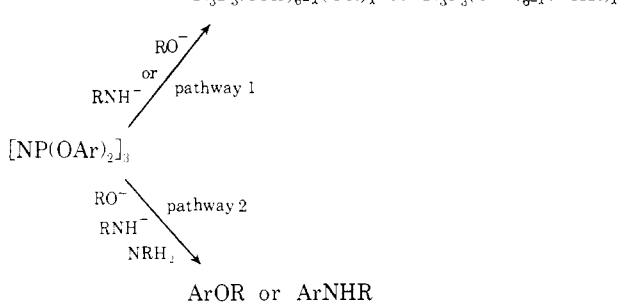
Two different reaction pathways were identified. The first involved simple replacement of one substituent group at

Table I. Reaction Conditions and Products for Ligand Exchange and Addition-Elimination Reactions[a]

Initial phosphazene	Nucleophile	Molar ratio of nucleophile: phosphazene	Solvent	Temp (°C)	Phosphazene products	Other products
I	$CF_3CH_2O^-$	1:1	DMF-THF[b,c]	65	V	VII, VIII-IX
		3:1			V (34%)	VII, VIII-IX
		6:1			V, VI	VII, VIII-IX
		3:1		25	V, VI	—
		3:1	HMPA[d]	65	V	VII, IX
		3:1	Dioxane	100	V, VI	—
		6:1	THF	65	V, VI	—
II		3:1	THF	25	X, XI	XII
III		6.6:1	THF	65	V (85%), XIII	—
IV		7:1	THF	65	V, XIX	—
III	$C_6H_5O^-$	6.6:1	THF	65	—[e]	—
I		6:1	DMF	45	—	XV, (VIII-IX)
II		6.6:1	THF	65	—	XVI, IX
I	$C_6H_5S^-$	7:1	DMF	45	—	XVII
III	$C_6H_5NH^-$	—	—	—	—	—
IV		7:1	THF	65	XVIII	—
II		8:1	THF	25	—	XIX
I or II	RNH_2	12:1	THF	65	—	XX, XXII, (VII)
I or II	R_2NH	18:1	THF	65	—	XXI, XXII
I	DMF	—	DMF	60	—[e]	—
I		—	DMF	120	—	XXIII

[a] I = $[NP(OC_6H_4NO_2\text{-}p)_2]_3$; II = $[NP(OC_6H_4NO_2\text{-}o)_2]_3$; III = $[NP(OC_6H_4Cl\text{-}p)_2]_3$; IV = $[NP(OC_6H_5)_2]_3$; V = $[NP(OCH_2CF_3)_2]_3$; VI = $N_3P_3(OC_6H_4\text{-}p)_{6-n}(OCH_2CF_3)_n$ (n = 1-5); VII = $O(C_6H_4NO_2\text{-}p)_2$; VIII = "phosphazane" of type, $[HN\text{-}P(O)C_6H_4\text{-}NO_2]_3$; IX = sodium cyclophosphazenate salt or organophosphate salt; X = $N_3P_3(OC_6H_4NO_2)_3(OCH_2CF_3)_3$—probably non-gem; XI = $N_3P_3(OC_6H_4NO_2)_2(OCH_2CF_3)_4$; XII = $CF_3CH_2OC_6H_4NO_2\text{-}o$; XIII = $N_3P_3(OC_6H_4Cl\text{-}p)_{6-n}(OCH_2CF_3)_n$ (n = 1-5); XIV = $N_3P_3(OC_6H_5)_{6-n}(OCH_2CF_3)_n$ (n = 1-5); XV = $C_6H_5OC_6H_4NO_2\text{-}p$; XVI = $C_6H_5OC_6H_4NO_2\text{-}o$; XVII = $C_6H_5SC_6H_4NO_2\text{-}p$; XVIII = $N_3P_3(OAryl)_5(NHC_6H_5)$, $N_3P_3(OAryl)_4(NHC_6H_5)_2$, etc; XIX = $C_6H_5NHC_6H_4NO_2\text{-}o$; XX = $RNHC_6H_4NO_2$; XXI = $R_2NC_6H_4NO_2$; XXII = phosphazene degradation products; XXIII = $(CH_3)_2NC_6H_4NO_2\text{-}p$. [b] DMF = dimethylformamide, THF = tetrahydrofuran. [c] DMF-THF in 5:1 vol ratio. [d] HMPA = hexamethylphosphoramide. [e] No reaction.

phosphorus by another via a nucleophilic attack at phosphorus (pathway 1). The second proceeded through nucleophilic attack by the reagent at an α-aromatic carbon atom of the aryloxy substituent to yield ethers or amines (pathway 2).



Results and Discussion

In the following sections the use of trifluoroethoxide ion as an attacking reagent will be discussed first together with the solvent effects in this system. The use of phenoxide and thiophenoxide ions will then be described, followed by a consideration of the reactions of amines and anilide ion with the aryloxyphosphazenes. The reaction mechanisms will be considered last.

Reactions of Phosphazenes I–IV with Trifluoroethoxide Ion. All four aryloxyphosphazenes (I–IV) reacted with trifluoroethoxide ion. Hexakis(p-nitrophenoxy)cyclotriphosphazene (I) reacted via pathways 1 and 2 to yield products identified as V–IX.

$$\underset{\text{I}}{[NP(OC_6H_4NO_2\text{-}p)_2]_3} \xrightarrow{NaOCH_2CF_3} \underset{\text{V}}{[NP(OCH_2CF_3)_2]_3} +$$

$$[NP(OC_6H_4NO_2)_{6-n}(OCH_2CF_3)_n]_3 +$$
VI (n = 1-5)

$$O_2N\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}NO_2 + [HNP(O)OC_6H_4NO_2]_3 +$$
VII VIII

"organophosphate" or cyclophosphazenate salt
IX

The distribution of the products under different reaction conditions is shown in Table I.

Pathway 1 (ligand exchange), to yield species such as V or VI, was favored in low polarity solvents such as dioxane or tetrahydrofuran. Phosphazene I is only poorly soluble in low polarity solvents, and these reactions were heterogeneous from the start. Moreover, sodium p-nitrophenoxide precipitated from the medium as the reactions progressed. The main reaction products in the temperature range, 65–100°, were mixed substituent cyclophosphazenes (VI) when a 3:1 ratio of nucleophile to I was employed, or both fully and partly substituted products (V and VI) when a 6:1 ratio of reagents was used. Substituent exchange was also the main pathway in a homogeneous system when a 5:1 DMF:THF solvent system was used at 25°. Compound V was the main product, together with all the stoichiometric combinations corresponding to formula VI. Of these mixed substituent derivatives, the tristrifluoroethoxytris-p-nitrophenoxy compound was formed in the largest amount. This compound was believed to have the nongeminal structure, $[NP(OC_6H_4NO_2)(OCH_2CF_3)]_3$.

However, pathway 2 (α-carbon attack) became evident in the 5:1 DMF:THF system when the temperature was raised to 65°. Under these conditions an equimolar mixture of I and $CF_3CH_2O^-$ ion yielded only a trace of V, no mixed substituent phosphazenes (VI), but substantial quantities of 4,4′-dinitro-

diphenyl ether (VII) and a compound believed to be phosphazane VIII. Dimethylformamide itself does not attack I under the conditions of this reaction, nor is it possible to synthesize VII from *p*-nitrophenol and base in DMF solvent. An increase in the molar ratio of $CF_3CH_2O^-$ to I from 1:1 to 3:1 gave a nearly 40% yield of V, together with 4,4′-dinitrodiphenyl ether and an organophosphate or phosphazenate-type product (IX). Similar results were obtained in hexamethylphosphoramide solvent at 65°, but larger amounts of IX were formed. A further increase in the molar ratio of $CF_3CH_2O^-$ to I to 6:1 in the DMF–THF system at 65° yielded mainly V (72%), but traces of VI and substantial amounts of VII and IX were formed as well.

Similar products were formed when the *o*-nitrophenoxyphosphazene (II) reacted with trifluoroethoxide ion. Compound II is more soluble in etheric solvents than is compound I. Hence, homogeneous systems in THF could be studied. At 25° in THF solvent a 3:1 molar ratio of $CF_3CH_2O^-$ to II yielded $[NP(OC_6H_4NO_2\text{-}o)(OCH_2CF_3)]_3$ in 71% yield together with smaller amounts of $N_3P_3(OC_6H_4NO_2\text{-}o)_2(OCH_2CF_3)_4$, bis(*o*-nitrophenyl) ether, and a detectable trace of $CF_3CH_2OC_6H_4NO_2\text{-}o$. This latter product was presumably formed by direct attack by $CF_3CH_2O^-$ on the α-carbon atom of II.

Pathway 1 appeared to be the exclusive route for the reaction of a sixfold excess of sodium trifluoroethoxide with $[NP(OC_6H_4Cl\text{-}p)_2]_3$ (III) or $[NP(OC_6H_5)_2]_3$ (IV) in THF or THF–DMF solution. Compound III yielded $[NP(OCH_2CF_3)_2]_3$ (V), $N_3P_3(OC_6H_4Cl\text{-}p)(OCH_2CF_3)_5$, and $N_3P_3(OC_6H_4Cl\text{-}p)_2(OCH_2CF_3)_4$. Compound IV yielded V, high yields of $N_3P_3(OC_6H_5)_3(OCH_2CF_3)_3$ and smaller amounts of $N_3P_3(OC_6H_5)_2(OCH_2CF_3)_4$ and $N_3P_3(OC_6H_5)(OCH_2CF_3)_5$.

Thus, the results suggest that the initial reaction involves a replacement of aryloxy groups at phosphorus by trifluoroethoxy groups. In solvents such as dioxane or THF, the aryloxide ion is removed from the system by precipitation, and pathway 2 cannot be followed easily. However, in more polar solvents, such as DMF–THF or hexamethylphosphoramide, the nitrophenoxide ion attacks the α-carbon atoms of the aryloxy groups still bound to phosphorus to generate bis(nitrophenyl) ether, with the concurrent formation of phosphazanes and ring cleavage products. Higher temperatures and longer reaction times presumably favor this latter process. *p*-Chlorophenoxy- and phenoxyphosphazenes show an intrinsically reduced tendency to follow pathway 2 since no evidence for α-carbon attack was obtained with these compounds.

Reactions of I–IV with Phenoxide and Thiophenoxide Ions. Sodium phenoxide did not react with hexakis(*p*-chlorophenoxy)cyclotriphosphazene (III) in boiling tetrahydrofuran. However, both sodium phenoxide and sodium thiophenoxide reacted with the *o*- or *p*-nitrophenoxyphosphazenes (II and I) in DMF–THF or DMF media to yield products characteristic of pathway 2. No phosphazenes at all could be isolated from the reactions of a 6:1 ratio of sodium phenoxide to I or II in DMF–THF. The reaction products included the appropriate nitrophenol, phenol, and nitrophenyl phenyl ether. The remaining products appeared to be phosphazanes or ring degradation products. Sodium thiophenoxide reacted with I in DMF solvent to yield *p*-nitrophenyl phenylsulfide.

Reactions of I–IV with Anilide Ion and Amines. Sodium anilide proved to be a powerful nucleophile for attack at the α-carbon atoms of the nitrophenoxyphosphazenes, I and II, even in THF solvent. For example, *N*-*o*-nitrophenylaniline was isolated from the reaction of II with sodium anilide, but no mixed substituent anilino–nitrophenoxyphosphazenes could be detected. By contrast, the reactions of the *p*-chlorophenoxy- and phenoxyphosphazenes (III and IV) with sodium anilide occurred exclusively via nucleophilic attack at phosphorus to yield mixed anilino–aryloxycyclotriphosphazenes. Specifically, a 7:1 molar mixture of sodium anilide and IV in THF yielded $N_3P_3(OC_6H_5)_5(NHC_6H_5)$ and $N_3P_3(OC_6H_5)_4(NHC_6H_5)_2$, together with smaller amounts of other mixed substituent trimers.

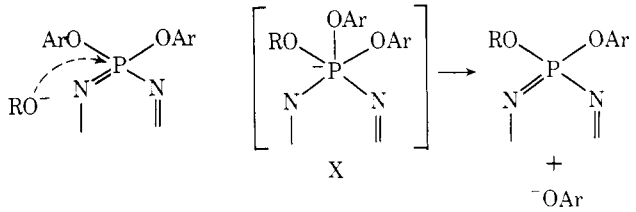
Primary and secondary amines are relatively weak nucleophiles compared to charged oxyanions or anilide ion. Hence, it was not surprising that only one previous report existed in which an uncharged amine reacted with an organophosphazene.[5] In this instance the reaction involved cleavage of a strained five-membered ring. Apart from this reaction, it appeared that most organophosphazenes were unreactive toward amines. In the present work this was found to be true for *p*-chlorophenoxy- and phenoxycyclophosphazenes (III and IV), which were found to be unreactive to propylamine, cyclohexylamine, or diethylamine.

However, the nitrophenoxycyclotriphosphazenes (I and II) were highly reactive to *n*-propylamine, *n*-butylamine, cyclohexylamine, diethylamine, di-*n*-propylamine, and diisopropylamine in THF solution. No simple ligand exchange products were detected. Instead, the products corresponded exclusively to those resulting from pathway 2. For example, *n*-propylamine reacted with II to yield *N*-propyl-*o*-nitroaniline. The residual phosphazane-type product eliminated 2,2′-dinitrophenyl ether on heating. *n*-Butylamine, diethylamine, di-*n*-propylamine, and cyclohexylamine yielded *N*-*n*-butyl-*o*-nitroaniline, *N*,*N*-diethyl-*o*-nitroaniline, *N*,*N*-dipropyl-*o*-nitroaniline, and *N*-cyclohexyl-*o*-nitroaniline, respectively. Ethyl glycinate reacted with II to yield *N*-*o*-nitrophenyl ethyl glycinate. However, the reactivity of the amine and the yield of the nitroaniline decreased sharply as the steric size of the amine was increased. This was especially evident with di-*n*-propylamine and diisopropylamine. Aniline and diphenylamine did not react with II, a fact that can be ascribed to the lower availability of the lone pair electrons in aromatic amines.

It should be noted that the phosphaz*ane*-type residues formed when II reacted with primary amines appeared to exist as "salt"-like adducts with excess primary amine, since the amine could be liberated by the addition of water. Presumably, these complexes resemble the well-known red or orange $NO_2\cdots H_2NR$ type adducts formed between aromatic nitro compounds and amines.[7,8]

Reaction Mechanism

The substituent exchange process (pathway 1) almost certainly takes place by a mechanism in which the incoming nucleophile attacks at phosphorus, probably via the formation of a pentacoordinate transition state (X). Close comparisons



can be drawn between this type of process and the hydrolyses of alkoxy- or aryloxycyclophosphazenes[9,10] and perhaps also with the reactions of halocyclo- or polyphosphazenes with alkoxides, aryloxides, or amines.[3] The limits of this pathway appear to be set by the nucleophilicity of the attacking reagent and by the leaving-group properties of the initial ligand. Trifluoroethoxide ion can displace aryloxy groups from phosphorus, but the ease of displacement of the leaving group decreases in the order: $OC_6H_4NO_2\text{-}o$- or -p > OC_6H_4Cl > OC_6H_5. Anilide ion can displace aryloxy groups from $[NP(OC_6H_4Cl\text{-}p)_2]_3$ or $[NP(OC_6H_5)_2]_3$, but it is too powerful a nucleophile for ligand exchange with nitrophenoxyphosphazenes.

One driving force for ligand exchange is the replacement of a bulky substituent by smaller group to reduce intramolecular steric crowding. The facile displacement of aryloxy by trifluoroethoxy groups may be a consequence of this effect. However, it should be recognized that the apparent preponderance of substituent exchange to α-carbon attack in some systems may merely reflect the fact that the displaced anion salt is insoluble in the medium.

When substituent exchange does occur, replacement could take place by a geminal or nongeminal mechanism. The experiments reported here do not distinguish between these two alternatives. However, the reaction of phosphazene I with trifluoroethoxide ion does yield a tris derivative, $N_3P_3(OC_6H_4NO_2\text{-}p)_3(OCH_2CF_3)_3$, in higher yield than the mono-, bis-, tetrakis-, or pentakis-substituted compounds. Hence, a nongeminal pathway may be preferred, with activation of the molecule following the introduction of the first two trifluoroethoxy groups.

Pathway 2 requires a nucleophilic attack on the α-carbon atom of an aryloxy group bound to phosphorus. This reaction is analogous to conventional addition-elimination type nucleophilic substitutions[11,12] and to the reactions of *o*- and *p*-nitrophenyl phosphate esters under nucleophilic attack.[13-15]

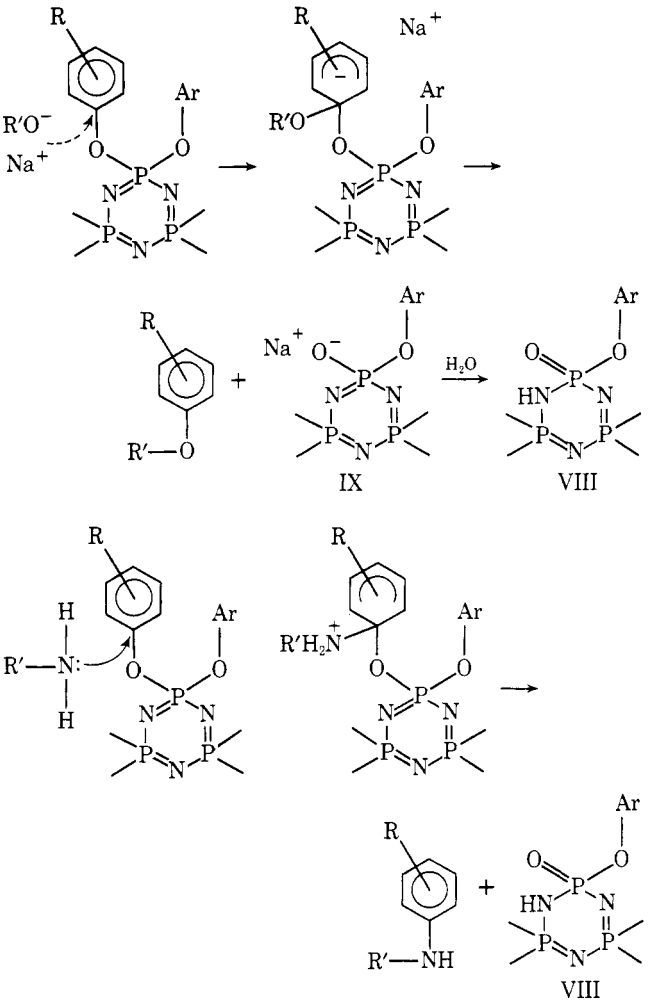
Liberation of an ether or an amine from an aryloxyphosphazene would be expected to leave a phosphazene salt or a phosphazane residue, as depicted in IX and VIII. The phosphorus-containing residues from these reactions could not be purified or identified unambiguously, but the infrared spectra were consistent with structures such as IX and VIII.

When both ligand exchange and α-carbon attack can occur in the same system, the latter process could involve either the initial anion or the anion released by the exchange reaction. When the nitrophenoxyphosphazenes react with trifluoroethoxide ion, the trifluoroethoxide ion is more reactive toward attack at phosphorus and it is rapidly consumed in the reaction. The released anion then undergoes α-carbon attack since the dinitrodiphenyl ether is the principal etheric product. Only traces of trifluoroethyl nitrophenyl ether were detected. When phenoxide or thiophenoxide ions react with I or II, it is the initial nucleophile that attacks by pathway 2. Hence, ligand exchange is probably slower than α-carbon attack in these particular systems.

Direct comparisons with related addition-elimination reactions were not made. However, it was shown that although the reaction of I with *p*-nitrophenoxide yielded 4,4′-dinitrophenyl ether, neither tris(*p*-nitrophenyl)phosphate nor *p*-nitroanisole showed evidence of α-carbon attack with sodium *p*-nitrophenoxide in THF-DMF solvent at 65°. Hence, the phosphazene ring has an activating effect for α-carbon attack when compared with a methyl group or a phosphate ester residue.

Experimental Section

Materials. *p*-Nitrophenol (Aldrich) was recrystallized twice from toluene to give material, mp 110-112°. *o*-Nitrophenol (Eastman) was recrystallized twice from 100% ethanol, then sublimed in vacuo to give yellow needles, mp 42-43.5°. Phenol was vacuum distilled before use. Tetrahydrofuran (THF) (Fisher) was refluxed over lithium aluminum hydride and then distilled before use. *N,N*-Dimethylformamide (DMF) (J. T. Baker) was shaken with barium oxide and vacuum distilled before use. 1,4-Dioxane (Fisher) was purified by boiling with aqueous hydrochloric acid, followed by treatment with potassium hydroxide pellets. It was then distilled from sodium and stored over molecular sieves. Diethyl ether (J. T. Baker) was refluxed over lithium aluminum hydride and distilled before use. Aniline (J. T. Baker) was boiled with zinc dust and fractionally distilled from the same reagent. *n*-Propylamine (Eastman), *n*-butylamine (Eastman), and diethylamine (Fisher) were shaken with a mixture of barium oxide (Fisher) and potassium hydroxide, then distilled from this mixture. Diphenylamine (Aldrich), cyclohexylamine (J. T. Baker), dipropylamine (Eastman), and diisopropylamine (Eastman) were used as received. Sodium carbonate (Fisher) was dried overnight in vacuo at 110°.



Preparations. Sodium 2,2,2-trifluoroethoxide was prepared from sodium and trifluoroethanol (Halocarbon Chemicals) in dry THF. Sodium thiophenoxide was synthesized by the addition of sodium to a solution of thiophenol (Aldrich) in diethyl ether. Sodium anilide was prepared by the reaction of sodium with aniline (J. T. Baker) in the presence of finely divided copper metal.[16] All preparations were carried out under an atmosphere of dry nitrogen. Sodium *p*-nitrophenoxide was made by the addition of potassium hydroxide to a solution of *p*-nitrophenol in ethanol.[17]

Hexachlorocyclotriphosphazene (El Monte Chemical Corp.) was recrystallized twice from *n*-hexane and then sublimed to give material, mp 113-114°. Hexakis(*p*-nitrophenoxy)cyclotriphosphazene (I) was prepared by the reaction of hexachlorocyclotriphosphazene with *p*-nitrophenol,[10,18] to give a white solid, mp 260-261°. Hexakis(*o*-nitrophenoxy)cyclotriphosphazene (II) was synthesized by the reaction of hexachlorocyclotriphosphazene with *o*-nitrophenol in the presence of sodium carbonate.[10] It was purified by recrystallization from nitromethane to give material, mp 155.5-157°. Hexakis(*p*-chlorophenoxy)cyclotriphosphazene (III) was synthesized by the reaction of sodium *p*-chlorophenoxide with hexachlorocyclotriphosphazene in THF solvent to yield material, mp 144-145.5°. Hexaphenoxycyclotriphosphazene (VI), mp 111.5-112°, was prepared from hexachlorocyclotriphosphazene and sodium phenoxide.[19]

Analytical Techniques. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory. Infrared spectra were recorded on a Beckman IR5A spectrometer or a Perkin-Elmer 621 grating spectrometer. Mass spectra were obtained with an AEI MS 902 spectrometer. The proton NMR spectra were recorded on a Varian A60A spectrometer. Vapor phase chromatography was carried out on a Hewlett Packard gas chromatograph using a 15-ft column of 10% Dexsil on Chromsorb W. Thin layer chromatography was performed on Mallinkrodt ChromAR chromatography sheet with elution by a variety of solvent systems and development by iodine vapor or identification in ultraviolet light. Column chromatography was

carried out on neutral alumina, Brockman Activity I, or silica gel, using standard glass column 2 ft × ⅞ in. (i.d.) with elution by a variety of solvent systems.

Reactions of I with Sodium 2,2,2-Trifluoroethoxide. (a) In THF–DMF with 1:1 Molar Ratio of Reactants. A solution of sodium trifluoroethoxide (4.88 g, 0.04 mol) in THF (100 ml) was added to a stirred solution of I (38.55 g, 0.04 mol) in DMF (500 ml). A yellow color became evident immediately after addition of the sodium trifluoroethoxide solution. The solution was stirred at 65° for 36 h, then concentrated to a volume of approximately 50 ml by vacuum distillation. Addition of water (500 ml) yielded a yellow precipitate which was collected, washed with water (4 × 500 ml), and dried to yield 34.45 g of a tan solid, mp 120–160°. This was chromatographed on neutral alumina. Elution with a petroleum ether–benzene mixture yielded a trace amount (0.17 g) of $[NP(OCH_2CF_3)_2]_3$ (V), identified by infrared and mass spectra. Elution with benzene produced a yellow solid (5.35 g) which was recrystallized from ethanol to yield yellow needles of VII, mp 143–144.5, identified by infrared spectrometry. Further elution of the column with ethanol yielded 28.47 g of a cream-colored solid (VIII or IX), mp 151–153°. The infrared spectrum of a Nujol mull of VIII or IX showed absorptions in the OH and NH regions, as well as absorptions at 1520 and 1350 (NO_2), 1220, 1164, 1040, 928, and 852 cm^{-1}. The proton resonance spectrum showed a sharp singlet at δ 2.78 ppm (N–H or O–H) and a complex multiplet centered at δ 7.6 ppm (aromatic H). The mass spectrum showed the presence of mass fragments greater than *m/e* 500, but no parent peak was observed. Elimination of VII (*m/e* 260) with the concurrent formation of a strong peak at *m/e* 461 occurred at temperatures greater than 250°. Acidification of VIII–IX in ethanol–water with 5% hydrochloric acid, yielded a fine white precipitate. This was washed with water and dried to give a white powder (IX), mp 231–234° (with yellow discoloration). The infrared spectrum contained nitrophenoxy absorptions and multiple bands on the 1250–1100-cm^{-1} region of the spectrum. No absorptions were present in the N–H or O–H region of the spectrum. A weak, shallow band at 2650 cm^{-1} was indicative of a P–O–H linkage. The proton resonance spectrum of a deuterioacetone solution showed a singlet at δ 3.7 ppm (O–H or N–H) and a complex multiplet centered at δ 7.6 ppm (aromatic H). Integration of the spectrum indicated a proton ratio of 1:4, respectively. The mass spectrum initially showed a base peak at *m/e* 139, but VII (*m/e* 260) was eliminated from the compound at higher temperatures. Further heating in the mass spectrometer caused rearrangements which resulted in the formation of a peak at *m/e* 461, which corresponded to tris(*p*-nitrophenyl) phosphate.

(b) In THF–DMF with 3:1 Molar Ratio. A solution of sodium 2,2,2-trifluoroethoxide (14.64 g, 0.12 mol) in THF (100 ml) was added to a stirred solution of I (38.55 g, 0.04 mol) in DMF (500 ml). The reaction mixture was stirred at 65° for 36 h, then concentrated by vacuum distillation. Addition of water (500 ml) produced a bright yellow solid which was collected, washed with fresh portions of water, and dried in vacuo to give 24.44 g of a tan solid, mp 60–150°. The presence of $[NP(OCH_2CF_3)_2]_3$ (V) (40%) was detected by vapor phase chromatography. The crude reaction product was passed through a column of neutral alumina. Elution with petroleum ether yielded pure $[NP(OCH_2CF_3)_2]_3$ (V) (6.84 g, 34.2%), identified by its melting point and infrared spectrum. Elution of the column with benzene provided 5.29 g (26.1%) of 4,4′-dinitrodiphenyl ether (VII), also identified by its infrared and mass spectra. Further elution of the column with ethanol yielded 7.74 g (39%) of a cream-colored solid, mp 149–151°. This material exhibited properties similar to those of compounds VIII–IX.

(c) In THF–DMF with 3:1 Molar Ratio at 25°. To a stirred solution of I (38.55 g, 0.04 mol) in DMF (1200 ml) was added dropwise a solution of sodium trifluoroethoxide (14.64 g, 0.12 mol) in THF. The reaction solution was stirred for 16 h at 25° under an atmosphere of nitrogen. Concentration of the solution by vacuum distillation, followed by addition of water (1000 ml), produced a dark yellow precipitate. This material was collected, washed with water, and dried to yield 25.94 g of a cream-colored solid, mp 75–150°. The product mixture was extracted with hot petroleum ether, and evaporation of the extracts yielded 6.16 g of $[NP(OCH_2CF_3)_2]_3$ (V). The petroleum ether-insoluble residue was then treated with hot acetone to give an acetone-soluble fraction and a pale yellow residue. This residue was dried in vacuo and recrystallized from nitromethane to yield 9.31 g of unreacted I, mp 259–261°. The acetone-soluble fraction was chromatographed on neutral alumina. Elution of the column with a benzene–acetonitrile solvent pair gave a mixture of $N_3P_3(OC_6H_4NO_2\text{-}p)(OCH_2CF_3)_5$ and $N_3P_3(OC_6H_4NO_2\text{-}p)_2(OCH_2CF_3)_4$. A mass spectrum of the mixture revealed parent peaks at *m/e* 768 and 807, respectively. Elution of the column with ethanol yielded a mixture of $[NP(OC_6H_4NO_2\text{-}p)(OCH_2CF_3)]_3$ and $N_3P_3(OC_6H_4NO_2\text{-}p)_4(OCH_2CF_3)_2$ cyclotriphosphazene; the molecular weights (mass spectrum) were 846 and 885 amu, respectively. The mixed phosphazene ester formed in the largest amount was the tris-substituted derivative. Further elution of the column with acetone gave a white solid, mp 243–245°. Its mass spectrum contained a parent peak at *m/e* 924, which corresponded to $N_3P_3(OC_6H_4NO_2\text{-}p)_5(OCH_2CF_3)$.

(d) In Dioxane with 3:1 Molar Ratio at 100°. A solution of sodium trifluoroethoxide (1.46 g, 0.012 mol) in dioxane (50 ml) was added dropwise to a stirred solution of I (3.86 g, 0.004 mol) in boiling dioxane (600 ml). The solution was stirred at reflux for 12 h. The orange-colored precipitate which formed during the reaction was filtered from solution and dried to give 2.2 g of sodium *p*-nitrophenoxide. Concentration of the filtrate under reduced pressure gave a yellow oil, which consisted of a mixture of phosphazene esters containing both trifluoroethoxy and *p*-nitrophenoxy substituents. The oil was dissolved in nitromethane, and addition of ethanol caused precipitation of 0.27 g of a white solid, mp 200–220°. A mass spectrum of the solid showed parent peaks at *m/e* 924 and 885, which corresponded, respectively, to $N_3P_3(OC_6H_4\text{-}p)_5(OCH_2CF_3)$ and $N_3P_3(OC_6H_4NO_2\text{-}p)_4(OCH_2CF_3)_2$. Further fractional crystallization from nitromethane–ethanol yielded 0.58 g of a white solid (mp 117–135°) which contained a mixture of $N_3P_3(OC_6H_4NO_2\text{-}p)_4(OCH_2CF_3)_2$ and $[NP(OC_6H_4NO_2\text{-}p)(OCH_2CF_3)]_3$. The molecular weights (mass spectrum) were 885 and 846 amu, respectively. Concentration of the nitromethane–ethanol filtrate under reduced pressure gave 1.86 g of a yellow oily solid, mp 85–120°. A mass spectrum of this material showed parent peaks at *m/e* 846, 807, 768, and 729, which corresponded respectively to $[NP(OC_6H_4NO_2\text{-}p)(OCH_2CF_3)]_3$, $N_3P_3(OC_6H_4NO_2\text{-}p)_2(OCH_2CF_3)_4$, $N_3P_3(OC_6H_4NO_2\text{-}p)(OCH_2CF_3)_5$, and V.

Reaction of II with Sodium Trifluoroethoxide in THF. A solution of sodium trifluoroethoxide (1.46 g, 0.012 mol) in THF (25 ml) was added dropwise to a stirred solution of II (3.86 g, 0.004 mol) in THF (100 ml). The resultant mixture was stirred at 26° for 16 h in an atmosphere of nitrogen. Sodium *o*-nitrophenoxide (2.01 g) precipitated from the solution. The solvent was removed from the filtrate on a rotary evaporator to yield an orange oil that contained a finely divided red solid. The mixture was suspended in benzene (50 ml) and the benzene solution was washed with water (3 × 50 ml). After the benzene layer was dried over anhydrous magnesium sulfate, evaporation of the benzene under reduced pressure yielded a viscous yellow oil. The oil solidified after standing overnight. Slow distillation at 40° (0.1 Torr), yielded *o*-nitrophenyl 2,2,2-trifluoroethyl ether (XII), identified from its infrared and mass spectra (*m/e* 221). A small amount of V codistilled with the ether under these conditions. The residue from the sublimation was recrystallized from 100% ethanol to yield a white solid, mp 104–106°. This material consisted mainly of $N_3P_3(OC_6H_4NO_2\text{-}o)_3(OCH_2CF_3)_3$ and a trace of $N_3P_3(OC_6H_4NO_2\text{-}o)_2(OCH_2CF_3)_4$. The molecular weights (mass spectrum) were 846 and 807 amu, respectively. The proton NMR spectrum of a deuterioacetone solution showed phenyl protons and α-methylene protons in a ratio of 4:2.

Reaction of III with Sodium Trifluoroethoxide in THF. A solution of III (4.5 g, 0.005 mol) in THF (25 ml) was added dropwise to a stirred solution of sodium 2,2,2-trifluoroethoxide (4.02 g, 0.033 mol) in THF (25 ml). The mixture was stirred at reflux for 36 h to give a yellow solution. The solvent was removed at reduced pressure to yield an off-white waxy solid. Thin layer chromatographic analysis in 2:1 heptane:benzene demonstrated the presence of *p*-chlorophenol. Vacuum sublimation of the crude product mixture at 40° (0.1 Torr) yielded 3.08 g (84.6%) of $[NP(OCH_2CF_3)_2]_3$ (V), mp 46–49°. The residue was treated with benzene (3 × 50 ml), and the combined extracts were evaporated to give 0.54 g of a white solid. A mass spectrum of this material revealed parent peaks at *m/e* 757 and 785, which corresponded respectively to $N_3P_3(OC_6H_4Cl\text{-}p)(OCH_2CF_3)_5$ and $N_3P_3(OC_6H_4Cl\text{-}p)_2(OCH_2CF_3)_4$. The remainder of the residue was sodium *p*-chlorophenoxide (4.32 g).

Reaction of I with Sodium Phenoxide. To a stirred solution of I (9.63 g, 0.01 mol) in DMF (300 ml), maintained at 45°, was added a solution of sodium phenoxide (7.66 g, 0.006 mol) in tetrahydrofuran (50

ml). After the addition was complete, the reaction solution was concentrated by vacuum distillation, and traces of solvent were removed overnight in vacuo to give a yellow-green oily solid. Thin layer chromatographic analysis of the crude product indicated the presence of four components: *p*-nitrophenol and phenol were identified by comparison with authentic samples. A component which eluted near the solvent front using 1:1 heptane:benzene as eluent was identified as *p*-nitrophenyl phenyl ether from its mass spectrum. In addition, another component was present at the origin of the thin layer chromatogram. Column chromatography on silica gel with 1:1 benzene:methanol as eluent yielded a white solid which became yellow and liquefied when exposed to the atmosphere. The sample decomposed in the mass spectrometer to give a base peak at 139 amu (*p*-nitrophenol). The material was insoluble in benzene, sparingly soluble in acetone, and soluble in water. Its infrared spectrum showed the presence of phenoxy and *p*-nitrophenoxy groups; other bands were broad and ill-defined. No P=N stretching frequency was observed.

Reaction of I with Sodium Thiophenoxide. Sodium thiophenoxide (7.5 g, 0.057 mol) was added slowly to a solution of I (8.0 g, 0.0083 mol) in DMF (250 ml). Addition of the nucleophile caused the temperature to rise to 50° and the color of the solution to change from light yellow to deep red-brown. The solution was stirred in an atmosphere of nitrogen for 18 h at 45°, then at 25° for an additional 72 h. Concentration of the solution in vacuum at 25° gave a yellow-brown resinous material. A portion of the crude reaction product was treated with hexane (5 × 50 ml). Evaporation of the combined hexane extracts yielded a yellow solid. Sublimation of the mixture at 35° (0.1 Torr) gave an off-white solid. The sublimate was recrystallized from 95% ethanol to yield white needles, mp 58–59°. The infrared and proton NMR spectra corresponded exactly to those of diphenyl disulfide. The residue which remained from the sublimation was identified as *p*-nitrophenyl phenyl sulfide (mp 54–55°) from its infrared, proton NMR, and mass spectra. The solid residue that remained from the hexane washes was a dark yellow powder which did not melt below 300°. The solid was suspended in water and acidified with 5% hydrochloric acid to yield an off-white gel. Its infrared spectrum indicated the presence of nitrophenoxy and phenyl sulfide groups. No P=N absorption was evident.

Reaction of II with Sodium Phenoxide. A solution of sodium phenoxide (7.66 g, 0.066 mol) in THF (50 ml) was added dropwise to a stirred solution of II (9.64 g, 0.01 mol) in THF (300 ml). After 16 h at 65°, the reaction mixture consisted of a reddish brown solution and a dark red solid. The red solid was sodium *o*-nitrophenoxide (3.84 g). Solvent was removed from the filtrate at reduced pressure. The resultant red-brown oil showed at least four distinct components on a thin layer chromatogram in 5:5:1 benzene:heptane:THF. Phenol was identified by means of its chromatographic retention time. A portion of the crude oily material was subjected to column chromatography on silica gel. Elution with a 2:1 hexane:benzene mixture yielded an orange oil which was identified by mass spectrometry as *o*-nitrophenyl phenyl ether (XVI). The presence of *o*-nitrophenol (*m/e* 139) was also established by mass spectrometry and thin layer chromatography.

Reaction of IV with Sodium 2,2,2-Trifluoroethoxide. A solution of IV (3.46 g, 0.005 mol) in THF (25 ml) was added dropwise to a stirred solution of sodium trifluoroethoxide (4.40 g, 0.036 mole) in THF (50 ml). The mixture was stirred at reflux for 3 days. Solvent was removed on a rotary evaporator to give a yellow, semisolid mixture. Thin-layer chromatography in 1:2 heptane:benzene indicated the presence of phenol and unreacted IV. The reaction mixture was dissolved in the minimum amount of hot *n*-heptane. The *n*-heptane solution was cooled to room temperature to yield a white, crystalline precipitate of IV. Evaporation of the *n*-heptane solution yielded a white, adhesive solid that contained IV, all the possible combinations of mixed phenoxy, 2,2,2-trifluororethoxycyclotriphosphazene esters (XIV), and the fully substituted derivative V. Mass spectrometry indicated the presence of significant amounts of V and a large amount of $N_3P_3(O\text{-}C_6H_5)_3(OCH_2CF_3)_3$. Very little $N_3P_3(OC_6H_5)_2(OCH_2CF_3)_4$ and almost no $N_3P_3(OC_6H_5)(OCH_2CF_3)_5$ were formed. Compound V sublimed readily from the product mixture, but the other derivatives could not be separated by sublimation or column chromatography.

Reaction of II with Sodium Anilide. A mixture of sodium anilide (2.76 g, 0.024 mol theoretical) and aniline was slowly added to a stirred solution of II (3.86 g, 0.003 mol) in THF (100 ml) under a blanket of nitrogen, and the mixture was stirred for 24 h at 65°. Solvent was removed on a rotary evaporator to yield a black, tar-like substance. This residue was extracted with diethyl ether (3 × 100 ml). The combined ether extracts were washed with 5% hydrochloric acid (100 ml) and water (100 ml), and then dried over anhydrous magnesium sulfate. Evaporation of the ether under reduced pressure gave a mixture which was chromatographed on neutral alumina. Elution of the column with benzene yielded *o*-nitrophenol and aniline. Further elution of the column with benzene gave a reddish brown oil that crystallized slowly at room temperature. Sublimation of this material yielded red needles, mp 74–75°, which were identified as *o*-nitrodiphenylamine from infrared and mass spectral data. Elution of the column with 95% ethanol produced several other unidentified dark-colored residues.

Reaction of IV with Sodium Anilide. A mixture of sodium anilide (4.14 g, 0.036 mol theoretical) and aniline was added dropwise to a solution of IV (3.46 g, 0.005 mol) in THF (100 ml). The mixture was stirred at 65° for 24 h and the solvent was removed under reduced pressure to give a black tar. A portion of the crude product mixture was dissolved in benzene and extracted twice with dilute hydrochloric acid and twice with water. The benzene layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to yield a dark brown tar. This was chromatographed on silica gel. Elution with 1:1 hexane:benzene yielded a single component which was identified as unreacted IV. The column was eluted with benzene to give a small amount of a brown oil which eventually yielded clear crystals of $N_3P_3(O\text{-}C_6H_5)_5(NHC_6H_5)$. The molecular weight (mass spectrum) was 692 amu. Elution of the column with THF afforded a brown oil which recrystallized slowly. A mass spectrum of this solid had a parent peak at *m/e* 691, which corresponded to $N_3P_3(OC_6H_5)_4(NHC_6H_5)_2$. Further elution with THF yielded small amounts of other mixed phenylaminophenoxyphosphazene derivatives.

Reaction of II with *n*-Propylamine. A solution of *n*-propylamine (2.84 g, 0.048 mol) and II (3.86 g, 0.004 mol) in THF (100 ml) was heated at reflux for 3 days. During this time, a finely divided solid formed in the reaction mixture. The solid was removed and recrystallization from nitromethane gave light yellow needles, mp 188–189.5°. The infrared spectrum showed an N–H stretching band at 3304 cm^{-1} and absorptions characteristic of the *o*-nitrophenoxy group. The P=N band at 1185 cm^{-1} was weak, and the P–O–C(phenyl) bands were shifted to longer wavelengths than in II. The proton NMR spectrum in acetone-d_6–D_2O solution indicated the presence of *n*-propyl and aromatic protons. The material decomposed in the mass spectrometer to give a base peak at *m/e* 139, which corresponded to *o*-nitrophenol. The THF filtrate was concentrated on a rotary evaporator to give a dark red-brown oil and some solid material. An orange oil was removed by low temperature vacuum distillation. The infrared, proton resonance, and mass spectra of this material corresponded to those *N*-propyl-*o*-nitroaniline. Attempted distillation of the crude mixture resulted in the formation of yellow needles of 2,2′-dinitrodiphenyl ether, mp 114–118°, in the distillation apparatus. The residue which remained after vacuum distillation was a dark tar. The infrared spectrum of the tar showed an N–H band at 3385 cm^{-1}, *o*-nitrophenoxy absorptions, and a complex series of absorptions between 1150 and 1260 cm^{-1}.

Reaction of II with *n*-Butylamine. A solution of *n*-butylamine (3.50 g, 0.048 mol) and II (3.86 g, 0.004 mol) in THF (100 ml) was stirred at reflux for 3 days. The solid precipitate was removed by filtration, washed with THF, and dried in vacuo to give a cream-colored solid, mp 181–185°. The infrared spectrum indicated an N–H band at 3295 cm^{-1} and absorptions characteristic of the *o*-nitrophenoxy group. A medium P=N stretch was observed at 1181 cm^{-1}, while the P–O–C(phenyl) absorptions were shifted to longer wavelengths. The proton NMR spectrum indicated *n*-butyl protons and aromatic protons in the ratio of 9:8. The THF filtrate was evaporated under reduced pressure to give a viscous, red-brown oil. When the mixture was placed under vacuum at room temperature, *N*-butyl-*o*-nitroaniline distilled into a cold finger condenser. The identification was based on its infrared, proton NMR, and mass spectra *m/e* 194). The residue was a black resinous material which contained *o*-nitrophenyl substituents. No phosphazene derivatives could be isolated from the resin.

Reaction of II with Cyclohexylamine. A solution of II (3.86 g, 0.004 mol) and cyclohexylamine (4.76 g, 0.048 mol) in THF (100 ml) was stirred at reflux for 3 days. Removal of the solvent in a rotary evaporator yielded a clear, viscous brown oil. The oil was chromatographed on a column of neutral alumina. Elution with benzene yielded 1.10 g of an orange solid, mp 104–106°, which was identified as *N*-cyclohexyl-*o*-nitroaniline from its infrared, proton NMR, and mass spectra.

Elution of the column with 10% methanol–acetone solution provided a brown oil. The infrared spectrum contained a broad band between 3200 and 3500 cm^{-1}, alkyl C–H absorptions, and absorptions characteristic of the *o*-nitrophenoxy group attached to phosphorus. The oil could not be induced to crystallize.

Reaction of II with Diethylamine. A solution of diethylamine (5.26 g, 0.072 mol) and II (3.86 g, 0.004 mol) was stirred for 3 days in boiling THF (100 ml). Evaporation of the solvent on a rotary evaporator yielded a viscous oil. *N,N*-Diethyl-*o*-nitroaniline distilled from the mixture under vacuum at 25°. A trace amount of *o*-nitrophenol sublimed from the mixture after several days, but an orange-colored solid residue did not sublime. The residue was recrystallized from benzene to give a light yellow solid, mp 147–148.5°. An infrared spectrum of this solid showed the following absorptions (in cm^{-1}): 1600 (aromatic C—C); 1527, 1351 (NO_2); 1215, 1200, 1175, 1162, 1150 (P═O, P—O—C (aromatic), P═N region); 922 (P-O-C (aromatic)); and 900–700 (aromatic C—H). The proton NMR spectrum in dimethyl-d_6 sulfoxide solution showed a complex multiplet at δ 7.5–8.5 ppm (aromatic H), a quartet centered at δ 2.92 ppm (methylene H), and a triplet (methyl H) at δ 1.19 ppm. The compound decomposed in the mass spectrometer to give a base peak at *m/e* 139 (*o*-nitrophenol). A phosphazane-type structure was postulated for this material.

Reaction of II with Di-*n*-propylamine. Di-*n*-propylamine (7.27 g, 0.072 mol) was added dropwise to a stirred solution of II (3.86 g, 0.004 mol) in THF (100 ml). The solution was stirred at reflux for 5 days. Evaporation of the solvent under reduced pressure gave a viscous orange-colored oil which crystallized slowly. Thin layer chromatographic analysis of the mixture indicated the presence of only two components. The mixture was gently heated in vacuo to distill 2.62 g of an oil which was identified as *N,N*-dipropyl-*o*-nitroaniline from its infrared, proton NMR, and mass spectra. The residue was recrystallized from ethanol to yield light yellow needles, mp 113–115° (with decomposition). An infrared spectrum (Nujol mull) showed the following absorptions (in cm^{-1}): 1590 doublet (aromatic C—C); 1523, 1341 (NO_2); 1216, 1202, 1191, 1155 (P—O—C (aromatic), P═O, P═N region); and 900–700 (aromatic C—H bond). The proton NMR spectrum of a deuteriochloroform solution indicated a complex multiplet between δ 7.2 and 8.4 ppm (aromatic H), a quartet at δ 3.82 ppm (δ methylene H), a broad signal between δ 2.6 and 3.3 ppm, a complex multiplet between δ 1.4 and 2.3 ppm (β-methylene H), and two triplets centered at δ 1.25 and δ 0.81 ppm (methyl H). The sample decomposed in the mass spectrometer to yield a base peak at *m/e* 139 (*o*-nitrophenol). These data would be consistent with a product of structure VIII.

Reaction of II with Diisopropylamine. Diisopropylamine (7.27 g, 0.072 mol) was added dropwise to a stirred solution of II (3.86 g, 0.004 mol) in THF (100 ml). After the solution was stirred at reflux for 5 days, the solvent was removed under reduced pressure to give a yellow solid. Thin layer chromatographic analysis indicated traces of a component near the solvent front which exhibited nearly identical retention times to those of other N-substituted *o*-nitroanilines. Recrystallization of the solid from acetonitrile gave 3.75 g of unreacted II, mp 154–155.5°.

Reaction of II with Glycine Ethyl Ester. A solution of glycine ethyl ester was prepared by the addition of triethylamine (9.0 g, 0.066 mol) to a stirred suspension of glycine ethyl ester hydrochloride (9.21 g, 0.066 mol) in THF (250 ml). The mixture was stirred at reflux for 3.5 h and filtered. The solution of glycine ethyl ester (6.79 g, 0.066 mol theoretical) in THF (250 ml) was added dropwise to a stirred solution of II (9.63 g, 0.010 mole) in tetrahydrofuran. After addition was complete, the solution was stirred at reflux for 24 h in an atmosphere of nitrogen. Removal of the solvent under reduced pressure yielded a yellow solid that showed three components by thin layer chromatography in 1:2 heptane:benzene. Unreacted II was identified by comparison with an authentic sample. The reaction mixture was treated with 1:1 heptane:benzene (3 × 25 ml). The combined extracts were evaporated to give 0.10 g of a yellow-orange oil which showed two components on a thin layer chromatogram. When the oil was placed under vacuum, traces of *o*-nitrophenol sublimed from the mixture. The remainder of the oil consisted of *N*-*o*-nitrophenylethyl glycinate. Its mass spectrum showed a parent peak at *m/e* 224. The yellow solid from the reaction mixture was recrystallized from acetonitrile to give 9.32 g of an unreacted II, identified by its infrared spectrum.

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References and Notes

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