Azidophosphazenes as Functionalized Intermediates

Harry R. Allcock,* Michael B. McIntosh, and Thomas J. Hartle

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

Received April 27, 1999

The synthesis of phosphazene cyclic trimers with azido side groups and aryloxy, alkoxy, or dialkylamino cosubstituent groups was accomplished. The compounds have the basic structure $N_3P_3(R)_x(N_3)_{6-x}$, where R represents phenoxy, trifluoroethoxy, dimethylamino, or diethylamino groups and $x = 3-5$. Experiments were also conducted to determine the ability of these materials to undergo a reaction unique to azido compounds known as nitrene insertion. The aryloxy derivative, $N_3P_3(OC_6H_5)_5(N_3)$, yielded a nitrene insertion product when heated with 1-phenylnonane at 280 °C. The alkoxy derivative, $N_3P_3(OCH_2CF_3)_5(N_3)$, produced a nitrene insertion product when ultraviolet irradiated in an aliphatic solvent. The dialkylamino derivative, $N_3P_3(N(CH_3)_2)_4(N_3)_2$, did not undergo nitrene insertion. The aryloxy and alkoxy azido trimers reacted with various phosphorus(III) compounds to form phosphinimines via the Staudinger reaction. Finally, sodium phenoxide displaced azides from both the alkoxy- and aryloxyphosphazene trimers while *n*-butylamine displaced only the azide on the alkoxy trimer.

Introduction

During the past 50 years, organic azides have developed into important synthetic reagents. Numerous alkyl, acyl, aryl, and vinyl azides have been utilized to prepare iminophosphoranes ($R-N{=}PR'_3$) which have been employed as building blocks in the construction of nitrogen-containing heterocycles via aza-Wittig chemistry.[1−3] Other organic azides have been developed for applications in photoresists, vulcanization, polymer coupling and cross-linking and for the surface modification of polymers and metals.[4−13] Aryl azides (PhN_3), sulfonyl azides (RSO_2N_3), and azidoformates ($ROC(=O)N_3$) have been the principal compounds analyzed due to their ability to form reactive nitrene intermediates that are capable of insertion into chemical bonds that are as unreactive as C−H (Scheme 1).

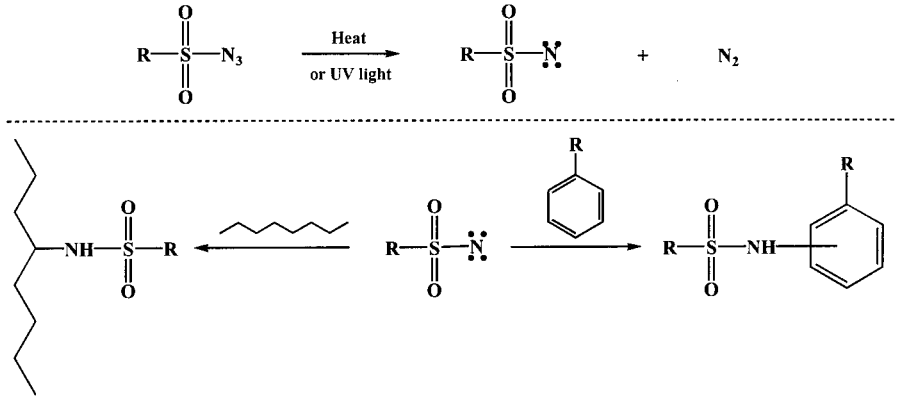
Phosphoryl azides ($RO_2P(=O)N_3$) also form nitrene compounds which undergo insertion reactions, but relatively little nitrene insertion chemistry appears to have been conducted with these materials.[14−19] Most of the recent work has utilized phosphoryl azide-promoted coupling or polymerization of organic monomers to produce polypeptides, polyamides, polyureas, or polyurethanes.[20−25] The lack of phosphoryl azide nitrene insertion chemistry may be due to the inherent moisture sensitivity of many phosphoryl azides or because of the difficulties encountered in preparing phosphoryl compounds with multiple azide groups.

Cyclic phosphazene trimers ($N_3P_3R_6$) offer a possible solution. The presence of three phosphorus atoms in these species allows easy access to compounds with two or three azido groups per molecule. Also, the properties of phosphazenes can be tailored by the organic cosubstituent groups that are connected to the phosphazene ring. For example, the incorporation of appropriate cosubstituent groups should provide azido compounds with acceptable stability.[26] Despite these potential advantages, only a few phosphazene azide compounds have been prepared. These include the shock-sensitive hexaazido cyclic trimer $[NP(N_3)_2]_3$,[27] a triazido−trichloro trimer ($N_3P_3Cl_3(N_3)_3$),[28] a pentafluoro−

(1) Molina, P.; Vilaplana, M. J. *Synthesis* **1994**, 1197.
(2) Palacios, F.; Alonso, C.; Rubiales, G. *J. Org. Chem.* **1997**, *62*, 1146.
(3) Gulolubov, Y. G.; Kaskhin, L. F. *Tetrahedron* **1992**, *48*, 1353.
(4) *Azides and Nitrenes-Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press Inc.: Orlando, FL, 1984.
(5) Tsunoda, T.; Yamaoka, T.; Nagamatsu, G. *Photogr. Sci. Eng.* **1973**, *17*, 390.
(6) Breslow, D. S.; Willis, W. D.; Amberg, L. O. *Rubber Chem. Technol.* **1970**, *43*, 605.
(7) Breslow, D. S.; Prosser, T. J.; Genge, C. A.; Marcantonio, A. F. *J. Am. Chem. Soc.* **1967**, *89*, 2384.
(8) Breslow, D. S.; Edwards, E. I.; Linsay, E. C.; Omura, H. *J. Am. Chem. Soc.* **1976**, *98*, 4268.
(9) McFarren, G. A.; Sanderson, T. F.; Schappell, F. G. *Soc. Plast. Eng. Technol. Pap.* **1976**, *22*, 19.
(10) Osteraas, A. J.; Olsen, D. A. *Nature* **1969**, *221*, 1140.
(11) Buckley, J.; Budziarek, R.; Nicholas, A. J.; Vickers, E. J. U.S. Patent 3,997,571, 1976.
(12) Hardy, W. B.; Adams, F. H. U.S. Patents 2,863,866, 1958; and 2,912,391, 1959.
(13) Susuki, S. U.S. Patents 3,526,644 and 3,547,843, 1970.
(14) Khanna, Y. P.; Bhattacharjee, H. R.; Kumar, R.; Williams, J. I.; Sibilia, J. P. U.S. Patent 4,876,127, 1989.
(15) Bhattacharjee, H. R.; Khanna, Y. P. U.S. Patent 4,906,708, 1990.
(16) Maslak, P. *J. Am. Chem. Soc.* **1989**, *111*, 8201.
(17) Breslow, R.; Herman, F.; Schwabacher, A. W. *J. Am. Chem. Soc.* **1984**, *106*, 5359.
(18) Gilyarov, V. A. *Russ. Chem. Rev.* **1982**, *51* (9), 909.
(19) Breslow, R.; Feiring, A.; Herman, F. *J. Am. Chem. Soc.* **1974**, *96*, 5937.
(20) Jin, S.; Mungara, P. M.; Gonslaves, K. E. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 499.
(21) Hicke, H.; Bohme, P.; Becker, M.; Schulze, H.; Ulbricht, M. *J. Appl. Polym. Sci.* **1996**, *60*, 1147.
(22) Nishi, N.; Naruse, T.; Hagiwara, K.; Nakajima, B.; Tokura, S. *Makromol. Chem.* **1991**, *192*, 1799.
(23) Zeng, J. N.; Magiera, D. J.; Krull, I. S. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1809.
(24) Nishi, N.; Masahiko, T.; Nakamura, K.; Tokura, S. *Makromol. Chem.* **1991**, *192*, 1811.
(25) Shioiri, T.; Ninomiya, K.; Yamada, S. J. *J. Am. Chem. Soc.* **1972**, *94*, 6203.
(26) Allcock, H. R. *Phosphorus−Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems*; Academic Press: New York, 1972; Chapters 5−7 and 12.
(27) Grundmann, C.; Ratz, R. *Z. Naturforsch.* **1955**, *10b*, 116.
(28) Muller, U.; Schmock, F. *Z. Naturforsch.* **1980**, *35b*, 1529.

10.1021/ic9904541 CCC: $18.00
Published on Web 11/04/1999

Scheme 1. General Acyl Nitrene Formation and Insertion Chemistry.



azido trimer ($N_3P_3F_5(N_3)$),[29] a pentaphenyl−azido trimer ($N_3P_3(C_6H_5)_5(N_3)$),[30] a hexaphenyl−diazido tetramer ($N_4P_4(C_6H_5)_6(N_3)_2$),[31] a tetraziridino−diazido trimer ($N_3P_3(C_2H_2N)_4(N_3)_2$,[32] and several ethylenediamino−tetrazido trimers.[33] Little investigation of the nitrene chemistry of phosphazene azides has been conducted, and no evidence of insertion chemistry has been described.

Recently, we reported in a communication the successful synthesis and nitrene insertion of alkoxy-, aryloxy-, and (dialkylamino)cyclotriphosphazene azides.[34] Here we provide a detailed description of our study, together with some additional findings. There were several objectives in our investigation. The primary goal of the research was to prepare new phosphazene azido cyclic trimers which also contain aryloxy, alkoxy, or dialkylamino cosubstituent groups. The target compounds are listed in Figure 1.

Also, a study was undertaken to examine the reactivity of the phosphazene azides toward phosphorus(III) compounds. Numerous organic aryl and acyl azides are known to react with phosphorus(III) species to form N═P bonds.[4,18,35−37] It was of interest to see if azidocyclophosphazenes would behave similarly, because phosphinimine formation with these species could be used as a route to cyclophosphazene-containing polymers.

Another objective of this work was to examine how organic substituents in both the cyclophosphazene azide and the phosphorus(III) species affect the formation of the P═N bonds. In addition, it was of interest to determine if the azido derivatives are capable of undergoing nitrene chemistry. It is known that aryloxy or alkoxy groups are necessary before phosphoryl compounds will undergo these reactions.[17−19] By contrast, compounds with direct carbon−phosphorus or amine−phosphorus linkages normally rearrange in preference to nitrene formation. Finally, the azido groups of other acyl azide compounds, especially sulfonyl azides, are cleaved by amines.[35] A series of experiments was undertaken to determine whether nucleophilic reagents would also displace the azido group of phosphazene azide trimers.

Results and Discussion

Aryloxy Azide Synthesis ($N_3P_3(OC_6H_5)_{6-x}(N_3)_x$) ($x = 1-3$) (2a−4a). $N_3P_3Cl_6$ (**1**) was converted to $N_3P_3(OC_6H_5)_3Cl_3$ (**2**), $N_3P_3(OC_6H_5)_4Cl_2$ (**3**), and $N_3P_3(OC_6H_5)_5Cl$ (**4**) by treatment with sodium phenoxide. The sodium phenoxide used in these preparations was generated either in the reaction flask by treatment of sublimed phenol with sodium metal or by a separate reaction between NaOH and phenol, with subsequent isolation of the sodium phenoxide salt.

The phenoxychlorophosphazene trimers were then converted to their corresponding phosphazene azides through reaction with sodium azide in the presence of tetrabutylammonium bromide (*n*-Bu_4NBr) (Scheme 2).

In refluxing 2-butanone (methyl ethyl ketone, MEK) or toluene, the conversion of the chlorophosphazene to the azidophosphazene was complete within 24 h. When THF was used as the solvent, 48 h was required for complete conversion. Complete azide formation was achieved in MEK even when *n*-Bu_4NBr was not present, but *n*-Bu_4NBr was needed when THF

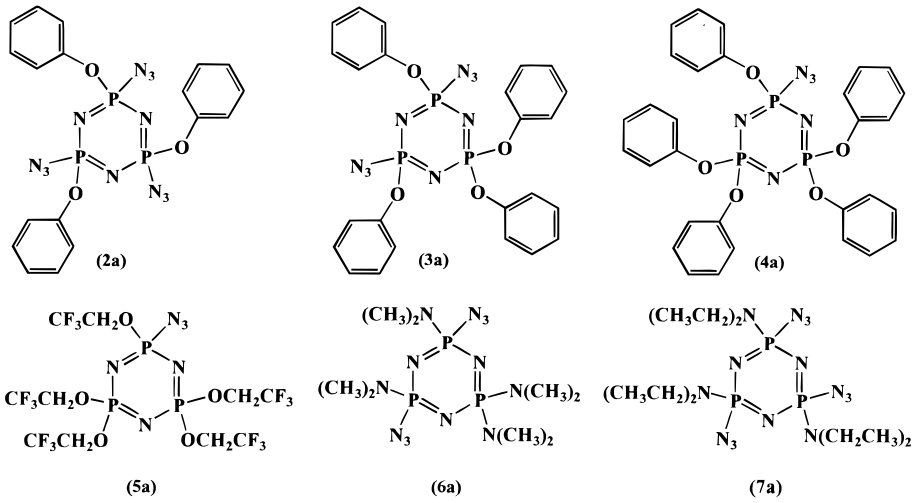
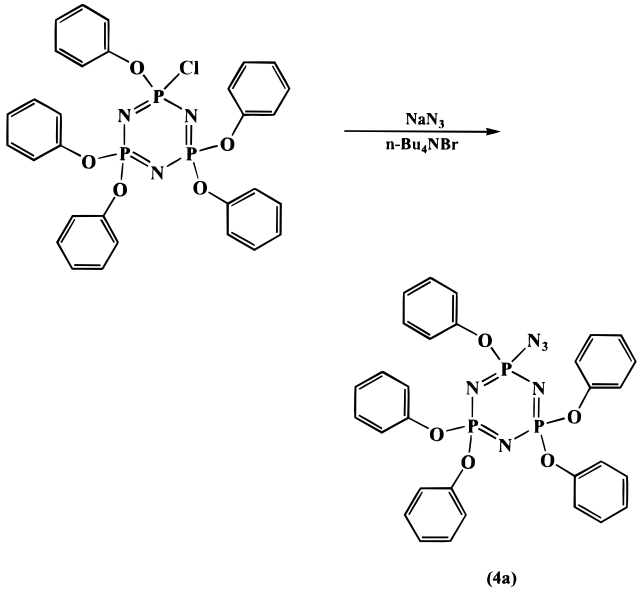


Figure 1. Phosphazene azide target trimers.

Scheme 2. Phosphazene Azide Synthesis ($N_3P_3(OC_6H_5)_5(N_3)$)



or toluene was the reaction solvent. This reflects the greater solubility of NaN_3 in methyl ethyl ketone. Even in the presence of *n*-Bu_4NBr, complete conversion to the azide did not occur in refluxing acetone after 48 h.

The identity of the azide compounds was confirmed by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, FTIR, FAB(+) mass spectrometry, and elemental microanalysis. FTIR confirmed the presence of the azido group with an azide stretch near 2150 cm^{-1}. The complete conversion to the azides was indicated by shifts in the ^{31}P NMR spectra. In the case of $N_3P_3(OC_6H_5)_5(N_3)$ (**4a**), azide formation was followed by the disappearance of the triplet resonance at 23 ppm, which is characteristic of the chlorine-substituted phosphorus atom of $N_3P_3(OC_6H_5)_5Cl$. In addition, a new triplet resonance appeared at 13 ppm. Similar shifts were observed in the reactions of $N_3P_3(OC_6H_5)_4Cl_2$ and $N_3P_3(OC_6H_5)_3Cl_3$ with NaN_3. However, in these cases, overlapping resonances appeared due to the formation of the cis and trans azides (Figure 2).

In the case of $N_3P_3(OC_6H_5)_3(N_3)_3$ (**2a**), the individual cis and trans isomers have recently been separated. The materials were nearly identical by FTIR and FAB(+) mass spectrometry. However, they have different ^{31}P, ^{1}H, and ^{13}C NMR spectra. The two isomers are also different in their room-temperature physical states. While the trans isomer is a clear colorless liquid at 22 °C, the cis isomer formed white crystalline needles (mp: 37−39 °C). It has not yet been possible to separate the cis and trans isomers of $N_3P_3(OC_6H_5)_4(N_3)_2$ (**3a**).

It was found that a mixture of the cis and trans isomers was obtained during the synthesis of $N_3P_3(OC_6H_5)_3(N_3)_3$ even when pure cis isomer of $N_3P_3(OC_6H_5)_3Cl_3$ was treated with NaN_3. This type of isomerization has been observed with arylphosphazene azides, $N_4P_4(C_6H_5)_6(N_3)_2$, in previous work.[31]

Alkoxy Azide Synthesis ($N_3P_3(OCH_2CF_3)_5(N_3)$) (5a). The alkoxy azide trimer $N_3P_3(OCH_2CF_3)_5(N_3)$ (**5a**) was also synthesized by treatment of its chlorophosphazene precursor ($N_3P_3(OCH_2CF_3)_5Cl$) (**5**) with NaN_3. However, an alternative route to $N_3P_3(OCH_2CF_3)_5Cl$ was needed in order to obtain pure $N_3P_3(OCH_2CF_3)_5(N_3)$. Normally, trifluoroethoxy cosubstituent trimers, $N_3P_3(OCH_2CF_3)_5(R)$, can be produced by treatment of $N_3P_3Cl_6$ with $NaOCH_2CF_3$ followed by an appropriate nucleophile to introduce R. The desired cosubstituent trimer is then obtained by isolation from a mixture of $N_3P_3(OCH_2CF_3)_4(R)_2$, $N_3P_3(OCH_2CF_3)_5(R)$, and $N_3P_3(OCH_2CF_3)_6$. However, when this method was utilized to produce azido trimers, the individual products could not be separated. To isolate the individual trimers, the mixture was treated with triphenylphosphine to produce the corresponding phosphinimines, $N_3P_3(OCH_2CF_3)_{6-x}(N{=}P(C_6H_5)_3)_x$. The individual products could then be separated by column chromatography on silica.

An alternative procedure was developed to obtain pure samples of both $N_3P_3(OCH_2CF_3)_5Cl$ and $N_3P_3(OCH_2CF_3)_5(N_3)$ (Scheme 3). In this process, $N_3P_3Cl_6$ was first converted completely to $N_3P_3(OCH_2CF_3)_6$. This cyclic trimer was then treated with NaOH in acetone to produce the monohydrolysis product, $N_3P_3(OCH_2CF_3)_5(O^-Na^+)$, which is easily purified due to its greater ionic character. The complete removal of $N_3P_3(OCH_2CF_3)_6$ was essential in order to avoid contamination of the final azido trimer. Species $N_3P_3(OCH_2CF_3)_5(O^-Na^+)$, was then converted to $N_3P_3(OCH_2CF_3)_5Cl$ by treatment with *n*-Bu_4NBr and PCl_5. Once the $N_3P_3(OCH_2CF_3)_5Cl$ was isolated, it could easily be converted to $N_3P_3(OCH_2CF_3)_5(N_3)$ by reaction with NaN_3. Column chromatography on silica gel yielded a clear, colorless liquid whose identity was confirmed by multinuclear NMR, elemental analysis, mass spectrometry, and FTIR. Attempts to purify by distillation gave an orange liquid with impurities evident by mass spectrometry and elemental analysis.

Dialkylamino Azides $N_3P_3(N(CH_3)_2)_4(N_3)_2$ (6a) and ($N_3P_3(N(CH_2CH_3)_2)_3(N_3)_3$ (7a). Both $N_3P_3(N(CH_3)_2)_4(N_3)_2$ (**6a**) and $N_3P_3(N(CH_2CH_3)_2)_3(N_3)_3$ (**7a**) were prepared by treatment of their chloro derivatives with NaN_3. Both azido cyclic trimers were isolated as clear, colorless liquids by column chromatography on silica gel. The (dialkylamino)phosphazene azides were the most difficult of the azido trimers to prepare. In MEK, 72 h at reflux was required for full conversion to the azides. The resistance to substitution is probably due to the electron-donating character of the amino groups which destabilizes the negatively charged reaction transition state.

(Aryloxy)phosphinimine Formation ($N_3P_3(OC_6H_5)_{6-x}(N{=}PR_3)_x$). One distinguishing attribute of azido compounds is their ability to react with phosphorus(III) molecules such as triphenylphosphine ($P(C_6H_5)_3$) to form phosphinimines ($-N{=}PR_3$) (Staudinger reaction). One of the goals of this investigation was to examine differences in reactivity of the phosphazene azides (**2a**−**7a**) with a variety of phosphorus(III) molecules which have different degrees of nucleophilic character. It was believed that these reactions might serve as models and yield information about the best combination of phosphazene azide and phosphorus(III) compounds to give a high reactivity. This information could then be utilized to synthesize or modify polymers via phosphinimine formation. The production of such polymers is currently under investigation.

Previous research has suggested that an optimum reactivity in the Staudinger reaction is obtained when an electron-deficient

(29) Roesky, H. W.; Banek, M. *Z. Naturforsch.* **1979**, *34b*, 752.
(30) Sharts, C. M. U.S. Patent 3,347,876, 1967.
(31) Sharts, C. M.; Bilbo, A. J.; Gentry, D. R. *Inorg. Chem.* **1966**, *5*, 2140.
(32) Willson, M.; Sanchez, M.; Labarre, J. *Inorg. Chim. Acta* **1987**, *136*, 53.
(33) Dave, P. R.; Forohar, F.; Axenrod, T.; Bedford, C. D.; Chaykovsky, M.; Rho, M.; Gilardi, R.; George, C. *Phosphorus, Sulfur Silicon* **1994**, *90*, 175.
(34) McIntosh, M. B.; Hartle, T. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1999**, *121*, 884.
(35) *The Chemistry of the Azido Group*; Patai, S., Ed.; John Wiley and Sons: London, 1971.
(36) Staudinger, H. S.; Hauser, E. *Helv. Chim. Acta* **1921**, *4*, 861.
(37) Staudinger, H. S.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.

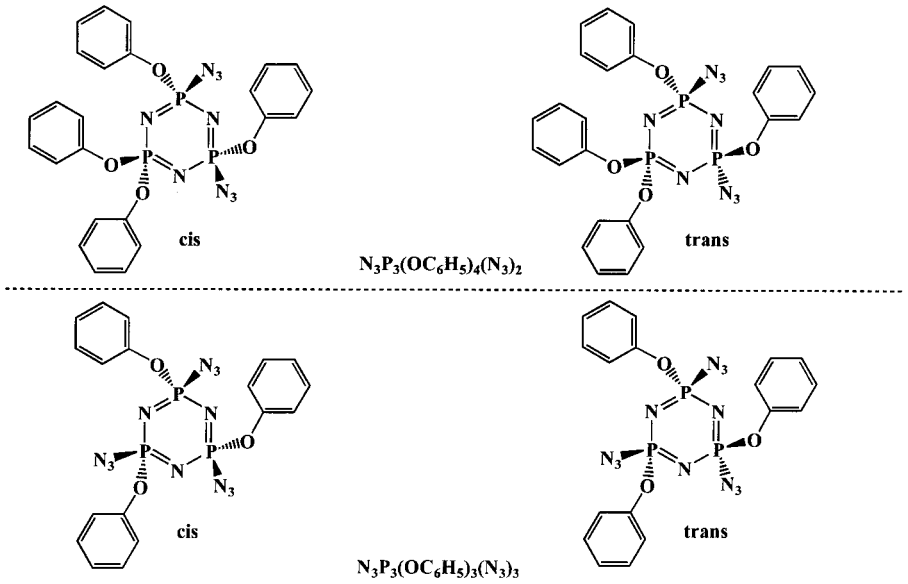
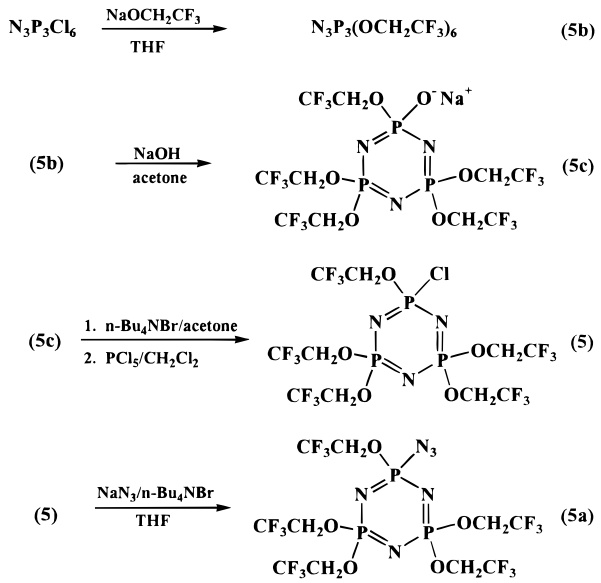


Figure 2. Cis and trans isomers of $N_3P_3(OC_6H_5)_4(N_3)_2$ and $N_3P_3(OC_6H_5)_3(N_3)_3$.

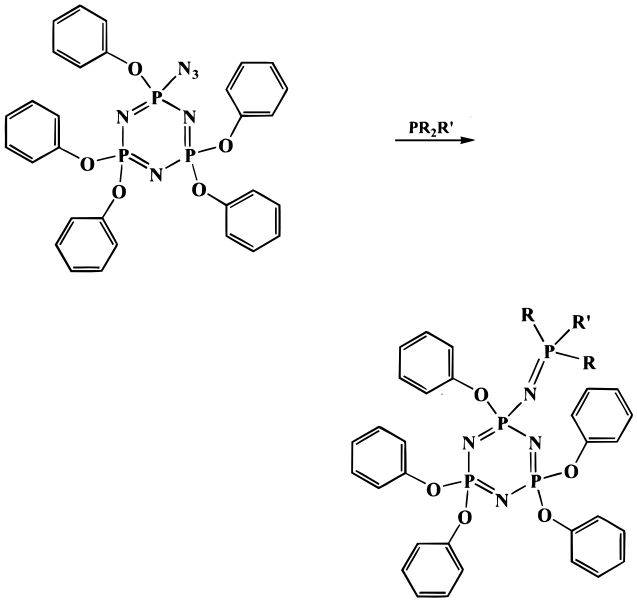
Scheme 3. Alternative Synthesis of $N_3P_3(OC_2CF_3)_5(N_3)$



azide is treated with an electron-rich phosphorus(III) compound.[32,36−39] Thus, phosphazene azides with electron-withdrawing groups and phosphorus(III) compounds with electron-donating substituents appeared to be the most promising candidates. However, it was necessary to examine other combinations as well in order to determine if they too might provide a useful synthetic protocol. The effect of multiple azide groups within the same phosphazene trimer was not known. A summary of the phosphinimines synthesized in this study and the reaction conditions employed is given in Table 1.

$N_3P_3(OC_6H_5)_5(N_3)$ served as the principal model compound for the reaction of (aryloxy)phosphazene azide trimers with phosphorus(III) compounds. This was due to the presence of only one azido group per molecule and the formation of only one isomer. These characteristics markedly simplified the isolation and characterization of phosphinimine reaction products.

Scheme 4. Phosphinimine Synthesis $[N_3P_3(OC_6H_5)_5(N{=}PR_2R')]$



$N_3P_3(OC_6H_5)_5(N_3)$ was treated with tri-*n*-butylphosphine ($P(n\text{-}C_4H_9)_3$), triphenylphosphine ($P(C_6H_5)_3$), triphenyl phosphite ($P(OC_6H_5)_3$), triethyl phosphite ($P(OCH_2CH_3)_3$), hexamethylphosphorus triamide ($P(N(CH_3)_2)_3$), chlorodiphenylphosphine ($P(C_6H_5)_2Cl$), dichlorophenylphosphine ($P(C_6H_5)Cl_2$), and dimethylphosphoramidous dichloride ($P(N(CH_3)_2Cl_2$) to form the corresponding phosphinimines (Scheme 4).

Most of the reactions were conducted in THF or toluene. Conversion of the azido trimer to the phosphinimine was indicated by the disappearance of the azido triplet in the ^{31}P NMR spectrum and by the emergence of a doublet resonance and a multiplet resonance from the phosphinimines. The relative

(38) Gilyarov, V. A.; Kudryavstev, R. V.; Kabachnik, M. I. *J. Gen. Chem. USSR (Engl.* Transl.) **1968**, *38*, 351.
(39) Goerdeler, J.; Ullmann, H. *Chem. Ber.* **1961**, *94*, 1067.

chemical shifts of these resonances varied depending on the phosphorus(III) compound utilized and the solvent.

The different groups attached to the phosphorus(III) moiety exerted profound effects on its reactivity toward $N_3P_3(OC_6H_5)_5(N_3)$, **4a**, and on the stability of the resultant phosphinimines. Tri-*n*-butylphosphine reacted vigorously and completely with $N_3P_3(OC_6H_5)_5(N_3)$, even at room temperature, to produce the phosphinimine, $N_3P_3(OC_6H_5)_5(N{=}P(n\text{-}C_4H_9)_3)$, as a clear, colorless, viscous oil that was stable in the atmosphere. Both triphenylphosphine and triethyl phosphite reacted completely with **4a** in refluxing THF or toluene to form their corresponding phosphinimines. $N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)_3)$ showed better long-term hydrolytic stability than $N_3P_3(OC_6H_5)_5(N{=}P(OCH_2CH_3)_3)$. The triphenylphosphinimine was hydrolytically stable over several months' exposure to the atmosphere whereas $N_3P_3(OC_6H_5)_5(N{=}P(OCH_2CH_3)_3)$ showed signs of decomposition over the same time period. This is probably due to the low hydrolytic stability of the phosphorus-alkoxy linkage. Hydrolysis of the phosphorus-alkoxy linkage may result in formation of a phosphorimic acid, $N_3P_3(OC_6H_5)_5(N{=}P(OCH_2CH_3)_2(OH)$. This acid can then undergo rearrangement which results in the hydrolysis of the phosphinimine linkage. $P(N(CH_3)_2)_3$ also underwent a relatively facile reaction with $N_3P_3(OC_6H_5)_5(N_3)$. Evidence of phosphinimine formation through the evolution of nitrogen gas was observable at room temperature; however, the reaction did not appear to be as vigorous as when tri-*n*-butylphosphine was utilized. The resultant phosphinimine, $(N_3P_3(OC_6H_5)_5(N{=}P(N(CH_3)_2)$, also demonstrated good atmospheric stability over several months. Treatment of $N_3P_3(OC_6H_5)_5(N_3)$ with $P(OC_6H_5)_3$ yielded the slowest reaction rates of the unhalogened phosphorus(III) species. Complete conversion to the phosphinimine, $N_3P_3(OC_6H_5)_5(N{=}P(OC_6H_5)_3)$, was possible. However, longer reaction times (72 h) and higher boiling solvents (toluene) were necessary. This is believed to be due primarily to the reduced nucleophilic character imparted to $P(OC_6H_5)_3$ by competition for electron density between the phosphorus atom and the phenoxy substituents.

Treatment of $N_3P_3(OC_6H_5)_5(N_3)$ with three halogenated derivatives [$P(C_6H_5)_2Cl$, $P(C_6H_5)Cl_2$, $P(N(CH_3)_2Cl_2$] provided widely differing results. $P(C_6H_5)_2Cl$ reacted in a manner similar to triphenylphosphine, and full conversion to the phosphinimine $N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)_2Cl)$ was possible within 24 h in toluene. On the other hand, $P(C_6H_5)Cl_2$ had a low reactivity. Seven days in refluxing toluene were required to obtain 90% conversion to $N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)Cl_2)$. This reduced reactivity can be ascribed to the presence of multiple electron-withdrawing chlorine substituents on the phosphorus(III) compound. It appears that the electron-donating character of the single phenyl substituent is insufficient to compensate for this. The nucleophilic character of the phosphine is thus reduced. Species $N_3P_3(OC_6H_5)_5(N_3)$ was treated with $P(N(CH_3)_2Cl_2$ in order to determine if the presence of a dialkylamino substituent might improve the nucleophilic character of the phosphine. Interestingly, $P(N(CH_3)_2)Cl_2$ demonstrated the least reactivity with $N_3P_3(OC_6H_5)_5(N_3)$ of any of the phosphorus(III) compounds studied. No evidence of any reaction was obtained when the reaction mixture was stirred at 70 °C in toluene for 24 h. After an additional 7 days in refluxing toluene, only 65% conversion to the phosphoranimine was detected by ^{31}P NMR spectroscopy. The result is surprising because amino groups generally act as good π donors. However, poor orbital overlap between the nitrogen lone pair of the $-N(CH_3)_2$ group and the phosphorus d-orbitals could hinder any π donation. In $P(N(CH_3)_2Cl_2$, the d-orbitals of the chlorine substituents may compete with those of the phosphorus atom for the nitrogen lone pair. If π donation by the amine is inhibited, the dimethylamino group would become an electron-withdrawing substituent due to the greater electronegativity of the nitrogen atom versus phosphorus. This would decrease the nucleophilic character of $P(N(CH_3)_2Cl_2$ and possibly lead to the results observed.

Most of the (aryloxy)phosphazene phosphinimine studies were conducted with $N_3P_3(OC_6H_5)_5(N_3)$, but several phosphinimine syntheses were carried out with the di- and triazido trimers as well. $N_3P_3(OC_6H_5)_4(N_3)_2$ reacted with triphenylphosphine in a manner similar to $N_3P_3(OC_6H_5)_5(N_3)$. Characterization of the resultant phosphinimine was difficult due to the presence of both the cis and trans isomers. Significant differences were found when $N_3P_3(OC_6H_5)_3(N_3)_3$ was utilized. When the triazido trimer was treated with $P(C_6H_5)_3$, several days reaction in refluxing toluene were required for full conversion to $N_3P_3(OC_6H_5)_3(N{=}P(C_6H_5)_3)_3$. Furthermore, complete formation of $N_3P_3(OC_6H_5)_3(N{=}P(OC_6H_5)_3)_3$ did not occur even after 7 days of reflux in toluene. These results can be explained by a combination of electronic and steric factors. Formation of a phosphinimine increases the electron density on the phosphazene trimer ring. The increased ring electron density then discourages further reaction of the remaining azido groups. Thus, more nucleophilic phosphorus(III) compounds ($P(C_6H_5)_3$) are required to form the di- and triphosphinimines. The formation of $-N{=}PR_3$ bonds where R is a bulky group also sterically inhibits further reaction of the remaining azido groups because the bulky R groups hinder the approach of other phosphorus(III) nucleophiles.

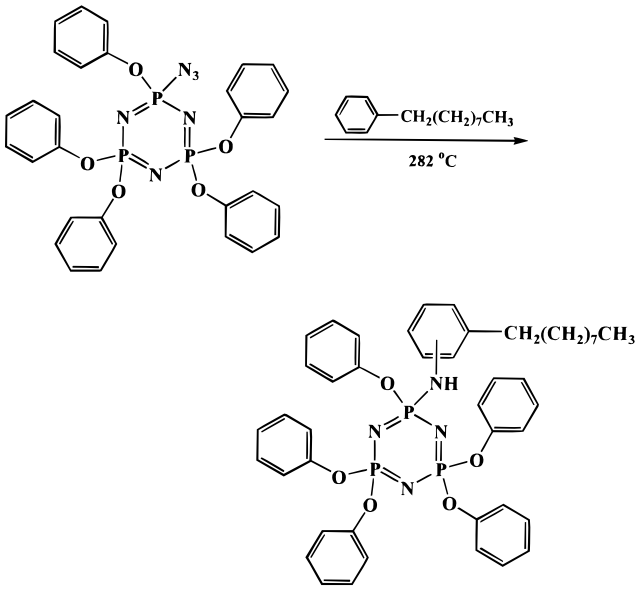
Alkoxyphosphinimine Azide Formation ($N_3P_3(OCH_2CF_3)_5(N{=}PR_3)$). Relatively few results were obtained regarding the synthesis of phosphinimines of the trifluoroethoxy trimers ($N_3P_3(OCH_2CF_3)_5(N{=}PR_3)$) due to the difficulty in establishing an effective synthesis of $N_3P_3(OCH_2CF_3)_5(N_3)$ until recently and the failure to isolate the diazido derivative, $N_3P_3(OCH_2CF_3)_4(N_3)_2$. However, reactions conducted with a $N_3P_3(OCH_2CF_3)_5(N_3)$ and $N_3P_3(OCH_2CF_3)_4(N_3)_2$ mixture suggest that the alkoxy azides behave similarly to their aryloxy counterparts.

Attempted (Dialkylamino)phosphinimine Azide Formation. The dialkylamino azido trimers, $N_3P_3(N(CH_3)_2)_4(N_3)_2$ (**6a**) and $N_3P_3(N(CH_2CH_3)_3(N_3)_3$ (**7a**), failed to undergo complete conversion to their corresponding phosphinimines when treated with triphenylphosphine, even when refluxed in toluene for more than 1 week. Instead, ^{31}P NMR spectroscopy showed a mixture of the unreacted azides and what is presumably the monophosphinimine $N_3P_3(N(CH_3)_2)_4(N_3)(N{=}P(C_6H_5)_3)$ or $N_3P_3(N(CH_2CH_3)_3(N_3)_2(N{=}P(C_6H_5)_3))$. However, the phosphinimines could not be separated. It is believed that phosphinimine formation is discouraged in the cases of **6a** and **7a** due to the electron-donating character of the dialkylamino substitutents on the trimer ring in addition to the steric and electronic effects imparted by the phosphinimine groups.

Rearrangement Chemistry of $N_3P_3(N(CH_3)_2)_4(N_3)_2$. Phosphorus azide compounds with dialkylamino substituents, $(R_2N)_2P(=O)N_3$, tend to rearrange to insoluble high molecular weight materials in preference to undergoing nitrene insertion. The exact mechanism of this reaction is unknown. However, it is believed that migration of the amino groups is involved.[19] It was the intent of this part of the study to determine if (dialkylamino)-phosphazene azides would react in a similar manner.

$N_3P_3(N(CH_3)_2)_4(N_3)_2$ was chosen as a model. The thermal decomposition temperature of the azide group was determined by differential scanning calorimetry (DSC) to be near 238 °C. When $N_3P_3(N(CH_3)_2)_4(N_3)_2$ was heated in refluxing butyl phenyl

Scheme 5. Thermal Nitrene Insertion of $N_3P_3(OC_6H_5)_5(N_3)$



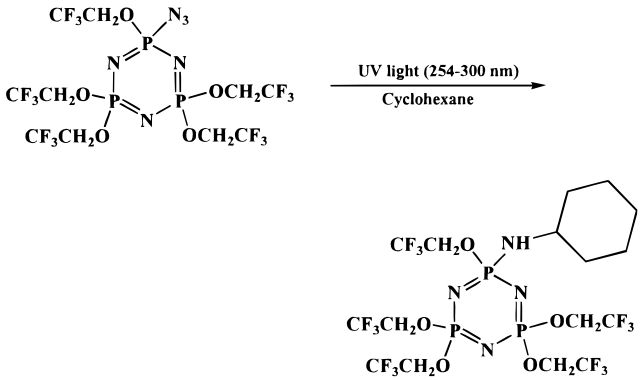
ether (bp: 210 °C), a white precipitate was formed. No resonances were detected in the ^{31}P NMR spectrum of the reaction mixture. This suggested that all the trimer material was in the precipitate. However, this could not be confirmed as no suitable solvent could be found to redissolve the solid for analysis. Because of the extreme insolubility, it is believed that $N_3P_3(N(CH_3)_2)_4(N_3)_2$ rearranges to yield a cross-linked material instead of undergoing nitrene insertion. This conclusion is based on similar results and conclusions obtained with $N_4P_4Ph_6(N_3)_2$ in previous work.[31]

Nitrene Insertion Chemistry of $N_3P_3(OC_6H_5)_5(N_3)$. DSC analysis of $N_3P_3(OC_6H_5)_5(N_3)$ showed that the azide decomposition occurred near 274 °C. Due to the higher decomposition temperature of the azide, a different reaction solvent was required. The azide was dissolved and heated to reflux in 1-phenylnonane (bp: 282 °C). Unlike the $N_3P_3(N(CH_3)_2)_4(N_3)_2$ reaction, clear evidence of azide decomposition was observed by vigorous gas evolution near the solvent reflux temperature. This was used to monitor the progress of the reaction. After about 10 min, the gas evolution had nearly ceased and the reaction mixture was allowed to cool. Only a very small amount of insoluble material was observed, and the ^{31}P NMR spectrum showed evidence of several soluble products. Due to the small quantity of material examined, only two of the reaction products could be recovered by column chromatography on silica gel. One of these was unreacted $N_3P_3(OC_6H_5)_5(N_3)$. Analysis of the other material suggested that it is the nitrene insertion product, $N_3P_3(OC_6H_5)_5(NHC_6H_4CH_2(CH_2)_7CH_3$. The overall reaction is depicted in Scheme 5. Species $N_3P_3(OC_6H_5)_4(N_3)_2$ and $N_3P_3(OC_6H_5)_3(N_3)_3$ have also been found to effectively cross-link polyolefins, presumably via nitrene insertion chemistry. This is of significance for the processing of organic polymers.[40]

Because some phosphoryl azides have also been found to form nitrenes through ultraviolet photolysis,[4,19] several experiments were conducted to determine if $N_3P_3(OC_6H_5)_5(N_3)$ would behave similarly. Initially, $N_3P_3(OC_6H_5)_5(N_3)$ was dissolved in toluene and subjected to ultraviolet irradiation (250−300 nm) for 24 h. No evidence of any reaction was observed. It was initially thought that the aromatic ring of toluene might be acting as an ultraviolet filter and hindering photolysis. However, when the azide was dissolved in cyclohexane and irradiated for 24 h, again no evidence of any insertion was found. The phenoxy groups on this trimer may also absorb the ultraviolet light and shield the azido groups since azido groups absorb only weakly in the ultraviolet region.

(40) Information provided by the Dow Chemical Co.

Scheme 6. Photolytic Nitrene Insertion of $N_3P_3(OCH_2CF_3)_5(N_3)$ into Cyclohexane



Nitrene Insertion Chemistry of $N_3P_3(OCH_2CF_3)_5(N_3)$. No definitive thermal nitrene insertion reactions could be conducted with $N_3P_3(OCH_2CF_3)_5(N_3)$ because this azido trimer volatilized before thermal azide decomposition could occur. However, evidence for nitrene insertion was obtained when $N_3P_3(OCH_2CF_3)_5(N_3)$ was irradiated with ultraviolet light in cyclohexane for 48 h at 35−40 °C (Scheme 6).

During this time, 70% conversion (by integration of the ^{31}P NMR spectrum) to $N_3P_3(OCH_2CF_3)_5(NHC_6H_{11})$ was obtained. It should be noted that this reaction appeared to proceed with fewer side products and less color formation than the thermal nitrene insertion reaction with $N_3P_3(OC_6H_5)_5(N_3)$. Subsequent ultraviolet irradiation of $N_3P_3(OCH_2CF_3)_5(N_3)$ in toluene for 48 h showed no evidence of any reaction, and ultraviolet exposure of $N_3P_3(OCH_2CF_3)_5(N_3)$ in cyclohexene has shown only minimal evidence for any reaction (<1% by ^{31}P NMR integration) after 48 h of irradiation.

Ultraviolet spectroscopy of $N_3P_3(OCH_2CF_3)_5(N_3)$ in 95% ethanol showed a broad absorbance attributable to azide absorption primarily over the wavelength range 200−230 nm with a tail extending out to 280 nm. The maximum molar absorptivity (ϵ_{max}) was found to be only 720 at 208 nm. By contrast, phenoxy groups of $N_3P_3(OC_6H_5)_6$ have a molar absorptivity of 50 000 at 206 nm. Furthermore, the aryloxy UV absorbance overlaps the entire wavelength range in which $N_3P_3(OCH_2CF_3)(N_3)$ absorbs. This supports the theory that the phenoxy groups shield the azido group from ultraviolet light and inhibit photolytic nitrene formation.

Nucleophilic Azide Displacement. The ability of nucleophiles such as amines or metal alkoxides to displace the azido group is another characteristic of acyl azides.[35] $N_3P_3(OC_6H_5)_5(N_3)$ and $N_3P_3(OCH_2CF_3)_5(N_3)$ were treated with nucleophiles to determine if their azido groups share this trait. When $N_3P_3(OC_6H_5)_5(N_3)$ was treated with sodium phenoxide in refluxing THF, the azido group was displaced, and $N_3P_3(OC_6H_5)_6$ was formed. However, replacement of the azido group was slow. Only 30% of the azido groups (by ^{31}P NMR integration) were cleaved after 48 h. For comparison, aniline, a weaker nucleophile than sodium phenoxide, replaces all of the azido groups of benzene sulfonyl azide within 24 h in refluxing benzene. When $N_3P_3(OC_6H_5)_5(N_3)$ was treated with *n*-butylamine, no azide displacement was detected over 48 h in refluxing THF even when several equivalents of the amine were utilized. By contrast,

50% of the azido groups on $N_3P_3(OCH_2CF_3)_5(N_3)$ had been displaced in 48 h under similar conditions. Complete azido group replacement to form $N_3P_3(OCH_2CF_3)_5(NHCH_2CH_2CH_2CH_3)$ was observed in 5 days. Similarly, total azide displacement to form $N_3P_3(OCH_2CF_3)_5(OC_6H_5)$ was attained within 24 h when $N_3P_3(OCH_2CF_3)_5(N_3)$ was treated with sodium phenoxide in refluxing THF. Although the electronegative character of the CF_3 group should promote azide displacement in the above reactions, the difference in reactivity between $N_3P_3(OC_6H_5)_5(N_3)$ and $N_3P_3(OCH_2CF_3)_5(N_3)$ can also be attributed to the steric constraints imposed by the phenoxy groups which may interfere with nucleophilic attack at the phosphorus atom. Steric effects also explain the difference in azido group displacement between the phosphazene azides and the more reactive sulfonyl azides. It is likely that the presence of two aryloxy or alkoxy substituents and the phosphazene ring restrict the approach of attacking nucleophiles to a much greater extent than in a simple arylsulfonyl group.

Conclusions

A variety of cyclic phosphazene trimers containing the azido group with aryloxy, alkoxy, or dialkylamino cosubstituents were synthesized. The aryloxy- and alkoxyphosphazene azides underwent complete reaction with numerous phosphorus(III) species to form phosphazene phosphinimines. The success of these reactions indicates that these materials are promising candidates for the synthesis or modification of polymers via phosphinimine formation.

Several of the phosphazene azides showed successful nitrene insertion chemistry. With (aryloxy)phosphazene azides, this was via a thermally initiated route. Nitrene insertion was initiated by UV light with the alkoxyphosphazene azide in an aliphatic solvent. No photolytic insertion was observed when aromatic species were involved due to their significantly stronger absorption in the UV region relative to the azido groups. The (dialkylamino)phosphazene azides rearranged in preference to nitrene insertion chemistry. (Aryloxy)phosphazene derivatives with multiple azide groups have been utilized to cross-link polyolefins using thermally initiated nitrene insertion chemistry.

The displacement of the azido group on $N_3P_3(OCH_2CF_3)_5(N_3)$ was found to occur much more readily than with $N_3P_3(OC_6H_5)_5(N_3)$. This difference is attributed to the steric constraints imposed by the phenoxy cosubstituents.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical) was purified by recrystallization from heptane. Sodium azide, sodium hydroxide, sodium metal, phosphorus pentachloride, tetrabutylammonium bromide, and dimethylamine were obtained from Aldrich and used without further purification. Phenol (Aldrich) was sublimed under vacuum (22 °C, 0.1 mmHg) (reactions with Na metal) or used without further purification (reactions with NaOH). 2,2,2-Trifluoroethanol (Aldrich) and diethylamine (Aldrich) were distilled from CaH_2 under nitrogen. Tri-*n*-butylphosphine, triphenylphosphine, triphenyl phosphite, triethyl phosphite, dichlorophenylphosphine, dimethylphosphoramidous dichloride, and chlorodiphenylphosphine (Aldrich) were used without further purification. Hexamethylphosphorus triamide (Aldrich) was used without further purification. Acetone and MEK (EM Science) were used without further purification. THF and toluene (both EM Science) were dried over and distilled from sodium/benzophenone under an argon atmosphere. Silica gel (Aldrich, 70−230 mesh, 60 Å) was used as received.

Instruments. ^{31}P, ^{13}C, and ^{1}H spectra were recorded with use of a Bruker AMX-360 NMR operated at 146, 90.27, and 360 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to tetramethylsilane. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. ^{19}F spectra were recorded on a Bruker WP-200 NMR and are referenced to $CFCl_3$. All heteronuclear NMR spectra were proton decoupled. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR using BaF_2 salt crystals (25 mm diameter, 4 mm thick). Fast atom bombardment mass spectrometry was performed on a Kratos MS-50 mass spectrometer with a magnetic sector using xenon atoms and nitrophenyl octyl ether or CH_2Cl_2 as the matrix. Differential scanning calorimetry measurements were performed by the Dow Chemical Co. Ultraviolet irradiation experiments were carried out in a Rayonet photochemical reactor (254−300 nm). Ultraviolet spectroscopy measurements were performed using a Hewlett-Packard 8452A diode array spectrophotometer using Fisherbrand quartz cuvettes and scanning the wavelength range 190−820 nm. Elemental analysis was performed by Quantitative Technologies, Inc.

Sodium Phenoxide Synthesis. Sodium phenoxide was prepared from NaOH and phenol on the basis of a previously reported procedure.[41]

Cyclophosphazene Precursor Syntheses. $N_3P_3(OC_6H_5)_3Cl_3$ (2), $N_3P_3(OC_6H_5)_4Cl_2$ (3) and $N_3P_3(OC_6H_5)_5Cl$ (4). These materials were synthesized by a previously reported procedure.[42] The cis form of $N_3P_3(OC_6H_5)_3Cl_3$ was isolated by crystallization from hexanes at −11 °C followed by several recrystallizations from petroleum ether (bp 40−60 °C) at −11 °C.

$N_3P_3(OCH_3CF_3)_5Cl$ (5). Initially $N_3P_3(OCH_2CF_3)_5Cl$ was prepared by a known procedure[43] which yielded a mixture of $N_3P_3(OCH_2CF_3)_4Cl_2$, $N_3P_3(OCH_2CF_3)_5Cl$, and $N_3P_3(OCH_2CF_3)_6$ from which the individual constituents could not be isolated. $N_3P_3(OCH_2CF_3)_5Cl$ was subsequently produced by a multistep procedure. The first step was the conversion of $N_3P_3Cl_6$ to $N_3P_3(OCH_2CF_3)_6$, which was carried out according to a literature procedure using THF instead of diethyl ether as the reaction solvent and distillation of the product under vacuum.[44] $N_3P_3(OCH_2CF_3)_6$ was subsequently hydrolyzed to $N_3P_3(OCH_2CF_3)_5(O^-Na^+)$, again by a previously reported method.[44] However, this reaction was conducted in refluxing acetone instead of diglyme. $N_3P_3(OCH_2CF_3)_5(O^-Na^+)$ was then converted to $N_3P_3(OCH_2CF_3)_5Cl$ through the following procedure. $N_3P_3(OCH_2CF_3)_5(O^-Na^+)$ (20.6 g, 0.0308 mol) was dissolved in acetone (50 mL). Tetrabutylammonium bromide (11.4 g, 0.0354 mol) was dissolved in another portion of acetone (50 mL) and was added to the sodium salt. The mixture was stirred for 2 h at room temperature. Next, solvent was removed by rotoevaporation and the residue was mixed with CH_2Cl_2 (100 mL). The mixture was filtered through Celite and the CH_2Cl_2 removed by rotoevaporation. The resultant oil was redissolved in freshly distilled CH_2Cl_2 (150 mL) under argon. Phosphorus pentachloride (10.0 g, 0.0480 mol) was dissolved in freshly distilled CH_2Cl_2 (150 mL) under argon. The $N_3P_3(OCH_2CF_3)_5(O^-n\text{-}Bu_4N^+)$ solution was then added to the PCl_5 solution via syringe. The reaction mixture was stirred at room temperature for 48 h. Excess PCl_5 was destroyed by pouring the reaction mixture into 4% aqueous $NaHCO_3$ (500 mL). The mixture was shaken in a separatory funnel and the CH_2Cl_2 phase (lower layer) collected. The CH_2Cl_2 was removed by rotoevaporation, and the resultant material was extracted between diethyl ether (200 mL) and 4% aqueous $NaHCO_3$ (200 mL). The ethereal layer was rinsed with distilled water (200 mL). Na_2SO_4 was then added to dry the solution. After the ether solution was stirred with Na_2SO_4 for 20 min, the sodium sulfate was filtered off, and the ether was removed by rotoevaporation. The resultant liquid was distilled under vacuum (95 °C, 0.2 mmHg). Yield: 16.3 g (68%) ($N_3P_3Cl_6$ to $N_3P_3(OCH_2CF_3)_5Cl$).

^{31}P NMR (CD_2Cl_2): δ 27.1 (t, 1P, $(CF_3CH_2O)P(Cl)$), 14.9 (d, 2P, $P(OCH_2CF_3)_2$). ^{1}H NMR (CD_2Cl_2): δ 4.58−4.53 (m, 2H, $CF_3CH_2O^-$), 4.49−4.38 (m, 8H, CF_3CH_2O-).

$N_3P_3(N(CH_3)_2)_4Cl_2$ (6). This compound was synthesized via a literature procedure.[45]

$N_3P_3(N(CH_2CH_3)_2)_3Cl_3$ (7). This material was synthesized by a previously reported procedure.[45] However, THF was used as the solvent instead of benzene.

(41) Kornblum, N.; Lurie, A. P. *J. Am. Chem. Soc.* **1959**, *81*, 2705.
(42) Dell, D.; Fitzsimmons, W.; Shaw, R. A. *J. Chem. Soc.* **1965**, 4070.
(43) Schmutz, J. L.; Allcock, H. R. *Inorg. Chem.* **1975**, *14*, 2433.
(44) Allcock, H. R.; Walsh, E. J. *J. Am. Chem. Soc.* **1972**, *94*, 119.
(45) Ray, S. K.; Shaw, R. A. *J. Chem. Soc.* **1961**, 872.

Azidocyclophosphazenes. Typical Synthesis. The chlorocyclophosphazenes, **2**−**7** (6.3×10^{-3} mol), were dissolved in MEK (60 mL) at room temperature. Tetrabutylammonium bromide (0.28 g, 8.7×10^{-4} mol) was added to the solution, followed by solid sodium azide, NaN_3 (1.5 equiv per P−Cl bond). The mixture was then heated to reflux for 48 h, allowed to cool to room temperature, and examined by ^{31}P NMR to check for complete conversion to the azide. MEK was then removed by rotoevaporation, and the resultant oily, white solid was extracted between diethyl ether (100 mL) and deionized water (100 mL). The ethereal layer was washed again with deionized water (100 mL) and then with 4% aqueous $NaHCO_3$ (100 mL). The ether layer was then dried with $MgSO_4$ or Na_2SO_4 and filtered to yield a clear, pale yellow solution. A slightly cloudy oil generally formed when the ether was removed by rotoevaporation. The oil was purified further by column chromatography on silica gel with 90% hexanes/10% diethyl ether as the eluent. The purified fractions were combined, and the solvent was removed to yield a colorless oil. The oil was dissolved in hot hexanes (50 mL), filtered, and allowed to cool to room temperature. A clear, colorless oil separated from solution on cooling the mixture to −11 °C. The hexanes were decanted off, and the oil was dried under vacuum. Additional purification procedures for individual trimers are described separately with the following characterization information.

$N_3P_3(OC_6H_5)_3(N_3)_3$ (2a). The cis and trans isomers were separated during column chromatography (90% hexanes/10% diethyl ether). The trans isomer was extracted by dissolving it in hexanes and cooling to −55 °C. The hexanes were poured off immediately before the solid could melt on warming since the trans isomer is an oil at room temperature. This extraction was repeated twice. The cis isomer was recrystallized several times from petroleum ether (−11 °C). The respective isomers were then dried under vacuum.

Data for the cis isomer: yield: 10%; mp 37−39 °C; ^{31}P NMR (CD_2Cl_2) δ 11.7 (s, 3P, $(C_6H_5O)P(N_3)$); ^1H NMR (CD_2Cl_2) δ 7.24−7.15 (m, 9H, ArH), 6.89 (d, 6H, ArH); ^{13}C NMR (CD_2Cl_2): δ 150.5 (s, ArC), 130.6 (s, ArC), 126.6 (s, ArC), 121.7 (s, ArC); $C_{18}H_{15}N_{12}O_3P_3$ calcd mass 540.33. FAB(+)-MS *m*/*z* 541.1 [MH^+]; FTIR (neat from CH_2Cl_2) 2158 cm^{-1}, asymmetric N_3 stretch). Anal. Calcd for $C_{18}H_{15}N_{12}O_3P_3$: C, 40.01; H, 2.80; N, 31.11; P, 17.20; Cl, 0.00. Found: C, 40.09; H, 2.44; N, 31.17; P, 17.26; Cl, <0.1.

Data for the trans isomer: yield: 5%; ^{31}P NMR (CD_2Cl_2) δ 13.1−10.8 (m, 3P, $(C_6H_5O)P(N_3)$); ^1H NMR (CD_2Cl_2) δ 7.44 (t, 2H, ArH), 7.39−7.27 (m, 9H, ArH), 7.14 (d, 4H, ArH); ^{13}C NMR (CD_2Cl_2) δ 150.4 (t, ArC), 150.2 (d, ArC), 130.3 (d, ArC), 127.0 (s, ArC), 126.8 (s, ArC), 122.2 (d, ArC), 121.9 (s, ArC)); $C_{18}H_{15}N_{12}O_3P_3$ calcd mass 540.33. FAB(+)-MS *m*/*z* 541.3 [MH^+]; FTIR (neat from CH_2Cl_2) 2148 cm^{-1}, asymmetric N_3 stretch. Anal. Calcd for $C_{18}H_{15}N_{12}O_3P_3$: C, 40.01; H, 2.80; N, 31.11; P, 17.20; Cl, 0.00. Found: C, 40.10; H, 2.78; N, 31.21; P, 17.27; Cl, 0.48.

$N_3P_3(OC_6H_5)_4(N_3)_2$ (3a). This species was a clear, colorless oil, presumably because it is a mix of the cis and trans isomers. Yield: 80%.

^{31}P NMR (CD_2Cl_2): δ 13.2−12.3 (overlapping d, cis + trans isomers, 2P, $(C_6H_5O)P(N_3)$), 8.5−7.2 (overlapping q, cis + trans isomers, 1P, $(C_6H_5O)_2P$) ^1H NMR (CD_2Cl_2) δ 7.6−6.9 (m, 20H, ArH); $C_{24}H_{20}N_9O_4P_3$ calcd mass 591.40. FAB(+)-MS *m*/*z* 592.1 [MH^+]; FTIR (neat) 2152 cm^{-1}, asymmetric N_3 stretch). Anal. Calcd for $C_{24}H_{20}N_9O_4P_3$: C, 48.74; H, 3.41; N, 21.32; P, 15.71; Cl, 0.00. Found: C, 48.14; H, 3.26; N, 21.14; P, 15.86; Cl, 424 ppm.

$N_3P_3(OC_6H_5)_5(N_3)$ (4a). This oil crystallized after several days (5−10) under vacuum or at atmospheric pressure to yield a white solid. Yield: 89%. Mp: 45−47 °C.

^{31}P NMR ($CDCl_3$): δ 13.6 (t, 1P, $(C_6H_5O)P(N_3)$), 8.6 (d, 2P, $(C_6H_5O)_2P$). ^1H NMR ($CDCl_3$): δ 7.3−6.9 (m, 25H, ArH). ^{13}C NMR ($CDCl_3$): δ 151.0 (m, ArC), 150.5 (d, ArC), 130.1 (d, ArC), 125.7 (d, ArC), 121.6 (m, ArC). $C_{30}H_{25}N_6O_5P_3$ calcd mass 642.77. FAB(+)-MS: *m*/*z* 643.2 [MH^+]. FTIR (neat as oil): 2148 cm^{-1}, asymmetric N_3 stretch. Anal. Calcd for $C_{30}H_{25}N_6O_5P_3$: C, 56.08; H, 3.92; N, 13.08; P, 14.46; Cl, 0.00. Found: C, 56.30; H, 3.76; N, 13.29; P, 14.23; Cl, 294 ppm.

$N_3P_3(OCH_2CF_3)_5(N_3)$ (5a). An attempt was made to purify this material by vacuum distillation (85 °C, 0.1 mmHg), but the resultant liquid was orange in color and was impure by elemental analysis. Instead, after extraction between diethyl ether and water, followed by drying with Na_2SO_4, the product was purified by column chromatography on silica gel (70% hexanes/30% diethyl ether). The fractions were combined, and the solvent was removed by rotoevaporation. Similar to *trans*-$N_3P_3(OC_6H_5)_3(N_3)_3$, this product was obtained by cooling in hexanes at −55 °C several times followed by drying under vacuum. The final product was obtained as a clear, colorless liquid. Yield: 74%.

^{31}P NMR (CD_2Cl_2): δ 17.6 (q, 1P, $(CF_3CH_2O)P(N_3)$), 16.2 (d, 2P, $(CF_3CH_2O)_2P$). ^1H NMR (CD_2Cl_2): δ 4.40−4.26 (m, 10H, CF_3CH_2O−). ^{13}C NMR (CD_2Cl_2): δ 123.7 (d of q, CF_3−), 63.9 (m, CF_3CH_2O−). ^{19}F (CD_2Cl_2): δ 51.1 (s, 9F, CF_3−), 51.0 (s, 6F, CF_3−); $C_{10}H_{10}F_{15}N_6O_5P_3$ calcd mass 672.15. FAB(+)-MS *m*/*z* 673.0 [MH^+]. FTIR (neat from CH_2Cl_2): 2165 cm^{-1}, asymmetric N_3 stretch. Anal. Calcd for $C_{10}H_{10}F_{15}N_6O_5P_3$: C, 17.87; H, 1.50; N, 12.51; F, 42.40; P, 13.82; Cl, 0.00. Found: C, 17.64; H, 1.28; N, 12.24; F, 42.29; P, 13.68; Cl, <0.1.

$N_3P_3(N(CH_3)_2)_4(N_3)_2$ (6a). After column chromatography, this material was purified furthered by multiple recrystallizations from hexanes at −55 °C followed by drying under vacuum. Yield: 53%.

^{31}P NMR ($CDCl_3$): δ 24.8 (t, 1P, $((CH_3)_2N)_2P$), 21.4 (d, 2P, $((CH_3)_2N)P(N_3)$). ^1H NMR ($CDCl_3$): δ 2.7−2.6 (m, 18H, (CH_3N−). ^{13}C NMR ($CDCl_3$): δ 36.6 (s, CH_3N−); $C_8H_{24}N_{13}P_3$ calcd mass 395.31. FAB(+)-MS: *m*/*z* 396.1 [MH^+]. FTIR (neat from CH_2Cl_2): 2138 cm^{-1}, asymmetric N_3 stretch. Anal. Calcd for $C_8H_{24}N_{13}P_3$: C, 24.30; H, 6.08; N, 46.08; P, 23.54; Cl, 0.00. Found: C, 24.54; H, 6.12; N, 45.21; P, 22.75; Cl, 0.31.

$N_3P_3(N(CH_2CH_3)_2)_3(N_3)_3$ (7a). This clear, colorless oil was dried directly after column chromatography. No extraction with hexanes was performed. Yield: 70%.

^{31}P NMR ($CDCl_3$): δ 18.7−17.2 (m) (appears to be a quartet 18.3 (1P) and doublet 17.4 (2P)). ^1H NMR ($CDCl_3$): δ 3.3−3.0 (m, 12H), 1.2−0.9 (overlapping triplets, 18H). ^{13}C NMR ($CDCl_3$): δ 39.7 (d, CH_3CH_2N−), 14.4 (s, CH_3CH_2N−). $C_{12}H_{30}N_{15}P_3$ calcd mass: 477.42. FAB(+)-MS: *m*/*z* 478.4 [MH^+]. FTIR (neat): 2153 cm^{-1}, asymmetric N_3 stretch. Anal. Calcd for $C_{12}H_{30}N_{15}P_3$: C, 30.19; H, 6.33; N, 44.02; P, 19.46; Cl, 0.00. Found: C, 31.17; H, 6.02; N, 43.78; P, 19.44; Cl, 524 ppm.

Table 1. Phosphazene Phosphinimines and Reaction Conditions

phosphinimine	reacn solvent (temp, °C)	reacn time
$N_3P_3(OC_6H_5)_5(N{=}P(n\text{-}C_4H_9)_3)$	THF (22)	24 h
$N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)_3)$	THF (65)	24 h
$N_3P_3(OC_6H_5)_5(N{=}P(OC_6H_5)_3)$	toluene (110)	72 h
$N_3P_3(OC_6H_5)_5(N{=}P(OCH_2CH_3)_3)$	2-butanone (80)	24 h
$N_3P_3(OC_6H_5)_5(N{=}P(N(CH_3)_2)_3)$	THF (65)	24 h
$N_3P_3(OC_6H_5)_4(N{=}P(C_6H_5)_3)_2$	toluene (110)	48 h
$N_3P_3(OC_6H_5)_3(N{=}P(C_6H_5)_3)_3$	toluene (110)	60 h
$N_3P_3(OCH_2CF_3)_5(N{=}P(C_6H_5)_3)$	toluene (110)	24 h
$N_3P_3(OCH_2CF_3)_5(N{=}P(OC_6H_5)_3)$	2-butanone (80)	24 h
$N_3P_3(OCH_2CF_3)_5(N{=}P(N(CH_3)_2)_3)$	THF (65)	24 h
$N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)_2Cl)$	toluene (110)	24 h
$N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)Cl_2)$	toluene (110)	7 days[a]
$N_3P_3(OC_6H_5)_5(N{=}P(N(CH_3)_2)Cl_2)$	toluene (110)	7 days[b]

[a] 90% conversion by ^{31}P NMR. [b] Only 63% conversion by ^{31}P NMR.

Phosphinimine Syntheses. General Synthesis Procedure. The reactions were generally carried out in distilled MEK, toluene, or THF. For specific reaction solvents and reaction times see Table 1. The azidophosphazene was dissolved in an appropriate solvent under nitrogen or argon. The phosphorus(III) compound (2 equiv/mol of azide) was added, and the reaction mixture was heated to reflux. The progress of the reaction was then followed by disappearance of the phosphorus azide resonance in the ^{31}P NMR spectrum. The reaction was allowed to cool to room temperature, and the solvent was removed by rotoevaporation. The product was dissolved in diethyl ether and extracted twice with deionized water. The ethereal solution was then extracted with 2% aqueous $NaHCO_3$, dried with $MgSO_4$, and filtered to yield a clear, colorless solution. The ether was then evaporated. Further purification procedures varied by product. The remaining purification details are given below for the individual phosphinimines.

$N_3P_3(OC_6H_5)_5(N{=}P(n\text{-}C_4H_9)_3)$ (8). This material was dissolved in hot hexanes (20 mL), filtered through filter paper, and cooled to −11 °C for 24 h. The hexanes were poured off while still cold to yield a clear, colorless oil. The oil was then dissolved in fresh hexanes and again cooled to −11 °C for 24 h. The hexanes were again poured off while still cold. This cold hexanes extraction procedure was repeated twice. The clear, colorless viscous oil was then dried under vacuum for 48 h. Yield: 48%.

^{31}P NMR (CD_2Cl_2): δ 30.4 (d, 1P, $(n\text{-}C_4H_9)_3P{=}N-$), 8.4 (d, 2P, $(C_6H_5O)_2P$), 7.6−6.4 (m, 1P, $(n\text{-}C_4H_9)_3P{=}N)P(OC_6H_5)$. ^{1}H NMR ($CD_2Cl_2$): δ 7.48−7.14 (m, 25H, ArH), 1.91−1.72 (m, 6H, $-PCH_2-$), 1.66−1.41 (m, 12H, $-PCH_2CH_2CH_2CH_3$), 1.05 (t, 9H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ 153.4 (d, ArC), 152.4 (d of t, ArC), 130.0 (d, ArC), 129.6 (s, ArC), 125.0 (d, ArC), 124.1 (s, ArC), 122.5 (d, ArC), 121.7 (m, ArC), 26.9 (d of d, $-PCH_2-$), 24.9 (d, $-PCH_2CH_2-$), 24.4 (d, $-PCH_2CH_2CH_2CH_3$), 14.2 (s, $-CH_3$). $C_{42}H_{52}N_4O_5P_4$ calcd mass: 816.75. FAB(+)-MS: *m*/*z* 817.4 [MH^+].

$N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)_3)$ (9). This product was crystallized from diethyl ether (20 mL) by addition of hexanes followed by cooling to −11 °C. The solvent was poured off, and the white crystalline product was rinsed twice with hexanes (10 mL). The product was then dried under vacuum for 24 h. Yield: 59%.

^{31}P NMR ($CDCl_3$): δ 10.4 (d, 1P, $(C_6H_5)_3P{=}N-$), 8.5 (d, 2P, $(C_6H_5O)_2P$), 6.9−5.6 (m, 1P, $(C_6H_5)_3P{=}N)P(OC_6H_5)$. ^{1}H NMR ($CDCl_3$): δ 7.6−7.2 (m, 15H, ArH), 7.1−6.8 (m, 25H, ArH). ^{13}C NMR ($CDCl_3$): δ 151.5 (d, ArC), 133.0 (d, ArC), 132.1 (d, ArC), 129.2 (s, ArC), 128.9 (s, ArC), 128.5 (d, ArC), 124.1 (d, ArC), 123.3 (s, ArC), 122.0 (d, ArC), 121.3 (d, ArC). $C_{48}H_{40}N_4O_5P_4$ calcd mass: 876.72. FAB(+)-MS: *m*/*z* 877.4 [MH^+].

$N_3P_3(OC_6H_5)_5(N{=}P(OC_6H_5)_3)$ (10). This product was crystallized from diethyl ether by the addition of hexanes. The final white solid was then dried under vacuum. Yield: 36%.

^{31}P NMR ($CDCl_3$): δ 8.5 (d, 2P, $(C_6H_5O)_2P$), 1.6 (q, 1P, $(C_6H_5O)_3P{=}N)P(OC_6H_5)$, −25.7 (d, 1P, $(C_6H_5O)_3P{=}N-$). ^{1}H NMR ($CDCl_3$): δ 7.22 (t, 7H, ArH), 7.16−6.94 (m, 31H, ArH), 6.76 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 151.2 (d, ArC), 150.3 (d, ArC), 129.7 (s, ArC), 129.1 (s, ArC), 128.7 (s, ArC), 125.6 (s, ArC), 124.2 (d, ArC), 123.4 (s, ArC), 121.4 (d, ArC), 121.0 (d, ArC), 120.5 (d, ArC). $C_{48}H_{40}N_4O_8P_4$ calcd mass: 924.72. FAB(+)-MS: *m*/*z* 925.0 [MH^+]. Anal. Calcd for $C_{48}H_{40}N_4O_8P_4$: C, 62.34; H, 4.36; N, 6.06, P, 13.40. Found: C, 62.44; H, 4.24; N, 6.21; P, 13.43.

$N_3P_3(OC_6H_5)_5(N{=}P(OCH_2CH_3)_3)$ (11). This material was further purified by dissolving it in hot hexanes (20 mL) and cooling the solution to −11 °C where a clear, colorless oil separated out. The hexanes were decanted off, and the product was dried under vacuum. Yield: 46%.

^{31}P NMR ($CDCl_3$): δ 8.3 (d, 2P, $(C_6H_5O)_2P$), 2.0 (q, 1P, $(CH_3CH_2O)_3P{=}N)P(OC_6H_5)$, −5.0 (d, 1P, $(CH_3CH_2O)_3P{=}N-$). ^{1}H NMR ($CDCl_3$): δ 7.34−7.09 (m, 25H, ArH), 4.19−4.00 (m, 6H, CH_3CH_2O-), 1.30 (t, 9H, CH_3CH_2O-); ^{13}C NMR ($CDCl_3$) δ 151.3 (d, ArC), 151.1 (d, ArC), 129.1 (s, ArC), 128.8 (s, ArC), 124.2 (s, ArC), 123.5 (s, ArC), 121.7 (d, ArC), 121.0 (d, ArC), 64.3 (d, CH_3CH_2O-), 15.8 (d, CH_3CH_2O-). $C_{36}H_{40}N_4O_8P_4$ calcd mass: 780.60. FAB(+)-MS: *m*/*z* 781.2 [MH^+].

$N_3P_3(OC_6H_5)_5(N{=}P(N(CH_3)_2)_3)$ (12). This compound was further purified by dissolving it in hot hexanes (30 mL) and cooling the solution to −11 °C for 12 h. The hexanes were decanted off to yield a viscous yellow oil. The oil was dried under vacuum. The oil crystallized into a yellow solid after several months, but this did not affect its NMR spectra. Yield: 34%.

^{31}P NMR ($CDCl_3$): δ 20.6 (d, 1P, $((CH_3)_2N)_3P{=}N-$); 8.4 (d, 2P, $(C_6H_5O)_2P$), 1.0 (q, 1P, $((CH_3)_2N)_3P{=}N)P(OC_6H_5)$. ^{1}H NMR ($CDCl_3$): δ 7.21−6.99 (m, 25H, ArH), 2.48 (d, 18H, $(CH_3)N$)). ^{13}C NMR ($CDCl_3$): δ 151.6 (d, ArC), 129.2 (d, ArC), 128.9 (s, ArC), 124.1 (d, ArC), 123.2 (s, ArC), 122.0 (d, ArC), 121.3 (q, ArC), 37.1 (d, $(CH_3)N-$); $C_{36}H_{43}N_7O_5P_4$ calcd mass: 777.65. FAB(+)-MS: *m*/*z* 778.0 [MH^+].

$N_3P_3(OC_6H_5)_4(N{=}P(C_6H_5)_3)_2$ Mixture of Cis- and Trans Isomers (13). This mixture was purified by several recrystallizations from THF and hexanes followed by drying under vacuum. (Note: The product usually remained a viscous oil during recrystallization, but it solidified with a great deal of foaming when dried under vacuum. Yield: 32%.)

^{31}P NMR (CD_2Cl_2): δ 9.1−7.8 (m, 3P, $(C_6H_5O)_2P$ and $(C_6H_5)_3P{=}N$), 6.6−5.9 (m, 2P, $(C_6H_5)_3P{=}N)P(OC_6H_5)$). ^{1}H NMR ($CD_2Cl_2$): 7.89−7.85 (m, 12H, ArH), 7.67 (t, 6H, ArH), 7.56−7.51 (m, 12H, ArH), 7.29−7.13 (m, 20H, ArH). $C_{60}H_{50}N_5O_4P_5$ calcd mass: 1059.90. FAB-(+)-MS: *m*/*z* 1060.8 [MH^+].

$N_3P_3(OC_6H_5)_3(N{=}P(C_6H_5)_3)_3$ Mixture of Cis- and Trans Isomers (14). This product precipitated from the reaction solution as a white powder. The solid was filtered off and was purified by several recrystallizations from CH_2Cl_2 followed by rinsing with hexanes. The resultant white powder was then dried under vacuum. Yield: 42%.

^{31}P NMR ($CDCl_3$): δ 6.7−6.5 (br m, 3P, $(C_6H_5)_3P{=}N$), 5.1−4.9 (br m, 3P, $(C_6H_5)_3P{=}N)P(OC_6H_5)$). ^{1}H NMR ($CDCl_3$): 7.60−6.60 (m, 60H, ArH). $C_{72}H_{60}N_6O_3P_6$ calcd mass: 1243.08. FAB(+)-MS: *m*/*z* 1243.2 [M^+].

$N_3P_3(OCH_2CF_3)_5(N{=}P(C_6H_5)_3)$ (15). Compound **15** was purified by column chromatography on silica gel (80% hexanes/20% diethyl ether). The solvent was removed by rotoevaporation, and the resultant clear, colorless oil was dried under vacuum. Yield: 62%.

^{31}P NMR ($CDCl_3$): δ 17.4 (d, 2P, $(CF_3CH_2O)_2P$), 13.6 (d, 1P, $(C_6H_5)_3P{=}N-$), 10.4 (m, 1P, $(CF_3CH_2O)P(-N{=}P(C_6H_5)_3)$). ^{1}H NMR ($CDCl_3$): δ 7.7−7.2 (m, 15H, ArH), 4.3−3.9 (m, 6H, CF_3CH_2O-), 3.8−3.6 (m, 4H, CF_3CH_2O-). ^{13}C NMR ($CDCl_3$): δ 133.1 (d, ArC), 133.0 (d, ArC), 130.3 (d, ArC), 129.1 (d, ArC), 123.3 (d of q, CF_3CH_2O-), 62.5 (m, CF_3CH_2O-). $C_{28}H_{25}F_{15}N_4O_5P_4$ calcd mass: 906.40. FAB(+)-MS: *m*/*z* 906.7 [MH^+]. Anal. Calcd for $C_{28}H_{25}F_{15}N_4O_5P_4$: C, 37.10; H, 2.76; N, 6.18; F, 31.44; Cl, 0.00. Found: C, 37.49; H, 2.76; N, 6.15; F, 31.15; Cl, <0.10.

$N_3P_3(OCH_2CF_3)_5(N{=}P(OC_6H_5)_3)$ (16). Compound **16** was further purified by column chromatography on silica gel using 67% dichloromethane/33% hexanes as the solvent. Fractions containing the desired product were combined, and solvent was removed by rotoevaporation. The resulting clear, colorless oil was dried under vacuum for 24 h. No yield could be calculated as this material was produced from the mixture of $N_3P_3(OCH_2CF_3)_4(N_3)_2$, $N_3P_3(OCH_2CF_3)_5(N_3)$, and $N_3P_3(OCH_2CF_3)_6$.

^{31}P NMR ($CDCl_3$): δ 17.2 (d, 2P, $(CF_3CH_2O)_2P$), 6.0 (q, 1P, $(CF_3CH_2O)P(-N{=}P(OC_6H_5)_3)$, −23.0 (d, 1P, $(C_6H_5O)_3P{=}N-$)). ^{1}H NMR ($CDCl_3$): δ 7.6−7.2 (m, 15H, ArH), 4.5−4.2 (m, 4H, CF_3CH_2O-), 4.2−4.0 (m, 4H, CF_3CH_2O-), 4.0−3.8 (m, 2H, CF_3CH_2O-). ^{13}C NMR ($CDCl_3$): δ 150.5 (d, ArC), 130.4 (s, ArC), 126.7 (s, ArC), 123.2 (d of q, CF_3-), 120.7 (s, ArC), 62.4 (m, CF_3CH_2O-); $C_{28}H_{25}F_{15}N_4O_8P_4$ calcd mass: 954.40. FAB(+)-MS: *m*/*z* 954.7 [MH^+]. Anal. Calcd for $C_{28}H_{25}F_{15}N_4O_8P_4$: C, 35.23, H, 2.64; N, 5.87; F, 29.86; Cl, 0.00. Found: C, 35.37; H, 2.58; N, 5.86; F, 28.67; Cl, 0.10.

$N_3P_3(OCH_2CF_3)_5(N{=}P(N(CH_3)_2)_3)$ (17). This compound was further purified by several recrystallizations from hexanes (20 mL) at −11 °C. Yield: 58%. Mp: 55−58 °C.

^{31}P NMR (CD_2Cl_2): δ 22.9 (d, 1P, $((CH_3)_2N)_3P{=}N-$)), 17.9 (d, 2P, $(CF_3CH_2O)_2P$), 4.8 (q, 1P, $(CF_3CH_2O)P(-N{=}P(N(CH_3)_2)_3)$). ^{1}H NMR ($CD_2Cl_2$): δ 4.40−4.30 (m, 8H, CF_3CH_2O-), 4.20−4.15 (m, 2H, CF_3CH_2O-), 2.72 (d, 18H, $(CH_3)N-$). ^{13}C NMR (CD_2Cl_2): δ 122.6 (d of q, CF_3-), 62.7 (m, CF_3CH_2O-), 37.3 (d, $(CH_3)N-$). $C_{16}H_{28}F_{15}N_7O_5P_4$ calcd mass: 807.33. FAB(+)-MS: *m*/*z* 808.4 [MH^+]. Anal. Calcd for $C_{16}H_{28}F_{15}N_7O_5P_4$: C, 23.80; H, 3.50; N, 12.15; P, 15.35. Found: C, 23.98; H, 3.37; N, 12.19; P, 15.47.

Halogenated Phosphinimines. General Methods. These materials were prepared by the same general procedure as described above. However, toluene was used as the reaction solvent. Because of the presence of the reactive P−Cl linkages, the halogenated phosphinimines were characterized in their reaction mixtures only by ^{31}P NMR.

$N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)_2Cl)$ (18). ^{31}P NMR (D_2O cap in toluene): δ 21.6 (d, 1P, $Cl(C_6H_5)_2P{=}N-$), 8.8 (d, 2P, $(C_6H_5O)_2P$), 7.2−6.0 (m, 1P, $(C_6H_5O)P(N{=}P(C_6H_5)_2Cl)$).

$N_3P_3(OC_6H_5)_5(N{=}P(C_6H_5)Cl_2)$ (19). ^{31}P NMR (D_2O cap in toluene): δ 14.4 (d, 1P, $Cl_2(C_6H_5)P{=}N-$), 9.0 (d, 2P, $(C_6H_5O)_2P$), 5.6−4.2 (m, 1P, $(C_6H_5O)P(N{=}P(C_6H_5)Cl_2)$).

$N_3P_3(OC_6H_5)_5(N{=}P(N(CH_3)_2)Cl_2)$ (20). ^{31}P NMR (D_2O cap in toluene): δ 8.9 (d, 2P, $(C_6H_5O)_2P$), 4.6−3.1 (m, 1P, $(C_6H_5O)P(N{=}P(N(CH_3)_2)Cl_2)$); 0.6 (d, 1P, $Cl_2((CH_3)_2N)P{=}N-$)).

Thermal Nitrene Insertion: $N_3P_3(OC_6H_5)(N_3)$ (4a) in $C_6H_5CH_2(CH_2)_7CH_3$. $N_3P_3(OC_6H_5)N_3$ (0.3 g, 5×10^{-4} mol) was dissolved in 1-phenylnonane (3.5 g, 0.017 mol), and the mixture was heated to reflux

at which point vigorous gas evolution commenced. After about 5 min, the gas evolution slowed, and the mixture was allowed to cool to room temperature. The mixture was purified by column chromatography on silica (20% Et_2O/80% hexanes). The solvent was removed by rotoevaporation and the product dried under vacuum to yield a clear, colorless oil. Yield: 26%.

^{31}P NMR (CD_2Cl_2): δ 11.7 (q, 1P, $(C_6H_5O)P(NHC_6H_4CH_2(CH_2)_7CH_3)$), 8.9 (d, 2P, $(C_6H_5O)_2P$). ^{1}H NMR (CD_2Cl_2): δ 7.2−6.7 (m, 29H, ArH), 4.51 (1H, $PNHC_6H_4-$), 2.10 (t, 2H, $-C_6H_4CH_2-$), 1.5−1.0 (m, 14H, $-C_6H_4CH_2(CH_2)_7-$), 0.80 (t, 3H, $-CH_2(CH_2)_7CH_3$). $C_{45}H_{49}N_4O_5P_3$ calcd mass: 818.79. FAB(+)-MS: *m*/*z* 819.8 [MH^+].

Photolytic Nitrene Insertion: $N_3P_3(OCH_2CF_3)_5(N_3)$ (5a) in Cyclohexane. $N_3P_3(OCH_2CF_3)_5(N_3)$ (2.0 g, 3.0×10^{-3} mol) was dissolved in cyclohexane (100 mL) at 35−40 °C. The solution was then placed in a photochemical reactor and subjected to ultraviolet irradiation (254−300 nm) for 48 h. Additional cyclohexane was added periodically to compensate for evaporation. Samples of the reaction mixture were analyzed by ^{31}P NMR spectroscopy after 24 and 48 h in the reactor. After 24 h, 20% insertion was indicated by ^{31}P NMR integration. After 48 h, 70% insertion was estimated. The remaining cyclohexane was allowed to evaporate in a fume hood. The resultant pale yellow oil was purified by column chromatography on silica gel (80% hexanes/20% diethyl ether). The presence of the insertion product in the resultant fractions was determined by ^{31}P NMR spectroscopy. Fractions containing the desired material were combined, and the ether/hexane solvent was allowed to evaporate. The product was then purified by recrystallization from hexanes (10 mL) at −11 °C. The hexanes were filtered off, and the resultant white crystalline solid was recrystallized from petroleum ether (bp: 40−60 °C) (10 mL) twice more. The final white solid was then dried under vacuum with gentle heat for 24 h. Yield: 0.30 g 14%.

^{31}P NMR (CD_2Cl_2): δ 20.6 (t, 1P, (CF_3CH_2O) *P* (NHC_6H_{11}), 17.4 (d, 2P, $(CF_3CH_2O)_2P$). ^{1}H NMR (CD_2Cl_2): δ 4.47−4.25 (m, 8H, CF_3CH_2O-), 4.25−4.14 (m, 2H, CF_3CH_2O-), 3.05 (br m, 1H, $-PNHC_6H_{11}$), 2.72 (t, 1H, cyclohexane: $-NHCHC_5H_{10}$), 1.93−1.89 (m, 2H, cyclohexane: $-CH_2-$), 1.74−1.68 (m, 2H, cyclohexane: $-CH_2-$), 1.62−1.54 (m, 1H, cyclohexane: $-CH_2-$), 1.43−1.05 (m, 5H, cyclohexane: $-CH_2-$). ^{13}C NMR (CD_2Cl_2): δ 123.6 (d of q, CF_3CH_2O-), 63.3 (m, CF_3CH_2O-), 51.4 (s, cyclohexane: $-PNHCHC_5H_{10}$), 36.2 (d, cyclohexane: $-CH_2-$), 25.6 (s, cyclohexane: $-CH_2-$), 25.2 (s, cyclohexane: $-CH_2-$). $C_{16}H_{22}F_{15}N_4O_5P_3$ calcd mass: 728.28. FAB(+)MS: *m*/*z* 729.0 [MH^+].

Azido Group Displacement: Reactions of $N_3P_3(OC_6H_5)_5(N_3)$ (4a) with $NaOC_6H_5$ and $CH_3CH_2CH_2CH_2NH_2$. $N_3P_3(OC_6H_5)_5(N_3)$ (2.32 $\times 10^{-3}$ mol) was dissolved in THF (50 mL) under nitrogen. The corresponding nucleophiles (sodium phenoxide or *n*-butylamine) (7.1×10^{-3} mol) were then added, and the mixtures were heated to reflux for 48 h. Azide displacement was measured by integration of the ^{31}P NMR spectrum. Specifically, the singlet resonance at 9.7 ppm for $N_3P_3(OC_6H_5)_6$ versus the doublet and triplet resonances of $N_3P_3(OC_6H_5)_5(N_3)$ was utilized in the phenoxide-induced displacement. No change was observed in the ^{31}P NMR spectrum when $N_3P_3(OC_6H_5)_5(N_3)$ was treated with *n*-butylamine.

Azido Group Displacement: $N_3P_3(OCH_2CF_3)_5(N_3)$ (5a) with $CH_3CH_2CH_2CH_2NH_2$. $N_3P_3(OCH_2CF_3)_5(N_3)$ (1.56 g, 2.32×10^{-3} mol) was dissolved in THF (30 mL) under N_2. *n*-Butylamine (1.02 g, 0.0139 mol) was added, and the reaction mixture was heated to reflux for 48 h. ^{31}P NMR spectroscopy indicated approximately 50% azide displacement after this time. The reaction mixture was then heated at reflux for an additional 72 h until no $N_3P_3(OCH_2CF_3)_5(N_3)$ was detected in the ^{31}P NMR spectrum. $N_3P_3(OCH_2CF_3)_5(NHCH_2CH_2CH_2CH_3)$ was isolated by removal of THF by rotoevaporation. The product was then dissolved in diethyl ether (50 mL) and extracted twice with 2% aqueous $NaHCO_3$ (70 mL). The ethereal layer was dried with Mg SO_4 and filtered. The ether was removed by rotoevaporation, and the resultant oil was purified by column chromatography on silica gel (80% hexanes/20% diethyl ether). The solvent was removed by rotoevaporation and the oil precipitated from petroleum ether (bp 40−60 °C) at −55 °C. The petroleum ether was poured off at while still cold, and the residue melted on warming to room temperature to yield a clear, colorless oil. Yield: 28%.

^{31}P NMR ($CDCl_3$): δ 21.8 (t, 1P, $(CF_3CH_2O)P(NHCH_2CH_2CH_2CH_3)$), 17.3 (d, 2P, $(CF_3CH_2O)_2P$). ^{1}H NMR ($CDCl_3$): δ 4.28−4.08 (m, 10H, CF_3CH_2O-), 2.95−2.89 (m, 2H, $-NHCH_2-$), 2.7 (br s, 1H, $PNHCH_2$), 1.50−1.44 (m, 2H, $-NHCH_2CH_2CH_2-$), 1.34−1.29 (m, 2H, $-NHCH_2CH_2CH_2CH_3$), 0.90 (t, 3H, $-NHCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 122.6 (d of q, CF_3CH_2O-), 62.9 (m, CF_3CH_2O-), 40.9, (s, $-NHCH_2CH_2CH_2-$), 33.8 (d, $-NHCH_2CH_2CH_2CH_3$), 20.0 (s, $-NHCH_2CH_2CH_2CH_3$), 13.8 (s, $NHCH_2CH_2CH_2CH_3$). $C_{14}H_{20}N_4O_5P_3$ calcd mass: 702.25. FAB(+)-MS: *m*/*z* 703.0 [MH^+].

Azido Group Displacement: $N_3P_3(OCH_2CF_3)_5(N_3)$ (5a) with $NaOC_6H_5$. Sodium metal (0.20 g, 8.7×10^{-3} mol) was added to distilled THF (50 mL) under a nitrogen atmosphere. Phenol (0.72 g, 7.6×10^{-3} mol) was dissolved in a separate flask in distilled THF (50 mL) under nitrogen. The phenol solution was then added to the sodium, and the reaction mixture was heated to reflux for 20 h. The mixture was cooled to room temperature, and the residual sodium metal was removed. $N_3P_3(OCH_2CF_3)_5(N_3)$ (2.15 g, 3.20×10^{-3} mol) was dissolved in distilled THF (20 mL) and was added to the sodium phenoxide solution. A white precipitate formed immediately. The mixture was stirred at room temperature for 3 h. It was then heated to reflux for an additional 17 h. ^{31}P NMR showed no remaining azido trimer. The THF was removed by rotoevaporation, and the product was extracted between diethyl ether (100 mL) and distilled water (100 mL). The ether layer was rinsed twice with distilled water (100 mL) and dried with sodium sulfate. The Na_2SO_4 was filtered off and the ether removed by rotoevaporation. The resultant oily material was purified by column chromatography on silica (50% CH_2Cl_2/50% hexanes). The purified fractions were combined solvents removed. The product was then recrystallized three times from hexanes (15 mL) at −11 °C. The white crystalline product was then dried under vacuum for 72 h. It should be noted that the product has a melting point near room temperature and thus also existed as a clear colorless liquid at times. Yield: 62%.

^{31}P NMR (CD_2Cl_2): δ 17.4 (d, 2P, $(CF_3CH_2O)_2P$, 13.9 (q, 1P, $(CF_3CH_2O)P(OC_6H_5)$). ^{1}H NMR (CD_2Cl_2): δ 7.45−7.34 (m, 2H, ArH−), 7.32−7.16 (m, 3H, ArH), 4.57−4.39 (m, 2H, CF_3CH_2O-), 4.38−4.20 (m, 4H, CF_3CH_2O-), 4.04−3.76 (m, 4H, CF_3CH_2O). ^{13}C NMR (CD_2Cl_2): δ 150.2 (d, ArC), 130.4 (s, ArC), 126.7 (d, ArC), 122.6 (m of q, CF_3CH_2O-), 121.6 (d, ArC), 64.5−62.2 (m of q, CF_3CH_2O-). $C_{16}H_{15}F_{15}N_3O_6P_3$ calcd mass: 723.22. FAB(+)-MS: *m*/*z* 724.0 [MH^+].

Acknowledgment. We thank the Dow Chemical Co. and the Federal Aviation Administration for their generous financial support.

IC9904541