

Synthesis and Reactivity of Alkoxy, Aryloxy, and Dialkylamino Phosphazene Azides

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The synthesis of cyclic trimeric phosphazene azides with aryloxy, alkoxy, or dialkylamino cosubstituents is described. The azide functional trimers were shown to react with various phosphorus(III) species to form phosphazene phosphinimines. The aryloxy azido trimers also undergo insertion chemistry typical of acyl nitrenes during thermal decomposition at temperatures above 250 °C.

During the past fifty 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 including unreactive examples such as C–H. 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 utilized phosphoryl azide-promoted coupling or polymerization of organic monomers to produce polypeptides, polyamides, polyureas, or polyurethanes.^{20–25} The lack of phos-

phoryl azide nitrene insertion chemistry may be due to the inherent moisture sensitivity of many phosphoryl azides or because of difficulties in the preparation of 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 controlled by the organic groups connected to the phosphazene ring. 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 hexa-azido cyclic trimer $[NP(N_3)_2]_3$, a triazido-trichloro trimer ($N_3P_3Cl_3(N_3)_3$), a pentafluoroazido trimer ($N_3P_3F_5(N_3)_3$), a pentaphenylazido trimer ($N_3P_3(C_6H_5)_5(N_3)_3$), a hexaphenyldiazido tetramer ($N_4P_4(C_6H_5)_6(N_3)_2$), and several ethylenediaminetetraazido trimers.^{27–32} Little investigation of the nitrene chemistry of phosphazene azides has been conducted, and no evidence of insertion chemistry has been reported.

The primary goal of this research was to prepare new phosphazene azido cyclic trimers which also contain aryloxy, alkoxy, or dialkylamino cosubstituent groups and to examine the reactivity of the phosphazene azides toward phosphorus(III) compounds. Numerous organic azides are known to react with phosphorus(III) species to form imine ($N=P$) bonds.^{4,18,33} An objective of this work was to determine how organic substituents in both the cyclophosphazene azide and the phosphorus(III) species affect the formation of the imine 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.

In this investigation, phenoxy groups were utilized in mono- ($N_3P_3(OPh)_5(N_3)_3$), di- ($N_3P_3(OPh)_4(N_3)_2$), and triazido phenoxy trimers ($N_3P_3(OPh)_3(N_3)_3$). 2,2,2-Trifluoroethoxy groups were employed in the alkoxy derivative ($N_3P_3(OCH_2CF_3)_5(N_3)_3$). The dimethylamino group was used in $N_3P_3(NMe_2)_4(N_3)_2$, and the diethylamino group was incorporated in a triaminotriazido phosphazene ($N_3P_3(NEt_2)_3(N_3)_3$).

The synthesis of the azido trimers, with the exception of $N_3P_3(OCH_2CF_3)_5(N_3)_3$, was accomplished through treatment of the corresponding chloro-organocyclophosphazene with sodium azide in the presence of a catalytic amount of tetrabutylammonium bromide.³⁴ The reactions were complete within 18 h in refluxing 2-butanone, toluene, or THF. A typical synthesis is illustrated in

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- (34) Isolation of pure $N_3P_3(OCH_2CF_3)_5(N_3)_3$ has so far been unsuccessful due to the difficulty of removal of $N_3P_3(OCH_2CF_3)_6$. However, its synthesis has been confirmed by ³¹P NMR spectrometry and the isolation of its phosphorus(III) imines: $N_3P_3(OCH_2CF_3)_5(N=PPh_3)$ and $N_3P_3(OCH_2CF_3)_5(N=P(OPh)_3)$.

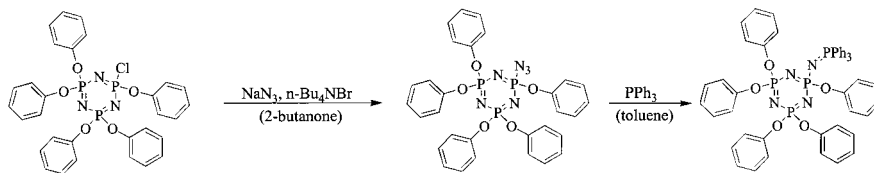


Figure 1. Example of phosphazene azide and phosphinimine synthesis.

Figure 1. The reactions also took place in refluxing acetone, but significantly longer reaction times were required (48 h) to achieve complete azide introduction.

The reactions proceeded cleanly in these solvents to give >90% yields of the appropriate cyclophosphazene azido trimer after liquid–liquid extraction between diethyl ether and 5% aqueous NaHCO_3 . These products were pure by ^{31}P NMR and ^1H NMR spectrometry but often were slightly orange in color. The orange color was easily removed via column chromatography on silica gel with a CH_2Cl_2 /hexane or diethyl ether/hexane solvent system. In all cases, the final products were clear, colorless oils except for $\text{N}_3\text{P}_3(\text{OPh})_5(\text{N}_3)$, which crystallized into a waxy, white solid during several weeks. All the other azides remained as oils. In some cases, such as $\text{N}_3\text{P}_3(\text{OPh})_4(\text{N}_3)_2$ and $\text{N}_3\text{P}_3(\text{OPh})_3(\text{N}_3)_3$, mixtures of the *cis* and *trans* isomers were obtained even when the pure *cis*-non-gem-dichlorophosphazene isomer was utilized. This type of racemization has been detected in other azido phosphazenes.³¹ So far, attempts to separate the individual isomers have been unsuccessful. All of the phosphazene azides prepared were characterized by ^{31}P NMR, ^1H NMR, ^{13}C NMR, FTIR, FAB mass spectrometry, and elemental analysis. None of the new compounds appeared to be shock sensitive, although care should be exercised in the handling of any azido derivative.

Treatment of the phenoxy or trifluoroethoxy azide derivatives with triphenylphosphine, triphenyl phosphite, triethyl phosphite, or hexamethylphosphorus triamide gave the corresponding phosphinimine-substituted trimers in about 50% yield after column chromatography or multiple recrystallizations (Figure 1). With the exception of non-gem $\text{N}_3\text{P}_3(\text{OPh})_3(\text{N}_3)_3$, triphenyl phosphite reacted completely with the phenoxy and trifluoroethoxy phosphazene azides. However, longer reaction times and higher boiling solvents, such as toluene, were necessary when using the triphenyl phosphite. Azides $\text{N}_3\text{P}_3(\text{NMe}_2)_4(\text{N}_3)_2$ or $\text{N}_3\text{P}_3(\text{NEt}_2)_3(\text{N}_3)_3$ interacted with triphenylphosphine or triphenyl phosphite to give mixtures of only partially reacted materials. Even when the reactions were allowed to proceed for several days in refluxing toluene, the monophosphinimine was the predominant reaction product. Presumably the electron-donating character of the amine groups discourages formation of the phosphinimine, which itself is also electron-donating. The phenoxy and trifluoroethoxy groups do not increase electron density on the phosphorus atom and thus allow for easier conversion to the phosphinimine.

The decomposition temperatures of $\text{N}_3\text{P}_3(\text{OPh})_5(\text{N}_3)$ and $\text{N}_3\text{P}_3(\text{NMe}_2)_4(\text{N}_3)_2$ were also investigated to determine if these azides might serve as useful cross-linking agents for commercial organic

polymers that melt above 200 °C. This is the decomposition temperature of most of the sulfonyl azides currently used for this purpose. DSC experiments revealed that $\text{N}_3\text{P}_3(\text{NMe}_2)_4(\text{N}_3)_2$ underwent a thermal decomposition (exotherm) near 238 °C, while $\text{N}_3\text{P}_3(\text{OPh})_5(\text{N}_3)$ decomposed thermally at 274 °C.

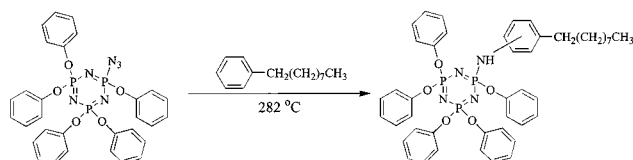


Figure 2. Phosphazene azide thermal insertion reaction.

Reactions to model the thermal insertion chemistry were also conducted. For example, it was found that the model compound 1-phenyl nonane (bp 282 °C) reacted with $\text{N}_3\text{P}_3(\text{OPh})_5(\text{N}_3)$ within 10 min at reflux (Figure 2). Column chromatography of the reaction mixture on silica gel with a CH_2Cl_2 /hexane solvent separated unreacted starting compounds and a nitrene insertion product, $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5(\text{NHC}_6\text{H}_4\text{CH}_2(\text{CH}_2)_7\text{CH}_3)$. This structure was indicated by ^{31}P NMR, ^1H NMR, ^{13}C NMR, and mass spectrometry. ^1H NMR results also suggested that insertion took place primarily at the aromatic C–H para to the nonane group.

Additional experiments were conducted to explore the possibility of photolytic nitrene insertion chemistry. However, $\text{N}_3\text{P}_3(\text{OPh})_5(\text{N}_3)$ showed no evidence of any reaction with either toluene or cyclohexane when UV-irradiated at 250–300 nm for 24 h.

In conclusion, cyclic trimeric phosphazene azides that bear aryloxy, dialkylamino, or alkoxy cosubstituent groups have been synthesized. The phenoxy-substituted phosphazene azides reacted with phosphorus(III) materials to form phosphinimine ($\text{P}=\text{N}$) linkages, but the alkylamino derivatives underwent incomplete reaction with all the phosphorus(III) compounds. The reaction of $\text{N}_3\text{P}_3(\text{OPh})_5(\text{N}_3)$ with 1-phenylnonane yielded a nitrene insertion product ($\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5(\text{NHC}_6\text{H}_4\text{CH}_2(\text{CH}_2)_7\text{CH}_3)$). Phenoxy azido phosphazenes, specifically $\text{N}_3\text{P}_3(\text{OPh})_4(\text{N}_3)_2$ and $\text{N}_3\text{P}_3(\text{OPh})_3(\text{N}_3)_3$, are currently under investigation as cross-linking or branching agents for organic polymers.

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