Nucleophilic Substitution of 2,2-Bis(arylthio)-4,4,6,6-tetrachlorocyclotriphosphazene with Ammonia, Phenoxide, and Thiophenoxide

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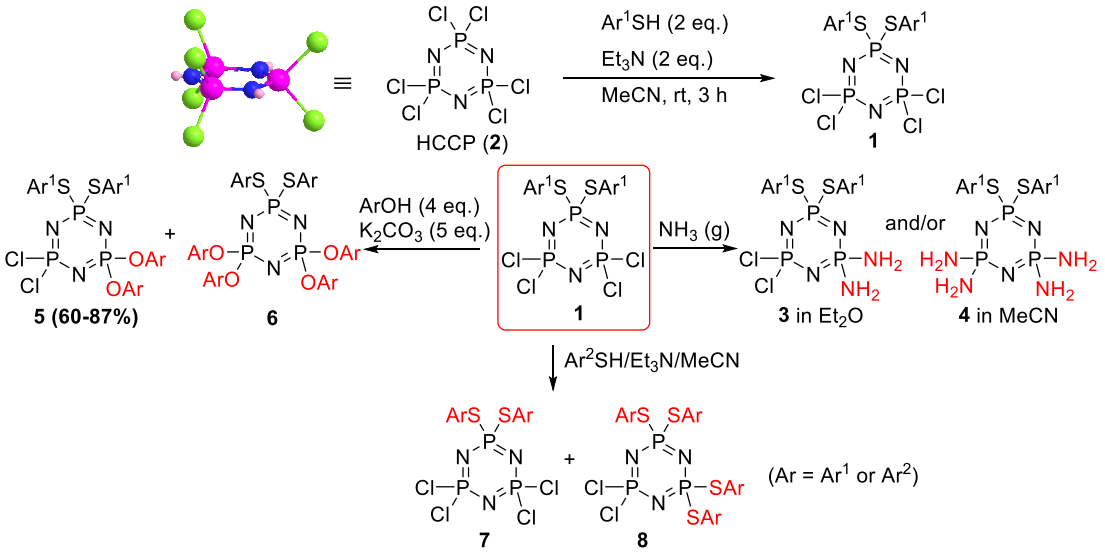
Cyclotriphosphazene $N_3P_3R_6$ has a N_3P_3 ring in which N and P atoms are connected alternately and two substituents are placed on the each phosphorus atom upper and lower sides of the ring. If the substituents can be introduced regio- and stereoselectively, multi-functionalyzed materials can be developed easily. For this purpose, we investigated synthesis of cyclotriphosphazene having two kinds of nucleophiles starting from 2,2-bis(arylthio)-4,4,6,6-tetrachlorocyclotriphosphazene $N_3P_3Cl_4$-*gem*-$(Ar^1S)_2$ (**1**).

Nucleophilic substitution of hexachlorocyclotriphosphazene (HCCP, **2**) with Ar^1SH/Et_3N (2/2 eq.) in MeCN gave **1**. Aminolysis of **1** with gaseous ammonia gave *gem*-disubstituted $N_3P_3Cl_2$-*gem*-$(NH_2)_2$-*gem*-$(Ar^1S)_2$ (**3**) in Et_2O and tetrasubstituted $N_3P_3(NH_2)_4$-*gem*-$(Ar^1S)_2$ (**4**) in MeCN, respectively. The reaction of **1** with $ArOH/K_2CO_3$ (4/5 eq.) gave a mixture of *gem*-disubstituted $N_3P_3Cl_2$-*gem*-$(ArO)_2$-*gem*-$(ArS)_2$ (**5**) (60 – 87%) and tetrasubstituted $N_3P_3(ArO)_4$-*gem*-$(Ar^1S)_2$ (**6**) which ratio depended on the reaction solvent. On the other hand, in a reaction of **1** with another arylthiol Ar^2SH, ArS-groups were scrambled, and a mixture of disubstituted $N_3P_3Cl_4$-*gem*-$(ArS)_2$ (**7**) and tetrasubstituted N_3P_3-*gem*-$Cl_2(ArS)_4$ (Ar = Ar^1 and/or Ar^2) (**8**) was obtained. In all cases, no isomers having odd number of Cl and/or non-*gem*-substituted products were obtained.



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