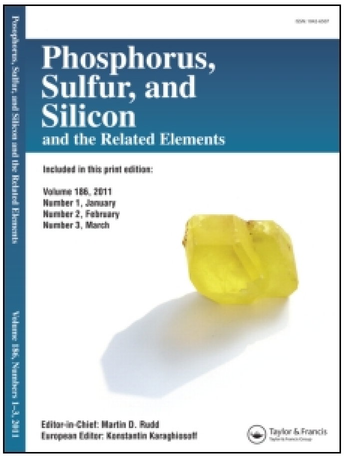

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NEW CYCLIC AND POLYMERIC PHOSPHAZENES DERIVED FROM N-SILYLPHOSPHORANIMINES

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NEW CYCLIC AND POLYMERIC PHOSPHAZENES DERIVED FROM N-SILYLPHOSPHORANIMINES

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Silicon-nitrogen-phosphorus compounds of the type $Me_3SiN{=}PR(R')X$ *(*X = *Cl, Br,* OCH_2CF_3*, OPh), known as N-silylphosphoranimines, are useful precursors to both cyclic and polymeric phosphazenes. Depending on the leaving group (X), thermolysis reactions afford either cyclic trimers,* $[N{=}PR(R')]_3$ *(when X = Cl, Br), or linear polymers,* $[N{=}PR(R')]_n$ *(when X =* OCH_2CF_3 *or OPh). Treatment of the P-trifluoroethoxy and P-phenoxy derivatives,* $Me_3SiN{=}PR(R')X$ *(X =* OCH_2CF_3*, OPh), with alcohols at lower temperature usually results in the formation of cyclic phosphazene trimers via silyl ether elimination. Recently, we have applied these synthetic methods to the preparation of some new phosphazene systems including a series of 4-aryl-functionalized trimers and polymers and a variety of non-geminal, mixed-substituent cyclic trimers. Representative examples of the synthesis, structural characterization, and reactivity of these new phosphazenes and their Si—N—P precursors are reported here.*

Keywords: Nongeminal; phosphazene; phosphorus-nitrogen; polymer; trimer

Depending on the substituents attached to phosphorus along the P—N backbone, poly(phosphazenes), $[R_2P{=}N]_n$, can have a wide range of physical and chemical properties as well as potential applications.[1] The structural and chemical diversity of poly(phosphazenes) is made possible by the two general and complimentary methods employed for their synthesis. The very well-studied ring-opening/substitution approach, developed by Allcock and coworkers,[2] is best suited

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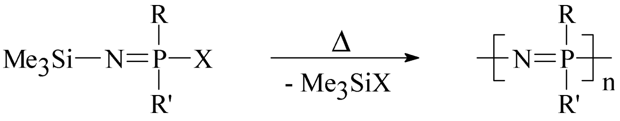
to the preparation of phosphazenes bearing alkoxy, aryloxy, or amino substituents. In contrast, the condensation polymerization of N-silylphosphoranimines (Eq. 1), developed by Wisian-Neilson and Neilson[3] and recently extended by others,[4] is commonly used for the synthesis of poly(*alkyl/aryl*phosphazenes) in which all of the side groups are attached directly by carbon-phosphorus bonds.



$$\mathrm{Me_3Si{-}N{=}\overset{R}{\underset{R'}{P}}{-}X} \xrightarrow[-\,\mathrm{Me_3SiX}]{\Delta} \left[\mathrm{N{=}\overset{R}{\underset{R'}{P}}}\right]_n \qquad (1)$$

R, R' = alkyl, aryl; X = Cl, Br, OCH_2CF_3, OPh

In the condensation method (Eq. 1), the substituents on phosphorus are introduced prior to polymerization beginning with the synthesis of suitable [bis(trimethylsilyl)amino]phosphines, $(Me_3Si)_2NPRR'$, via the Wilburn method.[5] Subsequent oxidative halogenation (e.g., with Br_2 or C_2Cl_6), followed by nucleophilic substitution at phosphorus (e.g., with $LiOCH_2CF_3$ or LiOPh), affords the typical phosphazene *polymer* precursors such as $Me_3SiN{=}P(X)Me_2$ and $Me_3SiN{=}P(X)(Ph)Me$ ($X = OCH_2CF_3$, OPh).[6] More recently, we have found that treatment of the same compounds with alcohols (especially CF_3CH_2OH), at room temperature, results in facile Si—N bond cleavage and formation of *cyclic* phosphazenes, $[R_2P{=}N]_{3,4}$, in high yield.[7]

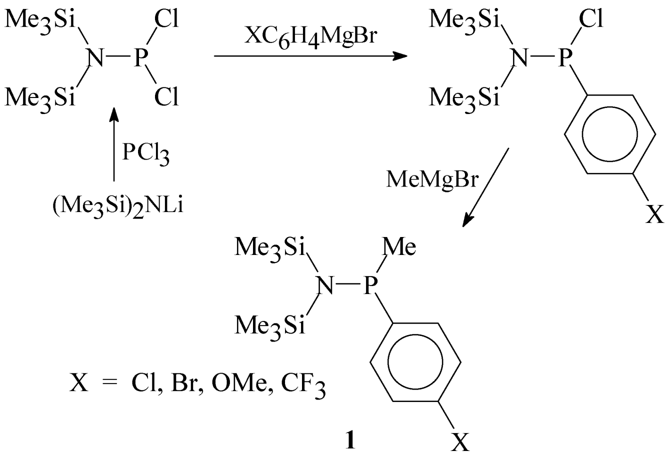
We report here on extensions of these synthetic routes to include the preparation of new types of cyclic and polymeric phosphazenes that contain 4-aryl functional groups directly attached to phosphorus or otherwise have a non-geminal, mixed-substituent pattern at phosphorus.

RESULTS AND DISCUSSION

4-Aryl Substituted Phosphazenes

In a modification of the Wilburn method,[5] treatment of the intermediate dichloro(disilylamino)phosphine with 4-aryl substituted Grignard reagents gave the expected 4-aryl(chloro)phosphines (Eq. 2). Subsequent addition of MeMgBr afforded the desired alkyl/arylphosphines

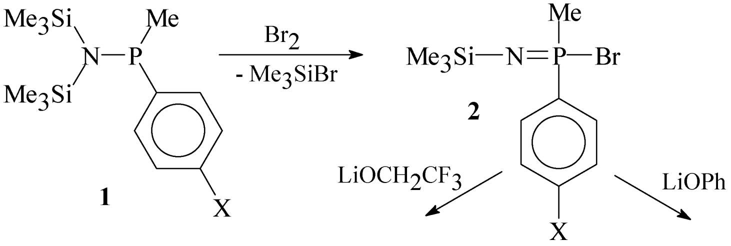
(**1**) in high yields as distillable liquids.[8]



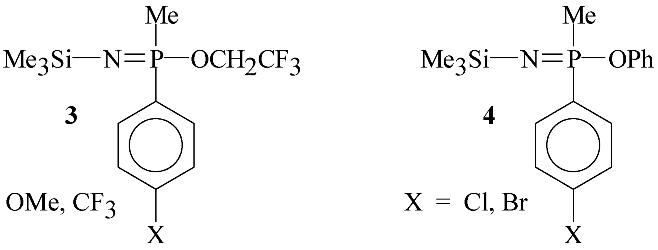
X = Cl, Br, OMe, CF_3

(2)

Oxidative bromination of phosphines **1** occurred smoothly to yield the P-bromo-phosphoranimines **2** (Eq. 3) that, in turn, were readily converted to the P-alkoxy (**3**) and P-phenoxy (**4**) derivatives by nucleophilic substitution reactions (Eq. 4).



(3)

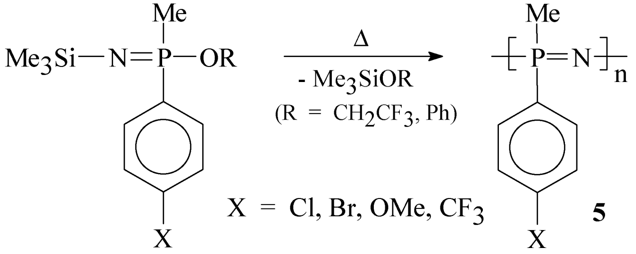


X = Cl, Br, OMe, CF_3

X = Cl, Br

(4)

Thermolysis of phosphoranimines **3** or **4** at ca. 200°C resulted in silyl ether elimination and clean formation of the expected polymeric phosphazenes **5** (Eq. 5). These new polymers have molecular weights in the 50,000–150,000 range, narrow polydispersities, and glass transition temperatures similar to the parent polymer, $[\mathrm{Ph(Me)P{=}N}]_n$.[3]

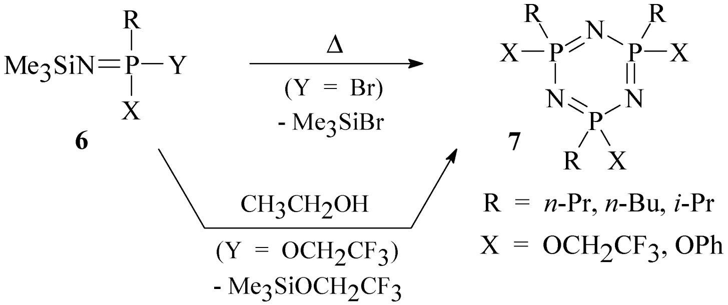


(5)

Alternatively, addition of an alcohol (CH_3CH_2OH in particular) to phosphoranimines **3**, at room temperature, readily afforded the corresponding cyclic trimers $[4\text{-X-}C_6H_4(Me)P{=}N]_3$ as mixtures of *cis* and *trans* isomers. All of these polymeric and cyclic phosphazenes have been fully characterized by NMR spectroscopy and elemental analysis. Further details of their synthesis, characterization, and reactivity will be reported elsewhere.

Mixed-Substituent Phosphazenes

By employing similar preparative chemistry, the details of which have been recently reported,[9] of the appropriate Si—N—P systems, we have prepared and characterized a wide variety of mixed substituent N-silylphosphoranimines **6**. Subsequently, these phosphoranimines were converted to a series of new, non-geminal, mixed-substituent cyclic trimers **7** by thermal elimination of Me_3SiBr or by treatment with CF_3CH_2OH at room temperature (Eq. 6).



(6)

The cyclic phosphazenes **7** all gave satisfactory elemental analyses and were identified as mixtures of *cis* and *trans* isomers by NMR spectroscopy.[10] In one case (R = *i*-Pr, X = OPh), the pure *trans* isomer was isolated by sublimation and structurally characterized by x-ray diffraction. Full details of the synthesis, characterization, and reactivity of these new nongeminal phosphazene products will be reported elsewhere.

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