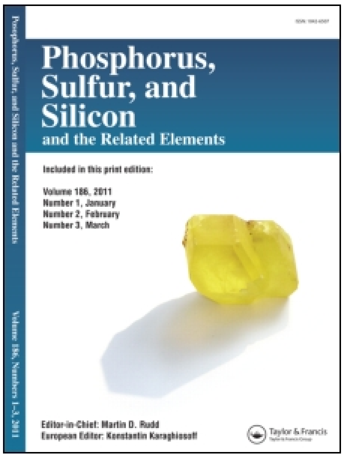

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SYNTHESIS AND REACTIVITY OF NEW PHOSPHORUS-NITROGEN AND PHOSPHORUS-NITROGEN-BORON CONDENSATION MONOMERS

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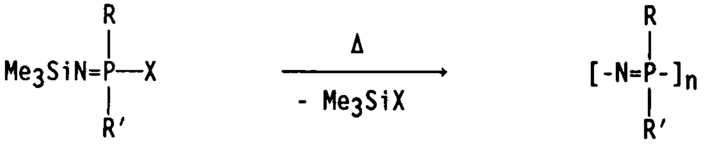
Abstract. The preparative chemistry of P-functional N-silylphosphoranimines, $Me_3SiN{=}P(X)R_2$, and the nature of the phosphazene products of their thermal decomposition are reported with particular emphasis on the effect that the leaving group (X) has on the polymerization/cyclization process. In a related study of potential precursors to novel B-N-P-N polymers, the preparation of a series of new phosphorus-(III) and -(V) derivatives of the 1,3,2-diazaboracyclohexane ring system is described.

In recent years, a new general method for the synthesis of linear and cyclic phosphazenes, $[R_2PN]_n$, has been under investigation in our laboratory.[1] This approach, which involves the *condensation polymerization* of appropriate N-silylphosphoranimines, $Me_3SiN{=}P(X)R_2$, is particularly well-suited to the synthesis of *fully* alkyl/aryl substituted polyphosphazenes.[2] In contrast, polyphosphazenes bearing alkoxy, aryloxy, or amino groups are best prepared by the ring-opening - substitution method developed by Allcock and coworkers.[3] We report here some recent results pertaining to the synthesis and reactivity of these phosphazene precursors and some related work on new P-N-B systems.

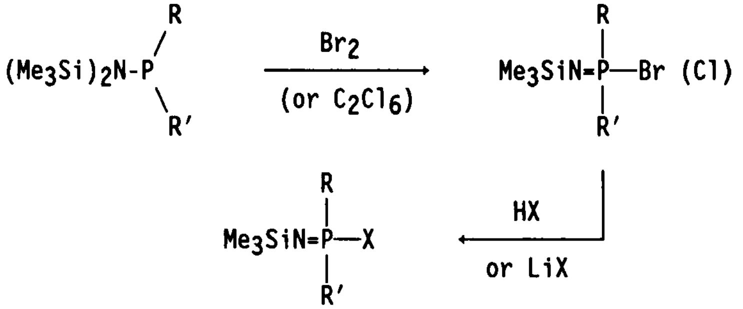


$$Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}X \xrightarrow[-\ Me_3SiX]{\Delta} [-N{=}\overset{R}{\underset{R'}{P}}-]_n \qquad (1)$$

PHOSPHAZENE PRECURSORS

Synthesis. The oxidative halogenation of (silylamino)phosphines[2,4] occurs smoothly and quantitatively with elimination of Me_3SiX to afford the P-*halo*phosphoranimines (eq 2). These compounds, which themselves are precursors to *cyclic* phosphazenes (see below), are readily converted via nucleophilic substitution reactions (eq 3) into other potential phosphazene precursors containing a wide variety of leaving groups on phosphorus.

When P-Me groups are present in the latter compounds, there is a convenient synthetic route to many new types of C-functionalized precursors. Previously, we have reported that deprotonation - substitution reactions[5-8] can be used to prepare new N-silyl-Ptrifluoroethoxyphosphoranimines bearing silyl,[5] phosphinyl,[6] and siloxy[7] substituents. More recently, we have used the P-CH_2SiMe_3 derivatives as substrates for the Peterson olefination process.[9] Some of the resulting vinyl-substituted precursors undergo facile copolymerization with $Me_3SiN{=}P(OCH_2CF_3)R_2$ to give soluble, linear polymers that have crosslinkable vinyl groups incorporated in a controlled fashion.[9b]



$$(\mathrm{Me_3Si})_2\mathrm{N{-}P}\begin{smallmatrix}\mathrm{R}\\ \mathrm{R'}\end{smallmatrix} \xrightarrow[\text{(or } \mathrm{C_2Cl_6})]{\mathrm{Br_2}} \mathrm{Me_3SiN{=}}\overset{\mathrm{R}}{\underset{\mathrm{R'}}{\mathrm{P}}}\mathrm{{-}Br\ (Cl)} \qquad (2)$$

$$\mathrm{Me_3SiN{=}}\overset{\mathrm{R}}{\underset{\mathrm{R'}}{\mathrm{P}}}\mathrm{{-}X} \xleftarrow[\text{or LiX}]{\mathrm{HX}} \qquad (3)$$

R, R' = alkyl, aryl; X = alkoxy, aryloxy, OCH_2CF_3

Thermolysis Reactions. The thermal decomposition of P-*trifluoroethoxy* substituted phosphoranimines (X = OCH_2CF_3) occurs smoothly in sealed glass or stainless steel containers at ca. 175-200°C with the elimination of $Me_3SiOCH_2CF_3$, a volatile, inert byproduct. The solid products of such reactions are exclusively *linear polymeric* phosphazenes. The characterization studies of a representative series of these polymers and copolymers show that *the poly(alkyl/arylphosphazenes) exist as extended, flexible chains in good solvents such as THF or $CHCl_3$, with average chain lengths of several hundred to a thousand repeat units and symmetrical molecular weight distributions* ($M_w/M_n \approx 2\text{-}3$).[1b] Since only relatively high molecular weight polymers ($M_w \approx 60{,}000$) and unreacted monomer are observed in the early stages of the reaction,[1b] *the polymerization mechanism appears to be a chain growth process*, probably initiated by heterolytic cleavage of the polar $P^{\delta+}{-}X^{\delta-}$ bond.

Information is also available on how the nature of the leaving group (X) at phosphorus affects the thermal stability and the decomposition products of the N-silylphosphoranimines, $Me_3SiN{=}P(X)R_2$. The tendency of these precursors to thermally eliminate Me_3SiX follows the approximate leaving group (X) order: halogen > aryloxy ≈ fluoroalkoxy > alkoxy ≈ amino. Thus, greater polarity of the P-X bond and the corresponding leaving-group ability of X^- generally favor the elimination of Me_3SiX. As a result, the P-*halo*phosphoranimines often decompose during distillation while most of the other types of phosphoranimines can routinely be distilled without decomposition. The leaving group also has a pronounced influence on the type of phosphazene (cyclic or polymeric) that is formed in these condensation processes. For example, the N-silyl-P-*halo*phosphoranimines (X = Br, Cl) decompose to yield *cyclic* phosphazenes, normally as mixtures of trimers and tetramers, rather than polymers as are obtained in the thermolyses of the trifluoroethoxy analogues. As part of a systematic study of the decomposition reactions of the P-bromophosphoranimines, we have prepared a series of cyclo*dialkyl*phosphazenes[10] that are not easily accessible by other methods. While mixtures of ring sizes (but no polymers) are generally obtained, ^{31}P NMR spectroscopy indicates that trimers are the major products when longer chain alkyl groups (e.g., *n*-Bu or *n*-Hx) are present.

At first glance, such a dramatic leaving group effect (i.e., X = Br vs. X = OCH_2CF_3) might be interpreted as an indication that two different mechanisms are involved. Other work, however, has shown that Me_3SiBr reacts with *polymeric* $[Me_2PN]_n$ and $[Me(Ph)PN]_n$, prepared from the P-OCH_2CF_3 derivatives, at high temperature (> 100°C) to cause chain degradation and formation of cyclic phosphazenes.[11] This observation illustrates the principle that condensation processes must produce an "inert" byproduct in order to be useful for polymerization reactions.[1a] Apparently, trifluoroethoxy- but not halosilanes are suitable elimination products in this sense.

Other questions about the polymerization mechanism prompted us to investigate alkoxy substituents other than -OCH_2CF_3 as possible leaving groups.[11] When non-fluorinated *alkoxy* groups are attached to phosphorus, the precursors are much more thermally stable than the OCH_2CF_3 derivatives. Furthermore, when more drastic conditions are used, the P-*alkoxy* compounds decompose to yield *cyclic* phosphazenes along with other products. For example, in the thermolysis of the *t*-butoxy derivative, the formation of the (silylamino)phosphine oxide, $Me_3SiN(H)P(=O)(Ph)Me$, probably occurs via a β-elimination of *iso*butylene.

In contrast to the results obtained with the alkoxy analogues, the thermal decomposition of the *aryloxy* substituted monomers is an efficient, high yield, and inexpensive new preparative route to the poly(alkyl/arylphosphazenes). The difference between these systems (i.e., alkoxy vs. aryloxy leaving groups) can be attributed to the inability of the aryloxy (or OCH_2CF_3) groups to undergo β-elimination and to the fact that OAr^- is a better leaving group than is OR^-.

PHOSPHORUS-NITROGEN-BORON COMPOUNDS

The success of this type of condensation polymerization in the phosphazene area has led us to investigate the possibility of applying similar methodology to the synthesis of other inorganic polymer systems. These include the poly(iminoboranes), $(RNBR)_n$, for which several precursors based on the 1,3,2-diazaboracyclohexane ring system have been prepared.[12,13] More recently, we have extended the scope of this project to include some related P-N-B-N compounds which are briefly noted here.

The N-lithio derivatives of the 1,3,2-diazabora-2-phenyl-cyclohexane ring systems can be treated with various P^{III} (eq 4) and P^{V} (eq 5) electrophiles to afford novel P-N-B-N derivatives. These products are generally obtained as distillable liquids in moderate to good yields (50 - 85%) and are readily characterized by multinuclear NMR spectroscopy and elemental analysis. Full details of the synthesis, characterization, and reactivity of these and related compounds will be published in forthcoming papers.

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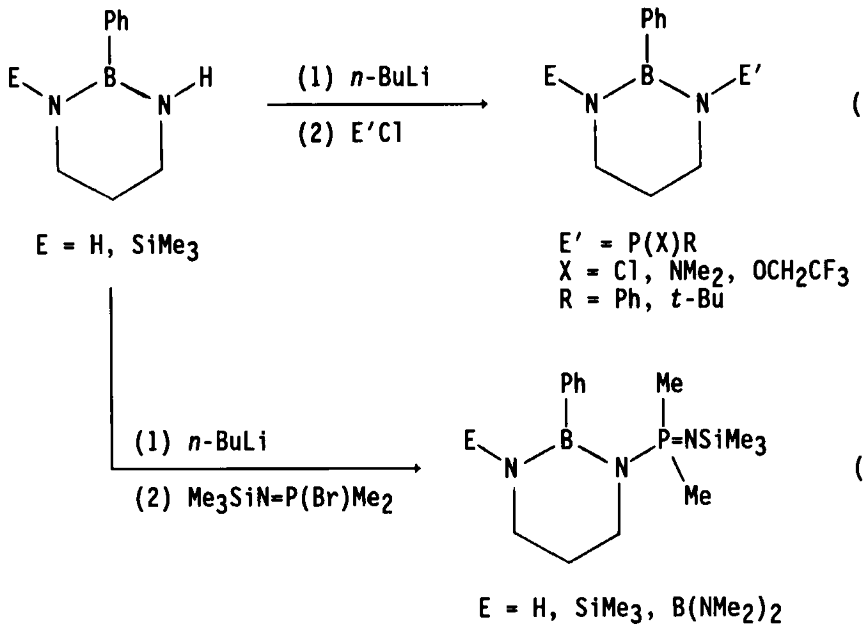

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