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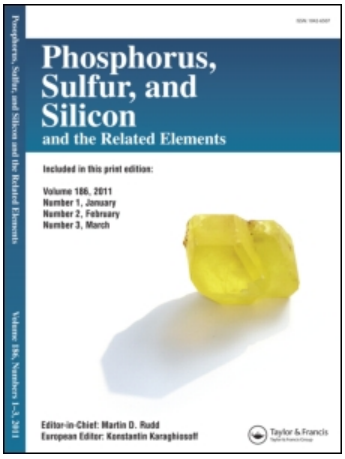

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POLY(ALKYL/ARYLPHOSPHAZENE) CHAINS AND RINGS VIA CONDENSATION REACTIONS OF Si-N-P PRECURSORS

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Abstract. The thermal decomposition of P-functional N-silylphosphoranimines, $Me_3SiN{=}P(X)R_2$, is an effective synthetic route to cyclic and polymeric phosphazenes that are fully substituted with P-alkyl/aryl side groups. Results of some recent studies of this condensation reaction and its products are reported, including: (1) the synthesis of a variety of new precursors with P-alkoxy and P-aryloxy substituents, (2) the effect of the leaving group (X) on the polymerization/cyclization process, and (3) the synthesis of a series of dialkyl cyclic phosphazenes, $[R_2PN]_n$ (e.g., n = 3, 4, 5; R = Et, *n*-Pr, *n*-Bu, *n*-Hx).

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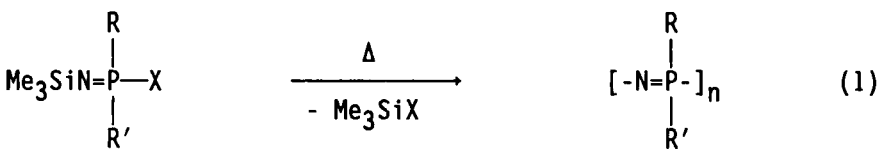
INTRODUCTION

Polyphosphazenes, $[R_2PN]_n$, which can be prepared with a wide variety of substituents at phosphorus, often exhibit useful properties including low temperature flexibility, resistance to chemical attack, flame retardancy, stability to UV radiation, and reasonably high thermal stability.[1-4] Compounds containing biologically, catalytically, or electrically active side groups are being investigated[5,6] as are some novel polyphosphazene-*graft*-polystyrene copolymers.[7,8]

The most well-studied synthetic route to polyphosphazenes is the ring-opening/substitution method developed by Allcock and coworkers.[1] This procedure involves the initial preparation of poly(dichlorophosphazene), $[Cl_2PN]_n$, by the ring-opening polymerization of the cyclic trimer followed by nucleophilic displacement of the chlorine atoms along the chain. In this process, the substituents at phosphorus must be introduced after polymerization since the fully substituted cyclic phosphazenes do not polymerize.[9] Polyphosphazenes prepared in this manner normally have the organic substituents bonded to phosphorus through oxygen or nitrogen links, thereby providing pathways for decomposition or depolymerization on heating above about 200°C. A number of partially alkylated

polymers, containing both P-alkyl/aryl and P-OR groups, have also been prepared, but attempts to achieve complete P-C substitution result in either incomplete substitution under mild conditions or undesired reactions such as chain cleavage and/or crosslinking under more vigorous conditions.[10]

In recent years, a new general method for the synthesis of linear and cyclic phosphazenes has been under investigation in our laboratory. This approach involves the thermal elimination of substituted silanes from appropriate N-silylphosphoranimines.[11] This type of *condensation polymerization* reaction (eq 1) has several attractive features, the most important of which is the ability to incorporate the desired phosphorus substituents directly into the starting Si-N-P compound. This procedure is particularly well-suited to the synthesis of *fully* alkyl/aryl substituted polyphosphazenes.[2]



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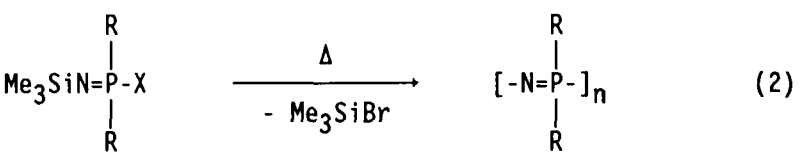
RESULTS AND DISCUSSION

P-Trifluoroethoxyphosphoranimines. The thermolysis of P-OCH_2CF_3 substituted phosphoranimines 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 of a representative series of these polymers and copolymers by NMR spectroscopy, dilute solution techniques (size exclusion chromatography, light scattering, membrane osmometry, and viscosity measurements), thermal analysis (DSC/TGA), and X-ray diffraction has been reported.[2b] In general, these studies 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* ($M_w/M_n \approx$ 2-3). Since only relatively high molecular weight polymers ($M_w \approx$ 60,000) and unreacted monomer are observed in the early stages of the reaction,[2b] *the polymerization mechanism appears to be a chain growth process*, probably initiated by

heterolytic cleavage of the polar $P^{\delta+} - X^{\delta-}$ bond.

P-Halophosphoranimines. 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 $P^{\delta+} - X^{\delta-}$ 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 (at ca. 150°C or less) 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 (eq 2)[12] that are not easily accessible by other methods.[13] 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. Details of the synthesis and characterization of these cyclic phosphazenes will be reported in a future paper.



$$Me_3SiN{=}\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{P}}}}{-}X \xrightarrow[-\ Me_3SiBr]{\Delta} [-N{=}\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{P}}}}{-}]_n \qquad (2)$$

R = Et, *n*-Pr, *n*-Bu, *n*-Hx; n = 3, 4, 5

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.[2a,14] This observation illustrates the principle that condensation processes must produce an "inert" byproduct in order to be use-

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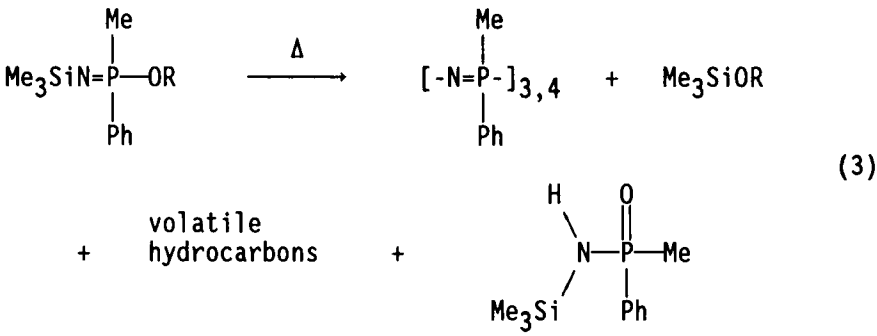
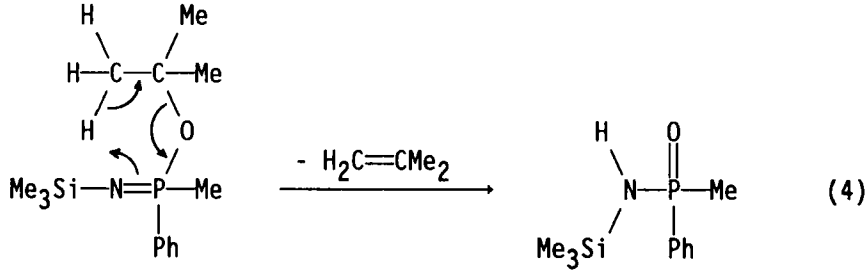
ful for polymerization reactions. Apparently, trifluoroethoxy- but not halosilanes are suitable elimination products in this sense.

P-Alkoxyphosphoranimines. Other questions about the polymerization mechanism prompted us to investigate alkoxy substituents other than $-OCH_2CF_3$ as possible leaving groups.[14] These types of compounds are readily prepared by treating the P-bromophosphoranimine, $Me_3SiN{=}P(Me)(Ph)Br$, with the appropriate alcohol in the presence of Et_3N. 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 (eq 3). For example, in the thermolysis of the *t*-butoxy derivative (eq 4), the formation of the (silylamino)phosphine oxide probably occurs via a β-elimination of *iso*butylene.



(3)

R = Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, *t*-Bu, *n*-Hx, *c*-Hx, etc.



(4)

P-Aryloxyphosphoranimines. We have also prepared a large series of P-*aryloxy*phosphoranimines by treatment of the P-bromophosphoranimine either with the appropriate

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phenol in the presence of Et_3N or with the corresponding lithium phenoxide.[14] 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) (eq 5). 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 ArO^- is a better leaving group than RO^-.

$$Me_3SiN{=}P(Me)(Ph){-}OAr \xrightarrow[-\ Me_3SiOAr]{\Delta} [-N{=}P(Me)(Ph)-]_n \qquad (5)$$

Ar = C_6H_5, *p*-MeC_6H_4, 2,6-$Me_2C_6H_3$, 3,5-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, *p*-ClC_6H_4, 2,4,6-$Cl_3C_6H_2$, *p*-$MeOC_6H_4$

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Although both the P-aryloxy and the P-OCH_2CF_3 substituted phosphoranimines lead to polymeric phosphazene products upon thermolysis, some differences are observed between the two systems. First, the reaction proceeds to completion faster in the case of the P-*aryloxy*phosphoranimines, typically requiring 2-4 days at 200°C compared to 6-12 days for the P-*trifluoroethoxy*phosphoranimines. Second, while the polymerization of the P-*trifluoroethoxy*phosphoranimines appears to occur by a chain growth process, the situation with the P-*aryloxy* monomers is more complicated. Analysis of incomplete polymerization mixtures of various $Me_3SiN{=}P(Me)(Ph)OAr$ precursors shows the presence of substantial amounts of lower molecular weight oligomers ($M_w \approx$ 3,000 - 10,000) in addition to polymer ($M_w \approx$ 40,000 - 100,000). The relative proportion of oligomer to polymer decreases as the percent polymerization increases. Further studies of the mechanism of this polymerization process are in progress.

In summary, our investigations of the condensation polymerization of N-silylphosphoranimines continue to yield results that are relevant to (1) the synthesis of new poly(alkyl/arylphosphazenes) with a wide variety of different substituents for structure/property studies, (2) the synthesis and characterization of new cyclic alkyl/arylphosphazenes, and (3) the further elucidation of the mechanisms of the polymerization and/or cyclization reactions.

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