STUDIES OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS INCLUDING A-N, ETC.

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ABSTRACT
The program of research has been directed toward the development of new synthesis of polyphosphazenes, particularly those with alkyl and/or aryl substituents, via the elimination of substituted silanes from N-silylphosphinimines. The synthesis and characterization of both the new polymers and their precursors has been investigated.
STUDIES OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS
INCLUDING A NEW SYNTHESIS OF PHOSPHAZENES

Final Report

by

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Our research conducted under ARO sponsorship has been directed toward the development of a new synthesis of alkyl and/or aryl substituted polyphosphazenes from Si-N-P precursor compounds. This synthesis is based on the premise that suitably constructed N-silylphosphinimines can be made to eliminate substituted silanes to form phosphazenes (see Scheme I).

Scheme I

\[
\begin{array}{c}
\text{Si-N=P-X} \\
\text{R} \\
\text{R'}
\end{array} \rightarrow \begin{array}{c}
\text{Si-X} \\
\text{P-N} \\
\text{n}
\end{array} \begin{array}{c}
\text{R} \\
\text{R'}
\end{array}
\]

In the earlier stages of this program our studies of the chemistry of silylaminophosphines were continued. The availability of the phosphines via the new "one-pot" synthesis (eq 1) greatly aided these studies, particularly the oxidation reactions (eq 2-4).

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{NH} & \xrightarrow{n-\text{BuLi}, 0^\circ} \text{LiN(SiMe}_3)_2 \xrightarrow{\text{PCl}_3, -78^\circ} \text{(Me}_3\text{Si)}_2\text{NPCL}_2 \\
\text{Et}_2\text{O} & \\
\text{RMgBr} \text{ or } \text{RLi} & \text{OSiMe}_3 \\
\text{(Me}_3\text{Si)}_2\text{NPR}_2 & \text{OSiMe}_3
\end{align*}
\]

(1)

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{NPR}_2 + \text{tBuO}_2\text{SiMe}_3 & \xrightarrow{} \text{Me}_3\text{SiN=PR}_2 + \text{tBuOSiMe}_3 \\
\text{(Me}_3\text{Si)}_2\text{NPMe}_2 + \text{Me}_3\text{SiBr} & \xrightarrow{} \text{Me}_3\text{SiN=PR}_2 + \text{Me}_3\text{SiBr}
\end{align*}
\]

(2) (3)

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{NPMe}_2 + \text{R}_2\text{C} = \text{O} & \xrightarrow{} \text{Me}_3\text{SiN=P-C-OSiMe}_3 \\
\text{Me} & \text{R}
\end{align*}
\]

(4)
An important, common feature of each of these oxidation reactions is subsequent cleavage of a Si-N bond as seen in the migration of Me₃Si from nitrogen to oxygen in eq 2 and 4 and in the elimination of Me₃SiBr in eq 3. Of particular importance is a similar Si-N bond cleavage upon thermolysis of the P-bromo, N-silylphosphinimine products in eq 3 to form exclusively cyclic phosphazenes (R₂PN)ₙ (n=3, 4, 5) (eq 5).

\[
\begin{align*}
\text{Me₃SiN} & \quad \text{P} - \text{Br} \quad \Delta \quad \text{Me₃SiBr} + \quad \text{P} - \text{N} \quad \text{n} \\
\text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R}
\end{align*}
\]

Since no evidence for polymer formation via Me₃SiBr elimination was observed, the effect of changing the leaving group from Br to NMe₂, OMe, and OCH₂CF₃ was studied. The N-silylphosphinimine precursors were prepared from the P-bromophosphinimines (eq 6). Although

\[
\begin{align*}
\text{Me₂NH} \quad & \quad \text{Me₃SiN} = \text{PR₂} \\
\text{MeOH} \quad & \quad \text{Me₃SiN} = \text{PR₂} \\
\text{Et₃N} \quad & \quad \text{Me₃SiN} = \text{PR₂} \\
\text{CF₃CH₂OH} \quad & \quad \text{Me₃SiN} = \text{PR₂} \\
\text{Et₃N} \quad & \quad \text{Me₃SiN} = \text{PR₂} \\
\end{align*}
\]

the NMe₂ and OMe derivatives were remarkably thermally stable, the OCH₂CF₃ substituted phosphinimine readily eliminated Me₃SiOCH₂CF₃ to give quantitative yields of poly(dimethylphosphazene) (eq 7). Polymerization occurs on heating at 175 to 190°C in a sealed glass
ampoule or in a stainless bomb, or in refluxing benzene, or under neat reflux. The phosphinimine also decomposes slowly on standing at room temperature for extended periods of time.

The process was extended to prepare a number of new alkyl and/or aryl substituted polymers (eq 8). In general, higher temperatures were required to facilitate polymer formation. Some of the physical properties that have been determined by AMMRC for \([\text{Ph(Me)PN}]_n\) are\(T_g=37^\circ\text{C}, [\eta]=0.396 \text{ dl/g}, M_n=53,900 \pm 1700 \text{ g/mole. Data for \([\text{Ph(Et)PN}]_n\) have not been received and no data is available for \((\text{Et}_2\text{PN})_n\) due to its insolubility. Thermolysis of \(\text{Ph}_2\text{P(OCH}_2\text{CF}_3)\equiv\ \text{NSiMe}_3\) at \(225^\circ\) for 10 days resulted in only trace amounts of polymer as well as cyclic trimer and tetramer and undecomposed starting material.

Copolymerization of mixtures of differently substituted phosphinimines was also investigated. Heating of equimolar amounts of \(\text{Ph(Et)P(OCH}_2\text{CF}_3)\equiv\ \text{NSiMe}_3\) and \(\text{Et}_2\text{P(OCH}_2\text{CF}_3)\equiv\ \text{NSiMe}_3\) or \(\text{Ph(Me)P(OCH}_2\text{CF}_3)\equiv\ \text{NSiMe}_3\) and \(\text{Me}_2\text{P(OCH}_2\text{CF}_3)\equiv\ \text{NSiMe}_3\) proceeded smoothly to give two new polymeric materials. Complete characterization of these compounds is in progress.
Publications


