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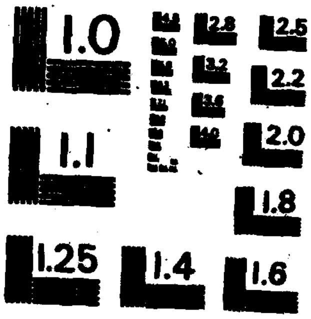

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Synthesis of Phosphorus-Nitrogen Polymers Using Si-N-P Reagents

by

Patty Wisian-Neilson, Aroop K. Roy,

Ze-min Xie, and Robert H. Neilson

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

→ Many small-molecule Si-N-P compounds of appropriate design can function as precursors to various oligomeric and polymeric P-N systems. For example, poly(dialkylphosphazenes), $(R_2PN)_n$, are readily obtained via the thermal condensation-polymerization of certain N-silylphosphinimines, $Me_3SiN{=}P(X)R_2$. →

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In addition, novel 3-coordinate phosphorus-V compounds including the bis(imino)phosphoranes, $RP(=NSiMe_3)_2$, can potentially lead to new polymers of formula $(RPN)_n$, the phosphorus analogs of electrically conducting $(SN)_n$. The synthesis of polyphosphazenes and their precursors and the synthesis of potential precursors to $(RPN)_n$ are discussed.

(SN) sub n

(RPN) sub n

SYNTHESIS OF PHOSPHORUS-NITROGEN POLYMERS USING Si-N-P REAGENTS

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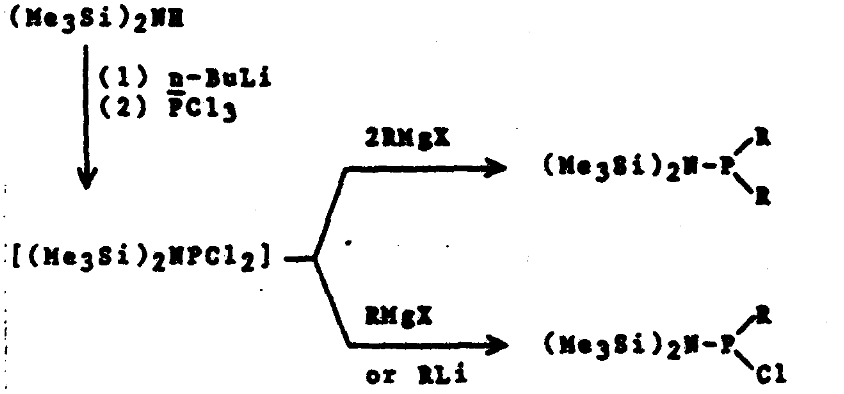
Many small-molecule Si-N-P compounds of appropriate design can function as precursors to various oligomeric and polymeric P-N systems. For example, poly(dialkylphosphazenes), $(R_2PN)_n$, are readily obtained via the thermal condensation-polymerization of certain N-silylphosphinimines, $Me_3SiN=P(X)R_2$. In addition, novel 3-coordinate phosphorus-V compounds including the bis(imino)-phosphoranes, $RP(=NSiMe_3)_2$, can potentially lead to new polymers of formula $(RPN)_n$, the phosphorus analogs of electrically conducting $(SN)_n$. The synthesis of polyphosphazenes and their precursors and the synthesis of potential precursors to $(RPN)_n$ are discussed.

The structural and chemical diversity of compounds containing the Si-N-P linkage is a result of both the variety of coordination numbers which phosphorus may assume and the reactivity of the Si-N bond. The combination of these features gives Si-N-P compounds very promising synthetic utility, particularly in the area of inorganic polymer synthesis.

Typically, the most common precursors to new Si-N-P systems are simple silylaminophosphines (eq 1). The difunctional character of these compounds, which is due to the nucleophilic site at phosphorus and a complementary electrophilic site at silicon, makes them very versatile reagents. They have been used in a new synthesis of alkyl and/or phenyl substituted phosphazenes $(R_2PN)_n$ (1) and have led to the preparation of promising precursors to potentially electrically conducting polymer systems of general formula $(RPN)_n$.

Synthesis of Polyphosphazenes

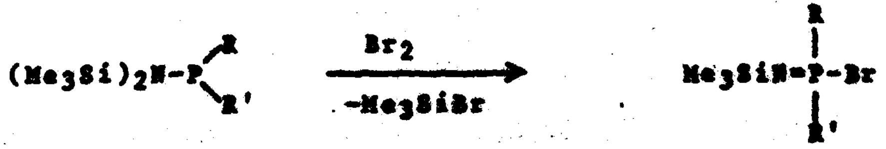
Work in the polymer synthesis area has been enhanced by a convenient "one-pot" synthesis which was developed by J.C. Wilburn (2) (eq 1). Yields of the phosphines prepared in this manner are typically 60 to



(1)

to 90% and quantities of 250 to 300 grams are easily obtained. The use of $PhPCl_2$ in place of PCl_3 allows for the introduction of phenyl/alkyl substitution at phosphorus.

Many simple oxidation reactions of tertiary alkyl or aryl phosphines are less straightforward in phosphines with silylamino substituents (3-8). Two such reactions have resulted in precursors to phosphazenes. The first of these is the reaction of bromine with disubstituted silylaminophosphines (7) to give Me_3SiBr and P-bromo-N-silylphosphinimines (eq 2).

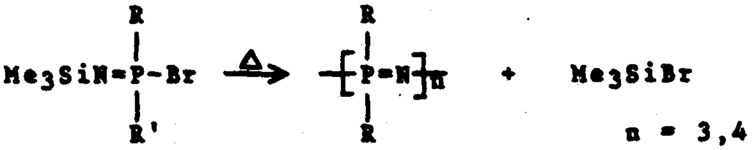


(2)

R,R' = Me, Et, i-Pr, Ph, OCH_2CF_3, CH_2Ph,

CH_2SiMe_3, $CH_2CH=CH_2$, etc.

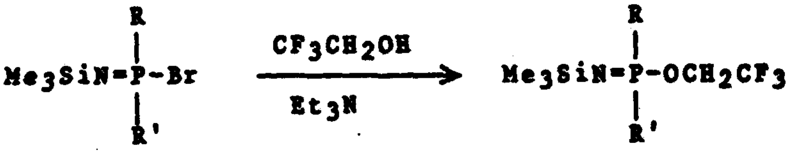
The phosphinimines are thermally unstable and readily eliminate Me_3SiBr at temperatures of greater than 100°C to form only cyclic phosphazenes (eq 3). (7)



$$\mathrm{Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}Br} \xrightarrow{\Delta} \left[\mathrm{\overset{R}{\underset{R}{P}}{=}N}\right]_{n} + \mathrm{Me_3SiBr} \qquad (3)$$

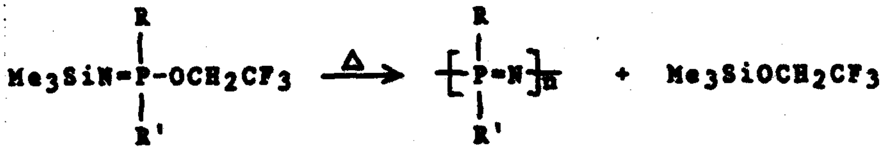
$$n = 3,4$$

More importantly, the P-bromophosphinimines react smoothly with CF_3CH_2OH in the presence of Et_3N to form P-(trifluoroethoxy)phosphinimines (eq 4) (7). On heating in either sealed glass ampoules or a stainless



$$\mathrm{Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}Br} \xrightarrow[Et_3N]{CF_3CH_2OH} \mathrm{Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}OCH_2CF_3} \qquad (4)$$

steel bomb these phosphinimines readily eliminate $Me_3SiOCH_2CF_3$ (eq 5) and form exclusively polymeric phosphazenes. (1)



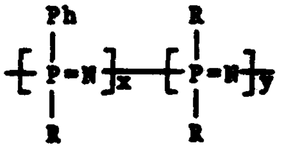
$$\mathrm{Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}OCH_2CF_3} \xrightarrow{\Delta} \left[\mathrm{\overset{R}{\underset{R'}{P}}{=}N}\right]_{n} + \mathrm{Me_3SiOCH_2CF_3} \qquad (5)$$

R	Me	Et	Ph	Ph	Ph
R'	Me	Et	Me	Et	Ch$_2$Ph

The physical properties of these polymers vary considerably as the substituents at phosphorus are changed. Poly(dimethylphosphazene) $(Me_2PN)_n$ is a white film-forming polymer with a weight averaged molecular weight ($\bar{M}_w$) of 50,000 as determined by light scattering. It is soluble in CH_2Cl_2, $CHCl_3$, CH_3CH_2OH, and THF/H_2O, and has a melting point of 158°C and a glass transition temperature of -42°C (1). The diethyl analog $(Et_2PN)_n$, on the other hand, is quite perplexing since its virtual insolubility in all solvents precludes most characterization other than elemental analysis.

In contrast to the alkyl substituted polymers, the P-phenyl compounds, $[Ph(Me)PN]_n$ and $[Ph(Et)PN]_n$, are brittle, brown colored materials which are quite soluble in THF and are readily plasticised by trace amounts of solvent. Determination of molecular weight by gel permeation chromatography for $[Ph(Me)PN]_n$ indicates $\bar{M}_n$ to be 54,000. Its glass transition temperature was found to be 37°C.

Phosphazene copolymers have also been prepared by the thermolysis of equimolar mixtures of the phenyl/alkyl and dialkyl substituted P-trifluoroethoxyphosphinimines.

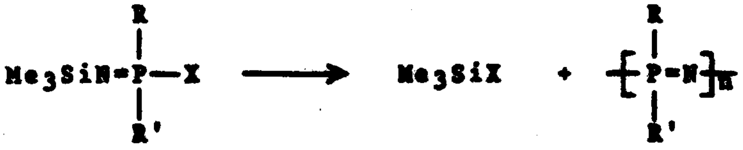


$$\left[\overset{Ph}{\underset{R}{P}}=N \right]_x - \left[\overset{R}{\underset{R}{P}}=N \right]_y$$

R = Me, Et

These materials are generally more elastomeric and rubber-like in appearance than either of the corresponding homopolymers. Such systems indicate that it should be possible to "custom design" polyphosphazenes by choosing precursors with desirable substituents.

In summary, this new and general method of synthesizing both cyclic and polymeric phosphazenes (eq 6)

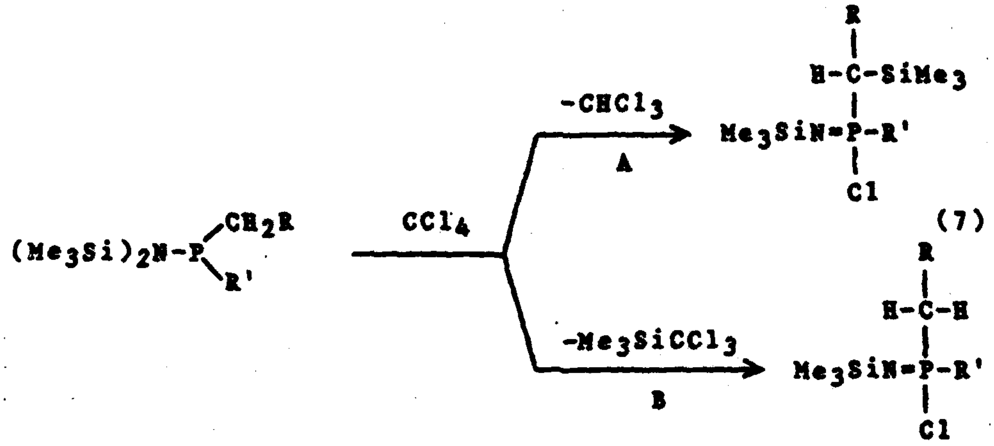


$$Me_3SiN=\overset{R}{\underset{R'}{P}}-X \longrightarrow Me_3SiX + \left[\overset{R}{\underset{R'}{P}}=N \right]_n \tag{6}$$

involves properly designed N-silylphosphinimines which contain a leaving group X and the desired substituents R and R' on phosphorus. Such compounds eliminate substituted silanes Me_3SiX and form cyclic or polymeric phosphazenes. When X is Br or, as reported earlier (9), F, only small ring compounds are formed, but when X is CF_3CH_2O, polymeric phosphazenes result. In contrast to the usual methods of preparing inorganic polymers via ring opening polymerization, this is an unusual example of a condensation-polymerization which gives an inorganic P-N polymer backbone. This method, therefore, has the advantage of allowing the initial construction of small molecule building blocks which incorporate desirable side groups. This is particularly useful for the preparation of alkyl and/or aryl substituted polyphosphazenes with direct carbon to phosphorus bonds, a system which is difficult to achieve by other methods.

CCl_4 Reactions of (Silylamino)phosphines

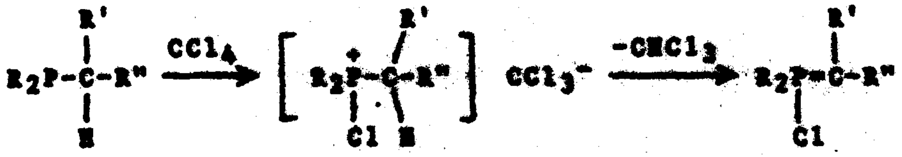
Other N-silylphosphinimines which are also suitably constructed phosphazene precursors, can be prepared by a second oxidation reaction of silylaminophosphines. When these phosphines react with carbon tetrachloride, two types of P-chlorophosphiminines may be formed by essentially two pathways (eq 7) (8).



(7)

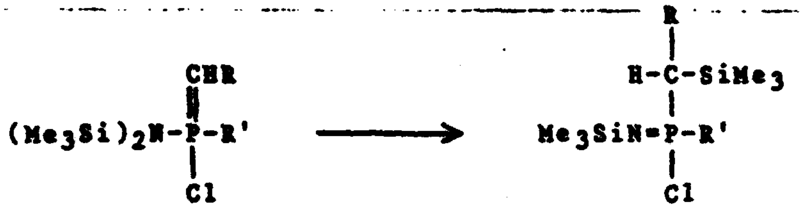
R = $SiMe_3$, Me, Ph, H
R' = CH_2SiMe_3, Me, Et, i-Pr, t-Bu, Ph, NMe_2, OMe, OCH_2CF_3

The elimination of $CHCl_3$ as shown in pathway A occurs in similar systems which contain a C-H moiety α to phosphorus. Presumably, initial formation of an ion pair intermediate $(R_3PCl^+)(CCl_3^-)$ (10) is followed by attack of the CCl_3^- anion at the hydrogen on the α carbon with elimination of $CHCl_3$ giving ylide products (eq 8) (11,12). However, in systems which



(8)

contain a silylamino substituent, the analogous ylides are presumably intermediates which rearrange via a [1,3]-silyl shift (eq 9) (4) to give the P-chlorophosphinimines shown in pathway A.



$$(Me_3Si)_2N\text{-}\overset{\overset{\textstyle CHR}{\|}}{\underset{\underset{\textstyle Cl}{|}}{P}}\text{-}R' \longrightarrow Me_3SiN{=}\overset{\overset{\overset{\textstyle R}{|}}{H\text{-}C\text{-}SiMe_3}}{\underset{\underset{\textstyle Cl}{|}}{P}}\text{-}R' \qquad (9)$$

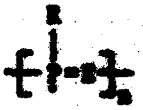
An alternate pathway is possible for systems containing silylamino substituents at phosphorus. This most likely involves attack of the CCl_3^- anion at the electrophilic silicon resulting in elimination of Me_3SiCCl_3 as shown in pathway B. In the systems investigated thus far, the reaction pathway preference appears to be influenced by: (1) solvent polarity, and (2) steric and electronic effects of the substituents at phosphorus (8).

Low-coordinate Phosphorus Systems

Regardless of which N-silylphosphinimine products are formed they all are potential precursors to phosphazenes via elimination of Me_3SiCl. Preliminary evidence indicates that the thermal elimination does indeed occur in some cases. The N-silylphosphinimines are also potential precursors to another type of novel Si-N-P compound, i.e. three-coordinate phosphoranes:

E = CRR', NR

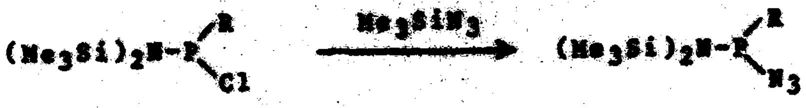
Our interest in such compounds stems mainly from the possibility that they might be useful precursors to new classes of phosphorus-containing polymers or cyclic oligomers. Functional linkages such as E = $NSiMe_3$ or $CR'SiMe_3$ could serve as sites for condensation-polymerization reactions, leading to novel cyclic or polymeric systems,



$$\left[\overset{\overset{\textstyle R}{|}}{P}{=}E\right]_n$$

where E = N or CR'. These materials are isoelectronic with the electrically conducting polymer, poly(sulfur nitride), $(SN)_x$.

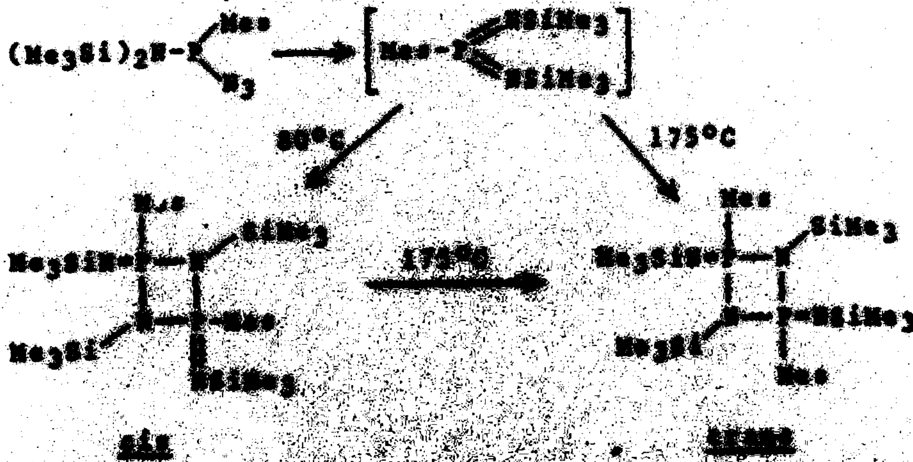
Silylaminophosphines, once again, are appropriate precursors to such low coordinate systems. Treatment of chloro substituted silylaminophosphines with Me_3SiN_3 at room temperature results in spectroscopically pure azido phosphines following removal of Me_3SiCl (eq 10). In the case where R is a mesityl group, heating the



$$(Me_3Si)_2N{-}P\begin{matrix}R\\Cl\end{matrix} \xrightarrow{Me_3SiN_3} (Me_3Si)_2N{-}P\begin{matrix}R\\N_3\end{matrix} \qquad (10)$$

R = CH_2SiMe_3, Ph, Mes, $N(SiMe_3)_2$

azido phosphine produces a loss of N_2 and a subsequent [1,3] silyl shift. At 80°C the *cis* 4-membered ring system (^{31}P δ-19.7) is formed while heating at 175°C produces the more thermodynamically stable *trans* isomer (^{31}P δ-24.7) (eq 11). The two crystalline isomers



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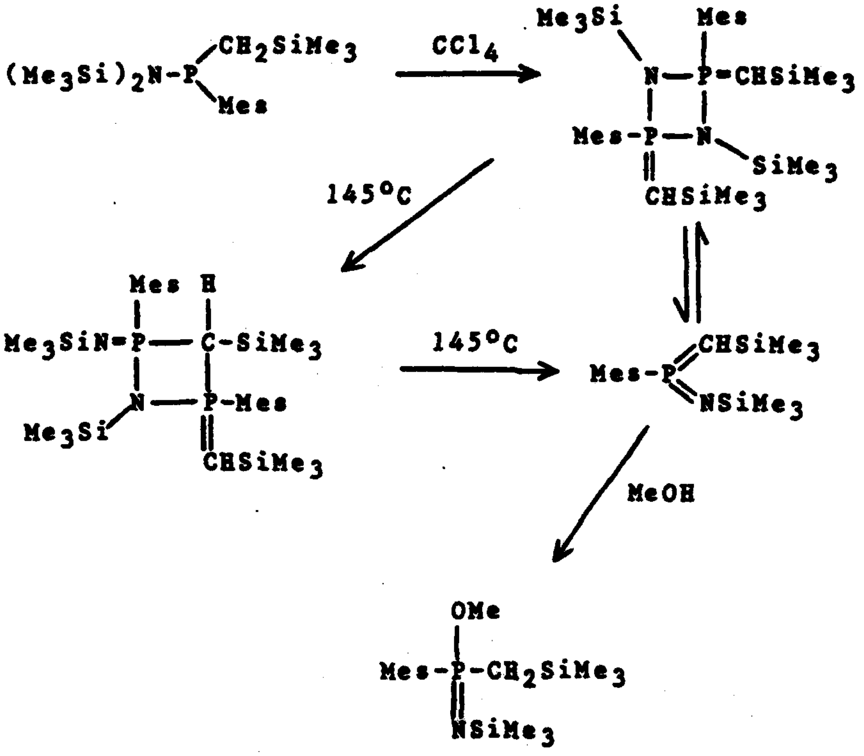

(12)

and Me_3SiCl and formation of a white crystalline solid which has been identified as the methylene substituted 4-membered P-N-P-N ring system (^{31}P δ+22.2). Upon distillation (b.p. 91-92°C/0.01 mm), the monomer $MesP(=NSiMe_3)(=CHSiMe_3)$ was collected as a colorless liquid (^{31}P δ+122.7). The monomer reverts to the dimer on standing at room temperature overnight. It readily adds methanol across the P=C bond to form the P-methoxy phosphinimine.

On heating at 145°C for two hours, both the monomer and dimer form a novel 4-membered P-N-P-C ring compound. The ^{31}P spectrum of this compound consists of two doublets of equal intensity at δ+10.9 and δ-10.6 with J_{PP} = 15.3 Hz. The downfield shift correlates with that of the phosphorus in the ring system containing $Me_3SiCH=$ substituents, while the upfield shift is similar to that of the 4-membered ring systems containing $Me_3SiN=$ substituents at phosphorus. The rings have also been characterized by ^{13}C and ^{1}H NMR, elemental analysis, and molecular weight measurements using both mass spectroscopy and cryoscopic techniques.

Preliminary studies indicate that the reactions of some of these dimers with $RPCl_2$ result in elimination of Me_3SiCl and ring opening reactions. Details of these investigations and complete characterization of these ring systems will be reported elsewhere.

Acknowledgments

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