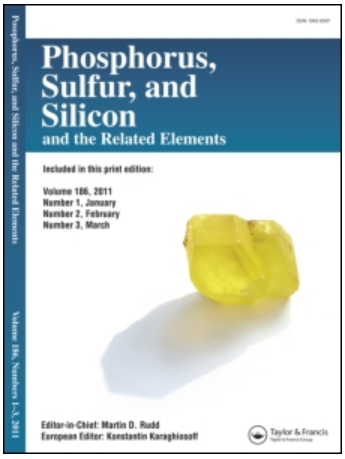

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Neilson, Robert H. , Azimi, Kaveh , Zhang, Goumin , Kucera, William R. and Longlet, Jon J.(1994) 'New Preparative Chemistry of Silicon-Nitrogen-Phosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 87: 1, 157 — 165
To link to this Article: DOI: 10.1080/10426509408037450
URL: http://dx.doi.org/10.1080/10426509408037450

Phosphorus, Sulfur, and Silicon, 1994, Vol. 87, pp. 157–165
Reprints available directly from the publisher
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NEW PREPARATIVE CHEMISTRY OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS

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WILLIAM R. KUCERA, and JON J. LONGLET
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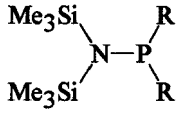
Compounds containing the Si-N-P linkage, especially (silylamino)phosphines, $(Me_3Si)_2NPR_2$, and N-silylphosphoranimines, $Me_3SiN{=}PR_2X$, are of interest as precursors to polyphosphazenes and/or other phosphorus-based polymer systems or to new types of organophosphorus or phosphorus-nitrogen compounds. In addition to reviewing the general preparative chemistry of these Si-N-P systems, this report describes some recent results on the synthesis and characterization of three new types of P-N compounds that either contain or were prepared from Si-N-P linkages. The new systems include: (1) a series of acetylene-substituted (silylamino)phosphines and N-silylphosphoranimines, (2) three types of aminoborane derivatives of N-silylphosphoranimines, and (3) several N-phosphoryl substituted phosphoranimines.

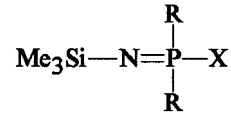
Key Words: (silylamino)phosphine, phosphoranimine, aminoborane, phosphazene, phosphoryl

INTRODUCTION

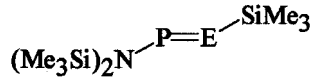
During the last 15 - 20 years, much of our research has centered on the synthesis, characterization, and derivative chemistry of the three types of silicon-nitrogen-phosphorus compounds that are illustrated below.[1] This presentation is specifically concerned with the chemistry of the first two classes, i.e., the (silylamino)phosphines and the N-silylphosphoranimines, while other recent work in our laboratories has dealt with the third type.[2] After a brief survey of the general synthesis and reactivity of (silylamino)phosphines and N-silylphosphoranimines, this paper will focus on some of our recent results in these areas.



(silylamino)phosphine

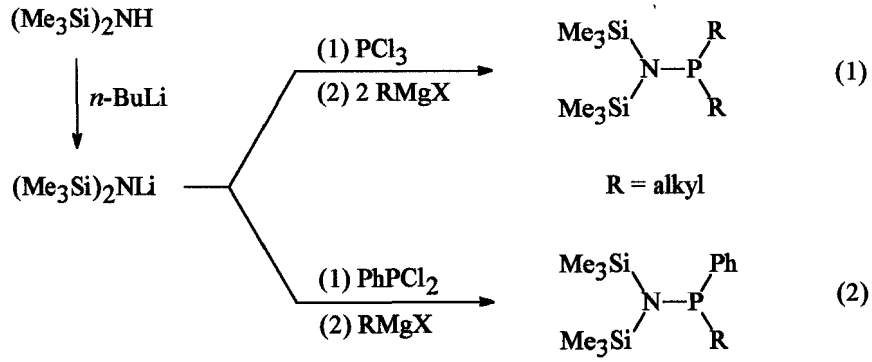


N-silylphosphoranimine



two-coordinate (silylamino)phosphines (E = N, CH)

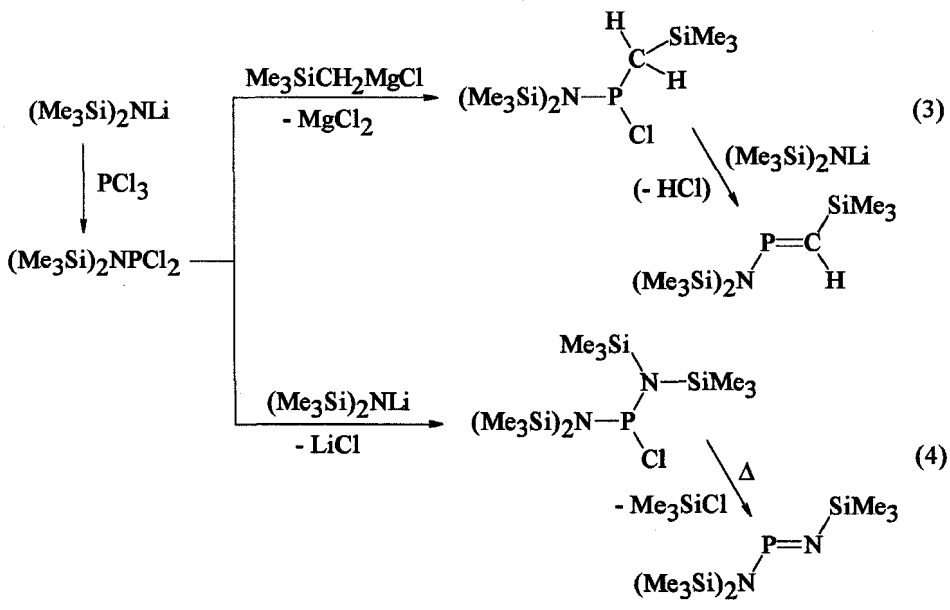
A variety of methods have been employed for the synthesis of (silylamino)phosphines including: (a) reaction of halophosphines with N-metalated silylamines;[3-5] (b) Si-N bond cleavage reactions of halophosphines with disilylamines;[4] and (c) reactions of silylphosphines with silyl azides.[3] By far the most general and practical approach to (silylamino)phosphines, however, is the "Wilburn Method"[5-7] which is a high-yield, one-pot synthesis of either symmetrical (eq 1) or unsymmetrical (eq 2) (silylamino)phosphines bearing alkyl and/or aryl groups on phosphorus.



(1)

(2)

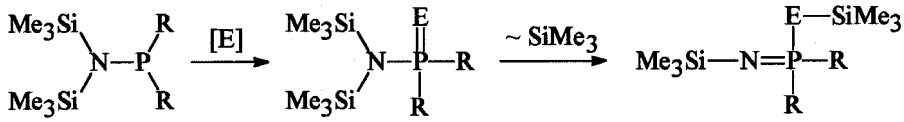
The chemistry of (silylamino)phosphines is quite diverse and encompasses synthetically useful routes to derivatives with either lower or higher coordination number at phosphorus. The former is illustrated by the preparation of stable two-coordinate (silylamino)phosphines by elimination of HCl (eq 3)[8] or Me_3SiCl (eq 4).[9]



(3)

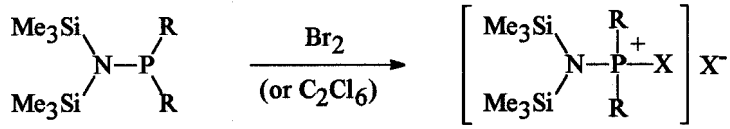
(4)

More commonly, (silylamino)phosphines undergo facile oxidation of the P^{III} center to the 4-coordinate P^{V} state. While many such oxidation reactions are accompanied by a silyl migration (eq 5),[5,10] oxidative halogenation occurs with halosilane elimination (eqs 6 and 7).[11] Both of these types of reactions result in the formation of products belonging to the second major class of Si-N-P compounds, the N-silylphosphoranimines. The P-halophosphoranimines can, in turn, be converted to a wide variety of P-alkoxy or P-aryloxy substituted phosphoranimines (eq 7). Thus, many types of functionalized N-silylphosphoranimines are readily accessible via straightforward reactions of (silylamino)phosphines. In contrast, most other methods[12] of preparing N-silylphosphoranimines generally afford symmetrically substituted compounds of the type $Me_3SiN{=}PR_3$ or $Me_3SiN{=}P(OR)_3$.



(5)

E = O, NR, CR_2



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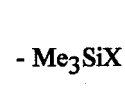
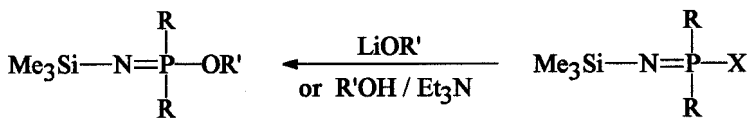
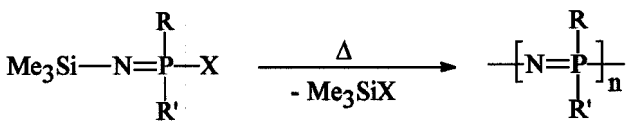




(7)

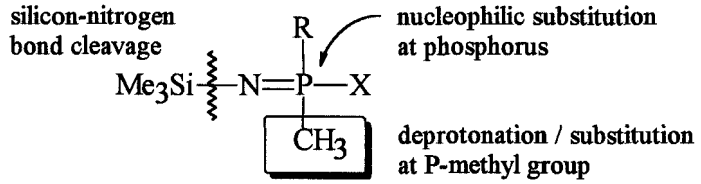
R' = CH_2CF_3, Ph X = Cl, Br

With a suitable leaving group (e.g., X = OCH_2CF_3 or OPh) at phosphorus, many of these N-silylphosphoranimines are useful precursors to poly(alkyl/arylphosphazenes) via a condensation polymerization process (eq 8).[1,13]



(8)

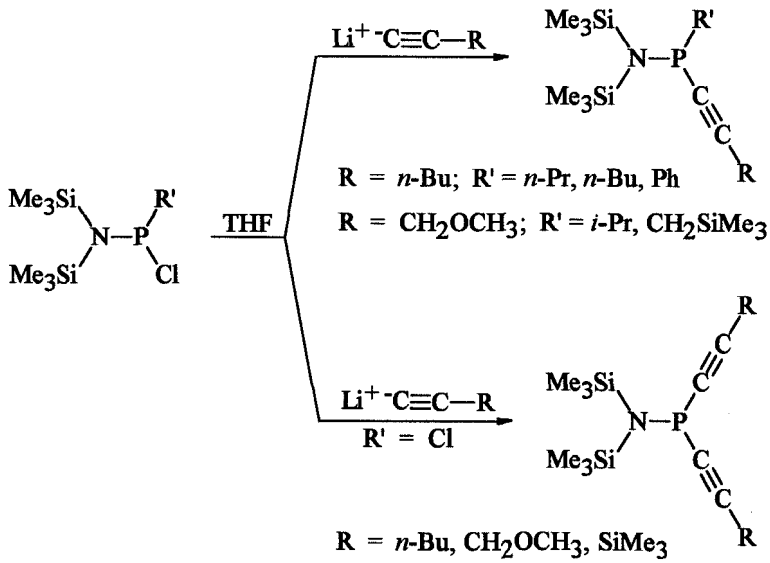
At the small molecule level, the N-silylphosphoranimines also have a very rich and synthetically useful derivative chemistry.[1] Three distinct modes of reactivity (as illustrated below) are well documented. Cleavage of the Si-N bond is typified by a series of transsilylation reactions with substituted chlorosilanes[14] while the deprotonation-substitution chemistry has led to a wide variety of P-CH_2-X derivatives containing silyl,[15] phosphinyl,[16] and organic[17] functional groups. Some of these latter reactions serve as useful model systems for similar derivative chemistry of the preformed phosphazene polymers such as $[Me(Ph)P{=}N]_n$.[1,18]



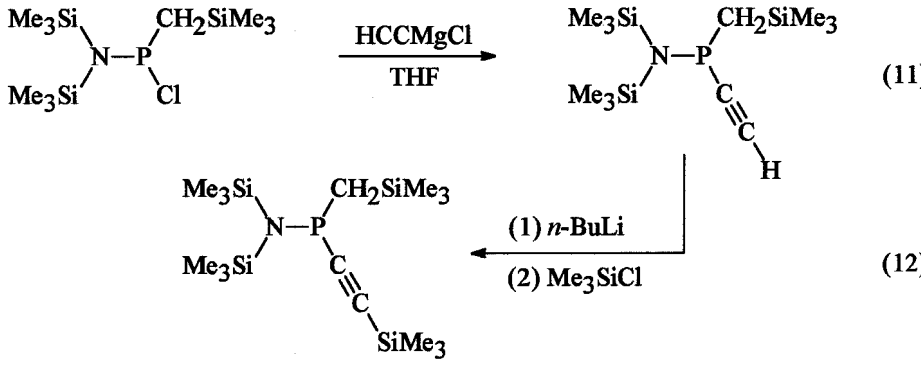
In addition to the synthesis of some new types of acetylene-substituted (silylamino)phosphines by a modification of the Wilburn method, we report here several new examples of these modes of reactivity of N-silylphosphoranimines. Specifically, the preparation of some new boryl- and phosphoryl-substituted phosphoranimines will be summarized.

ACETYLENE-SUBSTITUTED Si-N-P COMPOUNDS

We have recently been investigating the synthesis and derivative chemistry of some new (silylamino)phosphines that contain acetylenic moieties. These compounds are readily prepared by a variation of the Wilburn procedure which affords good yields of both mono- (eq 9) and di-acetylene (eq 10) derivatives.

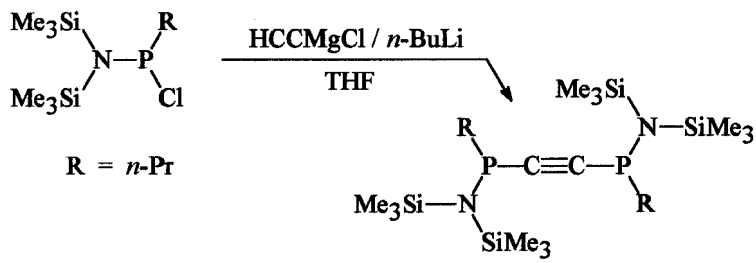


In a similar manner, it is possible to prepare the parent ethynylphosphine by the reaction of a chlorophosphine with HC≡CMgCl (eq 11). The terminal C-H group can then be selectively deprotonated and silylated (eq 12). Moreover, treatment of the ethynyl Grignard reagent with one equivalent of *n*-BuLi, followed by a chlorophosphine, gives a diphosphaacetylene product (eq 13). These acetylene derivatives generally undergo smooth and selective oxidative halogenation (eq 14) which leads to N-silylphosphoranimines bearing acetylenic side groups. Full details of the synthesis and characterization of all of these new compounds will be published elsewhere.

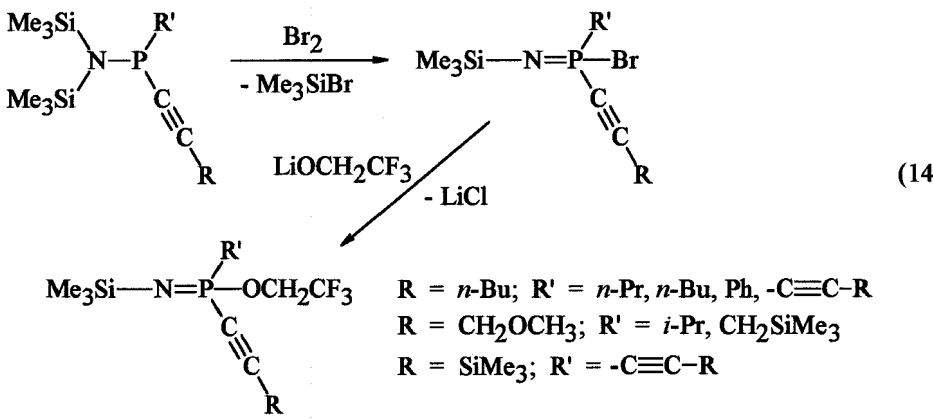


(11)

(12)



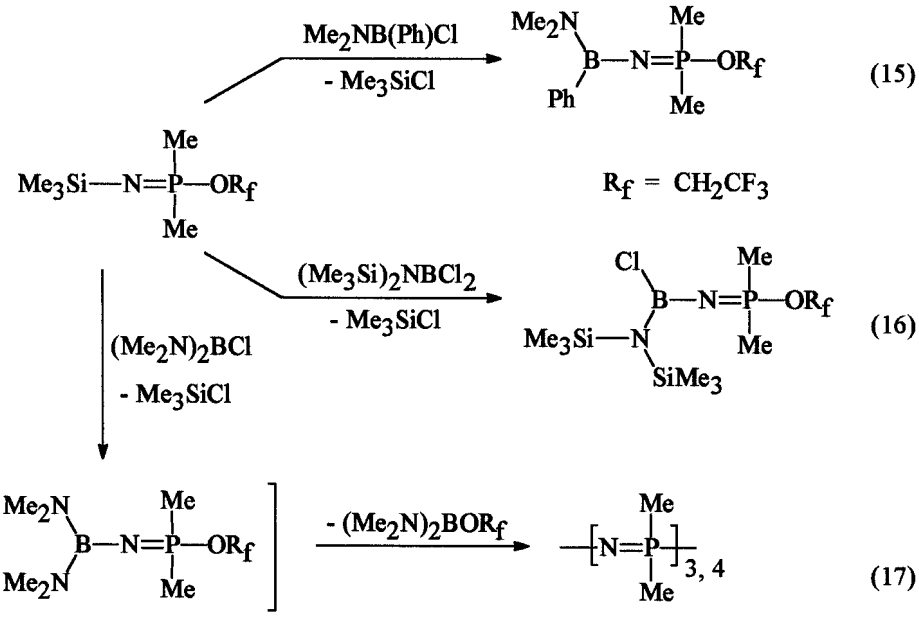
(13)



(14)

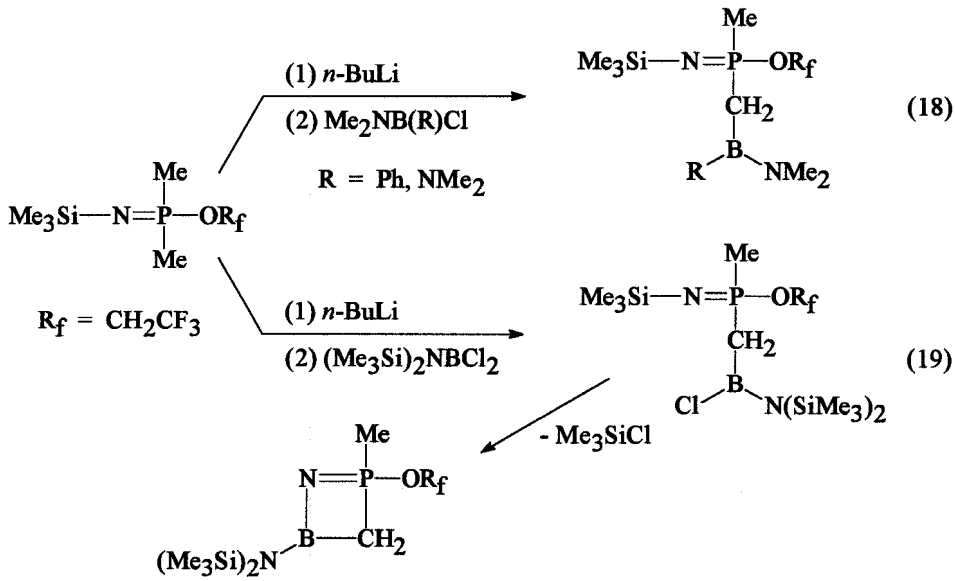
AMINOBORANE DERIVATIVES OF N-SILYLPHOSPHORANIMINES

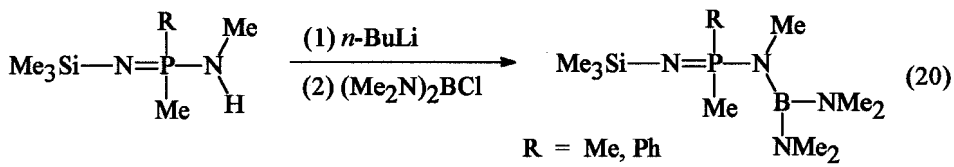
The three modes of reactivity of N-silylphosphoranimines mentioned above can all be adapted to the synthesis of new aminoboryl derivatives, some of which may be useful in the eventual synthesis of a novel PN/BN hybrid polymer system.[19] In the first method, facile elimination of Me_3SiCl takes place when N-silylphosphoranimines are treated with chloroboranes. In some cases (eqs 15 and 16), high yields of the expected N-boryl substituted phosphoranimines are cleanly obtained. On the other hand, a similar reaction with bis(dimethylamino)(chloro)borane (eq 17) results in the formation of cyclic dimethyl phosphazenes by a process in which the chloroborane appears to function as a low-temperature catalyst for the production of phosphazenes.

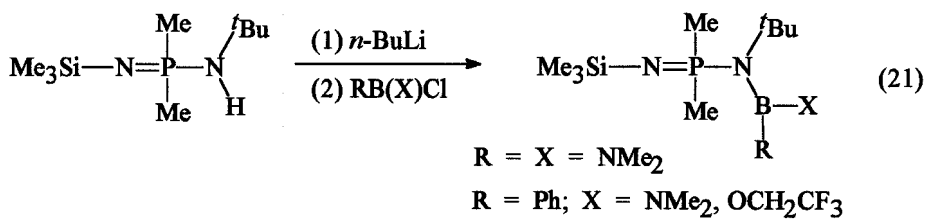


The second method of functionalization of N-silylphosphoranimines, i.e., the deprotonation/substitution reaction of the pendent P-CH_3 group, can also be applied to the synthesis of aminoboryl derivatives. These new P-CH_2-B systems are normally stable, distillable liquids (eq 18). If a B-Cl moiety is still present, however, elimination of Me_3SiCl leads to the formation of a novel PNCB four-membered ring (eq 19).[19] Current work is aimed at the synthesis of a crystalline analog of this ring system that can be structurally characterized by X-ray diffraction.

The third successful route to boryl derivatives of N-silylphosphoranimines that we have explored involves deprotonation/substitution reactions at the N-H site of appropriate amino-substituted phosphoranimines (eqs 20 and 21).[19a] These compounds were generally obtained in good yield as high-boiling liquids that were fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and elemental analysis.

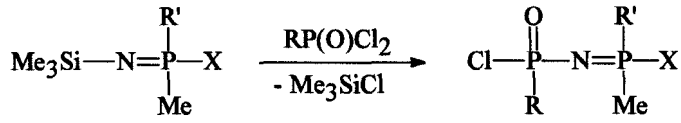






N-PHOSPHORYL SUBSTITUTED PHOSPHORANIMINES

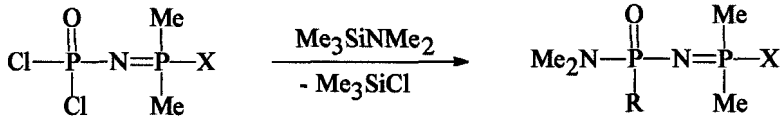
As part of our overall program on the development of new precursors for the synthesis of poly(alkyl/arylphosphazenes) (eq 8), we are studying possible Si-N bond cleavage reactions of the N-silylphosphoranimines with various reactive halides. In addition to the chloroborane reactions described above (eqs 15 - 17), we find that phosphoryl halides such as $P(O)Cl_3$ and $MeP(O)Cl_2$ react very smoothly with both the dimethyl- and the phenyl(methyl)phosphoranimines (eq 22) to afford high yields of new P-N=P systems. Although these P-Cl derivatives are routinely obtained as fully-characterized, distillable liquids, they are easily converted to their P-dimethylamino derivatives via treatment with Me_3SiNMe_2 (eq 23).



(22)

X = OCH_2CF_3, OPh
R' = Me, Ph

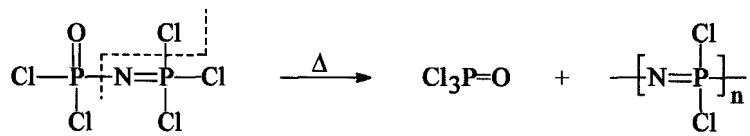
R = Cl, Me



(23)

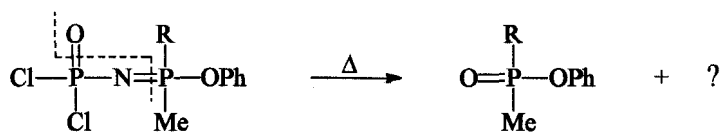
R = NMe_2, Me, Cl

Only a few other examples of N-phosphoryl-phosphoranimines have been previously reported. Most notable of these is the perchloro analog which has been shown to be an effective precursor to poly(dichlorophosphazene) via the thermal elimination of $P(O)Cl_3$ (eq 24).[20]



(24)

Interestingly, our phosphoryl derivatives, which contain various substituents at the P=N phosphorus center other than chlorine, do not decompose in the same manner. We find, instead, that the only significant volatile product is a phosphine oxide that probably results from the type of fragmentation indicated in equation 25. The non-volatile, possibly polymeric, products of this decomposition process are not readily identifiable and must await further study.



(25)

R = Me, Ph

In combination with the production of cyclic phosphazenes from some of the chloroborane reactions (eq 17), these results clearly indicate that investigation of Si-N bond cleavage reactions of N-silylphosphoranimines should be continued.

Acknowledgment. The authors thank the U.S. Army Research Office, the National Science Foundation, the Robert A. Welch Foundation, and the TCU Research Fund for generous financial support of these research projects.

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