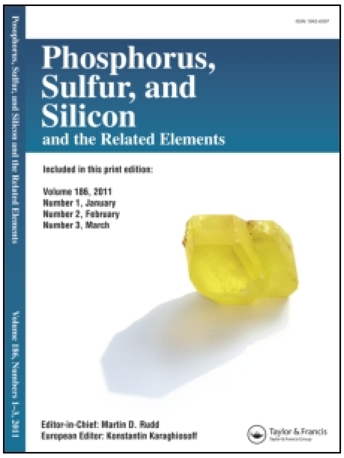


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Silylated Phosphines and Phosphoranimines

Robert H. Neilson[a]; Bruce A. Boyd[a]; Donn A. Dubois[a]; Rahim Hani[a]; Gary M. Scheide[a]; John T. Shore[a]; Urszula G. Wettermark[a]
[a] Department of Chemistry, Texas Christian University, Fort Worth, Texas, USA

To cite this Article Neilson, Robert H. , Boyd, Bruce A. , Dubois, Donn A. , Hani, Rahim , Scheide, Gary M. , Shore, John T. and Wettermark, Urszula G.(1987) 'Silylated Phosphines and Phosphoranimines', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 463 — 466

To link to this Article: DOI: 10.1080/03086648708080620

URL: http://dx.doi.org/10.1080/03086648708080620

Phosphorus and Sulfur, 1987, Vol. 30, pp. 463–466
Photocopying permitted by license only

SILYLATED PHOSPHINES AND PHOSPHORANIMINES

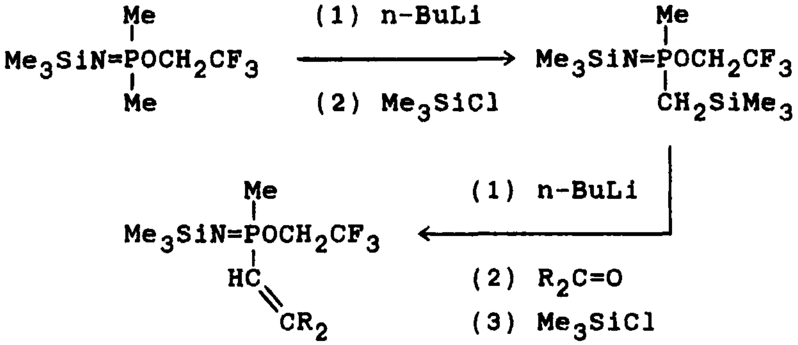
ROBERT H. NEILSON*, BRUCE A. BOYD, DONN A. DUBOIS, RAHIM HANI, GARY M. SCHEIDE, JOHN T. SHORE, AND URSZULA G. WETTERMARK
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

Abstract The N-silylphosphoranimines [e.g., $Me_3SiN{=}P(OCH_2CF_3)Me_2$] undergo a variety of reactions including deprotonation/substitution of the P-Me groups, transilylation, and condensation with reactive phosphines. Some new 1,2-addition and oxidation reactions of the P=C systems, $R_2NP{=}CHR$, $R_2NP({=}NR){=}CHR$, and $R_2NP{=}CR{-}CH{=}CHR$ ($R = SiMe_3$) are also reported.

The chemistry of compounds containing Si-N-P and/or Si-C-P linkages is usually markedly different from that of the nonsilylated analogues. On the one hand, the Si-N or Si-C bonds may function as reactive sites so that processes such as transilylation and condensation reactions via silane elimination are commonly found. Alternatively, the steric and electronic properties of the silyl groups can impart both kinetic stability and interesting chemical reactivity to a variety of low-coordinate phosphorus systems. We report here several illustrative examples of these principles.

REACTIONS OF N-SILYLPHOSPHORANIMINES

Various P-functionalized N-silylphosphoranimines are useful precursors to cyclic and polymeric phosphazenes. Recently, the synthetic utility of such compounds has been greatly expanded through two general types of reactions. First, deprotonation/silylation of the P-methyl group followed by a Peterson olefination affords a series of vinyl derivatives (eq 1). Some of these

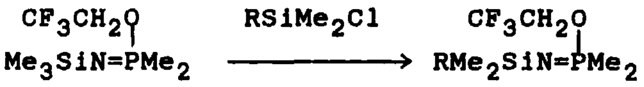


$$Me_3SiN{=}\overset{Me}{\underset{Me}{P}}OCH_2CF_3 \xrightarrow[(2)\ Me_3SiCl]{(1)\ n\text{-}BuLi} Me_3SiN{=}\overset{Me}{\underset{CH_2SiMe_3}{P}}OCH_2CF_3 \xrightarrow[(2)\ R_2C{=}O \quad (3)\ Me_3SiCl]{(1)\ n\text{-}BuLi} Me_3SiN{=}\overset{Me}{\underset{HC{=}CR_2}{P}}OCH_2CF_3 \qquad (1)$$

$R_2C(O) = Me_2C(O)$, PhC(O)H, PhC(O)Me, $PhC(O)CF_3$, $PhC(O)CH{=}CH_2$, $Me_2C{=}CH{-}C(O){-}CH{=}CMe_2$

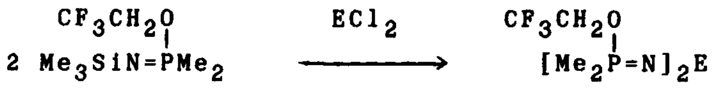
"monomers" undergo condensation polymerization to yield poly(phosphazenes) bearing substituted C=C side groups.

Second, we have studied a broad spectrum of Si-N bond cleavage reactions. For example, transilylation processes yield a series of novel N-silylphosphoranimines (eq 2) bearing reactive substituents on silicon as well as some bis(phosphoranimino)silanes and -siloxanes (eq 3). The related reactions involving cleavage of the Si-N bond in $Me_3SiN{=}P(X)Me_2$ [X = Cl, Br, OCH_2CF_3, and $N(SiMe_3)_2$] by reactive phosphines, e.g., Ph_2PY (Y = Cl, OCH_2CF_3), are generally more complex.



$$Me_3SiN{=}\overset{CF_3CH_2O}{P}Me_2 \xrightarrow{RSiMe_2Cl} RMe_2SiN{=}\overset{CF_3CH_2O}{P}Me_2 \qquad (2)$$

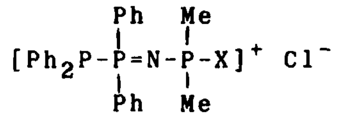
R = Ph, $CH{=}CH_2$, Cl, $(CH_2)_3CN$, $CH_2CH_2C(O)Me$, $SiMe_2(CH_2)_2SiMe_2Cl$



$$2\ Me_3SiN{=}\overset{\overset{CF_3CH_2O}{|}}{P}Me_2 \xrightarrow{ECl_2} [Me_2\overset{\overset{CF_3CH_2O}{|}}{P}{=}N]_2E \qquad (3)$$

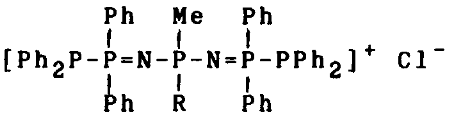
E = $SiMe_2$, $SiMe_2(CH_2)_2SiMe_2$, $Me_2Si(OSiMe_2)_n$
$n = 1\text{-}5$

These reactions occur with elimination of Me_3SiY and, depending upon the choice of reactants, lead to various open-chain ionic species (e.g., **A** and **B**).



$$[Ph_2P-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{P}}{=}N-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{P}}-X]^+\ Cl^-$$

A: X = Cl, Br, OCH_2CF_3



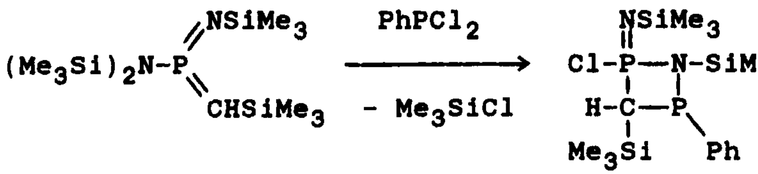
$$[Ph_2P-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{P}}{=}N-\underset{\underset{R}{|}}{\overset{\overset{Me}{|}}{P}}-N{=}\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{P}}-PPh_2]^+\ Cl^-$$

B: R = Me, Ph

Surprisingly, the permethylated analoque of **A** (X = OCH_2CF_3) is produced in high yield in the "transilylation" of Me_2SiHCl with $Me_3SiN{=}P(OCH_2CF_3)Me_2$.

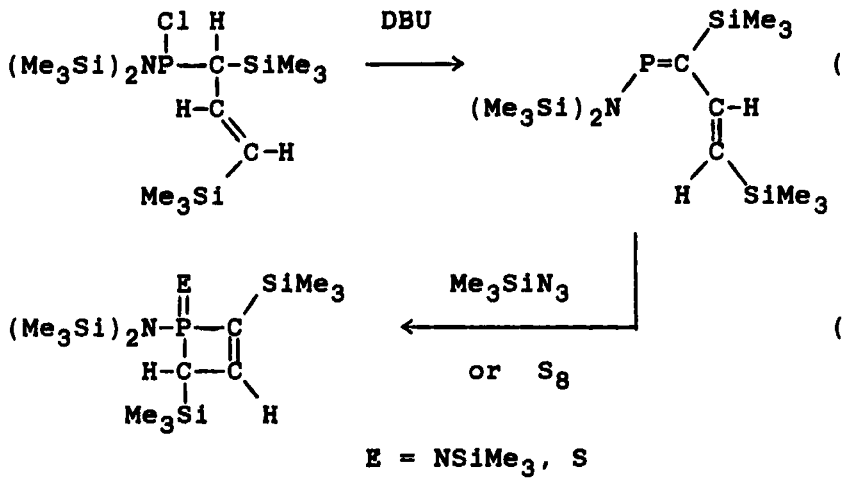
REACTIONS OF SILYLATED P=C COMPOUNDS

In this area our recent work has included a comparative study of the reactivity of the P=C bonds in the analogous P(III) and P(V) compounds, $(Me_3Si)_2NP{=}CHSiMe_3$ and $(Me_3Si)_2NP({=}NSiMe_3){=}CHSiMe_3$, respectively. In general, the 1,2-addition of polar reagents to the P=C bond occurs more readily in the P(V) system. For example, while the former does not react with $PhPCl_2$, the latter undergoes Si-N cleavage and ring formation (eq 4) subsequent to the 1,2-addition process. Some reagents, on the other hand, react smoothly with both substrates. Cyclopentadiene, for example, affords a Diels-Alder adduct in each case.



(4)

A stable, acyclic 1-phosphadiene has also been prepared (eq 5) and we have begun to investigate its derivative chemistry. Interestingly, simple oxidation reactions (e.g., with sulfur or Me_3SiN_3) are accompanied by isomerization to four-membered ring products (eq 6). In the sulfur reaction, a three-membered disulfide ring, $(Me_3Si)_2NP(S)-S-C(SiMe_3)CH=CHSiMe_3$ is also produced.



(5)

(6)

ACKNOWLEDGEMENTS

This research is generously supported by the U.S. Army Research Office, the U.S. Office of Naval Research, and the Robert A. Welch Foundation.