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Oxidation and Methylation Reactions of P–H-Substituted (Silylamino)phosphines[1]

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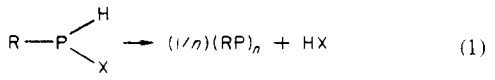
The reactions of a representative series of secondary (silylamino)phosphines $(Me_3Si)_2NP(R)H$ [R = $N(SiMe_3)_2$, *t*-Bu, *i*-Pr, Ph] with the reagents Me_3SiN_3, MeI, and *t*-BuO_2SiMe_3 are reported. The products of the Staudinger reaction with Me_3SiN_3 are generally isomeric mixtures of the P–H phosphoranimines $(Me_3Si)_2NPR(H)=NSiMe_3$ and the N–H phosphines $(Me_3Si)_2NP(R)N(H)SiMe_3$. The isomers are not readily interconvertible, and formation of the P–H product is favored by bulky R groups. Two of these systems are also obtained by reduction of the iodophosphoranimines $(Me_3Si)_2NP(R)I=NSiMe_3$ (R = *t*-Bu, *i*-Pr) with $LiAlH_4$. Deprotonation of either the N–H or P–H products with *n*-BuLi, followed by addition of MeI, yields only the *P*-methylphosphoranimines $(Me_3Si)_2NP(R)Me=NSiMe_3$ (R = *t*-Bu, *i*-Pr). Treatment of an N–H derivative (R = Ph) with CCl_4 smoothly affords the *P*-chlorophosphoranimine $(Me_3Si)_2NP(R)Cl=NSiMe_3$. The starting phosphines are easily methylated by MeI, yielding the P–H phosphonium salts $[(Me_3Si)_2NP^+(R)(Me)H]I^-$, which react rapidly with a second equivalent of MeI via a desilylation process to give the dimethyl N–H derivatives $[Me_3SiN(H)P^+(R)Me_2]I^-$. Both of these types of phosphonium salts can be dehydrohalogenated by reaction with *n*-BuLi, giving the known phosphines $(Me_3Si)_2NP(R)Me$ and phosphoranimines $Me_3SiN=P(R)Me_2$, respectively. Oxidation of the same series of phosphines by the silyl peroxide *t*-BuO_2SiMe_3 is accompanied by [1,3]-silyl shift from nitrogen to oxygen and sometimes by proton transfer from phosphorus to nitrogen. Thus, depending on what substituent is present, the reaction may yield a P–H siloxyphosphoranimine $Me_3SiN=P(H)(R)OSiMe_3$ [R = $N(SiMe_3)_2$], an N–H siloxyphosphine $Me_3SiN(H)P(R)OSiMe_3$ (R = Ph), or complex mixtures (R = *t*-Bu, *i*-Pr). Proton, ^{13}C, and ^{31}P NMR data are reported for the new compounds obtained from all of these reactions. The P–H phosphoranimines $(Me_3Si)_2NP(R)H=NSiMe_3$ [R = $N(SiMe_3)_2$, *t*-Bu, *i*-Pr, $OSiMe_3$] are fluxional, and energy barriers of ca. 12–19 kcal/mol are reported for the [1,3]-silyl exchange process.

Introduction

Generally, aminophosphines containing P–H bonds are thermally unstable due to the facile α elimination (eq 1), which



$$R{-}P(H)(X) \longrightarrow (1/n)(RP)_n + HX \qquad (1)$$

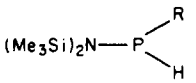
X = NR_2, OR, halogen

normally results when there is an electronegative atom attached to the P–H-substituted phosphorus center. The stabilization of such compounds, however, has been recently accomplished by two methods: (1) complexation to transition metals[2] and (2) the use of bulky groups, especially $(Me_3Si)_2N$, to provide kinetic stability.[3-7] Examples of the latter type include the novel primary phosphine $(Me_3Si)_2NPH_2$ reported by Niecke[5] and several secondary phosphines $(Me_3Si)_2NP(R)H$ prepared in our laboratory[6] and elsewhere.[3,4,7]

In addition to their stabilizing influence, the silyl groups are also reactive sites with the result that Si–N–P compounds are useful as synthetic reagents in several areas. An obvious question to be addressed is how the chemistry of the Si–N–P linkage might be modified and extended by the added presence of a reactive P–H bond. Toward this objective, we report here some "simple" derivative chemistry of the secondary (silylamino)phosphines $(Me_3Si)_2NP(R)H$. Specifically, the reactions of these phosphines with two oxidation reagents (Me_3SiN_3, *t*-BuO_2SiMe_3) and a methylation reagent (MeI) leading to new P^{III} and/or P^V compounds are described.

Results and Discussion

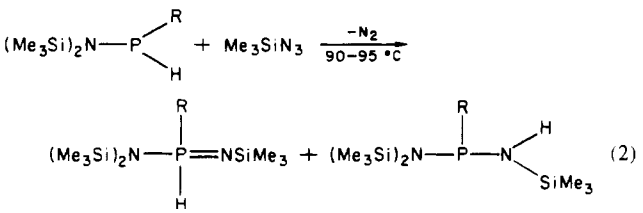
Compounds **1–4** were used in this study as representative examples of P–H-substituted (silylamino)phosphines. They are easily prepared by the $LiAlH_4$ reduction of the corresponding chlorophosphines and are conveniently purified by fractional distillation.[6] They differ primarily in the steric bulk



1, R = $N(SiMe_3)_2$
2, R = *t*-Bu
3, R = *i*-Pr
4, R = Ph

of the substituent (R), although compound **1** was included because it also contains a greater number of Si–N groups than do the others. The reagents Me_3SiN_3, MeI, and *t*-BuO_2SiMe_3 were selected for this preliminary study of the reactivity of P–H-substituted (silylamino)phosphines since the reactions of the same reagents with the *P*-alkyl analogues are already well-studied.[8-10]

Reactions with Me_3SiN_3.[8] When the P–H phosphines **1–4** were allowed to react with azidotrimethylsilane at 90–95 °C, without solvent, two types of products were generally formed (eq 2). Depending on the nature of the R group on phosphorus, the products are the expected P–H phosphoranimines **5a–8a** and/or the isomeric N–H phosphines **5b–8b**, resulting from proton transfer from phosphorus to nitrogen.



$$(Me_3Si)_2N{-}P(R)(H) + Me_3SiN_3 \xrightarrow[90\text{–}95\ ^\circ C]{-N_2}$$

$$(Me_3Si)_2N{-}P(R)(H){=}NSiMe_3 + (Me_3Si)_2N{-}P(R){-}N(H){-}SiMe_3 \qquad (2)$$

	R	% yield		R	% yield
5a	$N(SiMe_3)_2$	71	5b	$N(SiMe_3)_2$	0
6a	*t*-Bu	60	6b	*t*-Bu	26
7a	*i*-Pr	19	7b	*i*-Pr	54
8a	Ph	0	8b	Ph	52

The data suggest that the relative proportion of the two isomers is dependent on the steric demands of the substituents

(1) Taken in part from: O'Neal, H. R. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1983.
(2) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488 and references cited therein.
(3) Niecke, E.; Ringel, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 486.
(4) Cowley, A. H.; Kemp, R. A. *J. Chem. Soc., Chem. Commun.* **1982**, 319.
(5) Niecke, E.; Rüger, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 62.
(6) O'Neal, H. R.; Neilson, R. H. *Inorg. Chem.* **1983**, *22*, 814.
(7) Cowley, A. H.; Kemp, R. A. *Inorg. Chem.* **1983**, *22*, 547.
(8) Wilburn, J. C.; Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 1429.
(9) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347.
(10) Neilson, R. H.; Wisian-Neilson, P.; Wilburn, J. C. *Inorg. Chem.* **1980**, *19*, 413.

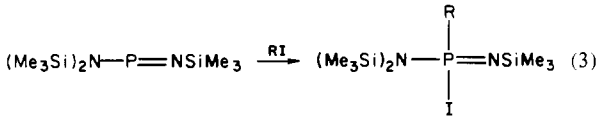
0020-1669/84/1323-1372$01.50/0

attached to phosphorus. The most sterically hindered phosphine **1** [R = $N(SiMe_3)_2$] affords the highest yield of the P–H phosphoranimine **5a** while the phenylphosphine **4** yields only the N–H phosphine product **8b**. The alkylphosphines **2** and **3**, however, both give mixtures of the corresponding P–H phosphoranimines (**6a** and **7a**) and N–H phosphines (**6b** and **7b**).

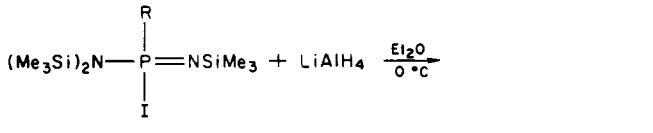
The products of these Me_3SiN_3 reactions are readily identified by NMR spectroscopy (Table I) and are further characterized by IR spectroscopy and elemental analysis (Table II). The P–H phosphoranimines **5a–7a** all show relatively high-field ^{31}P chemical shifts (ca. −13 to +10 ppm) and large $^1J_{PH}$ coupling constants of ca. 500 Hz as well as intense IR bands (2200–2400 cm^{-1}) indicative of the P–H stretching modes. On the other hand, the N–H phosphines **6b–8b** have ^{31}P shifts at lower fields (ca. 50–110 ppm, characteristic of P^{III} (silylamino)phosphines), do not show any P–H coupling, and exhibit N–H stretching bands (ca. 3200–3400 cm^{-1}) in the IR spectrum. Some derivative chemistry of these products (see below) is also consistent with their assigned structures.

The mixtures of products obtained from the phosphines **2** (R = *t*-Bu) and **3** (R = *i*-Pr) could not be completely separated by fractional distillation through a 10-cm column. Therefore, the yields reported here are based on ^1H and ^{31}P NMR integrations, and the elemental analyses (Table II) were obtained on the mixtures. The product mixtures could, however, be partially separated so as to provide enriched samples of the individual isomers, thus facilitating the interpretation of their ^1H and ^{13}C NMR spectra. These mixtures are colorless liquids while the phosphoranimine **5a** and the N–H phosphine **8b** are white solids (mp 81–85 and 30–31 °C, respectively) that crystallize on standing after distillation.

As part of this study, some of these products were prepared by an alternate procedure that makes use of the recently reported iodophosphoranimines[11] (eq 3). Equation 4 summa-



(3)

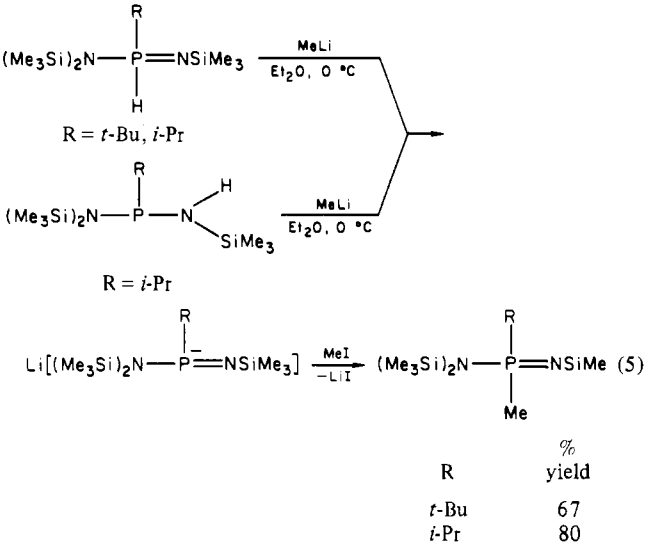


(4)

	R	% yield		R	% yield
6a	*t*-Bu	89	6b	*t*-Bu	0
7a	*i*-Pr	55	7b	*i*-Pr	48

rizes the results obtained when ether solutions of these P–I compounds are treated with $LiAlH_4$ at 0 °C. Interestingly, when this synthetic approach is used, only a single isomer **6a** is obtained in the *t*-Bu-substituted system. In the case of R = *i*-Pr, however, both isomers are again produced, although the relative percentage of the P–H form is much higher than in the Me_3SiN_3 reaction (eq 2).

For the purpose of further characterization, compound **6a** and the mixture of **7a**/**7b** were treated with MeLi, followed by addition of MeI. As expected, only the previously reported dialkylphosphoranimines[11] were obtained (eq 5). These results are consistent with the work of Cowley and Kemp[4] in which

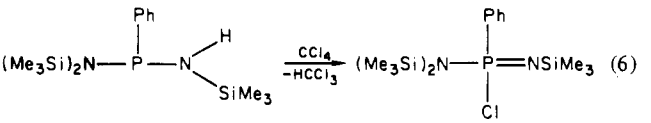


(5)

R	% yield
t-Bu	67
i-Pr	80

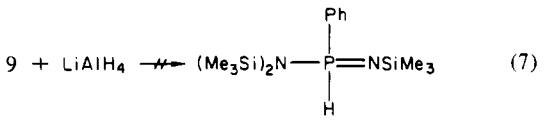
a single anionic intermediate is generated in a similar system. With compound **5a** [R = $N(SiMe_3)_2$], however, no reaction with MeLi is observed after 24 h at room temperature. This may be a result of the steric bulk of the four Me_3Si groups that serve to protect the P–H bond.

We were also interested in preparing the phenyl-substituted P–H phosphoranimine **8a** in order to determine whether it would rearrange to the N–H isomer **8b** obtained in the Me_3SiN_3 reaction (eq 2). We therefore attempted a two-step process (eq 6 and 7) starting with the N–H phosphine **8b**.



(6)

8b **9**

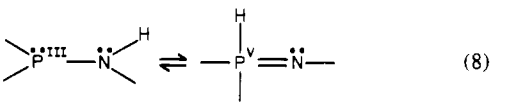


(7)

8a

When excess CCl_4 was added to a neat sample of the phosphine **8b**, a 91% yield of the desired *P*-chlorophosphoranimine **9** was obtained. Scherer and Gick[12] have reported similar results for the CCl_4 reaction of another N–H-substituted (silylamino)phosphine. Unfortunately, the chlorophosphoranimine **9** was found to be completely resistant to reduction by $LiAlH_4$ (eq 7), thereby precluding the synthesis of isomer **8a** by this method.

While it was not our intention to attempt any detailed mechanistic studies, our results do relate to the question of possible tautomerism in these P–N–H systems (eq 8) as



(8)

studied, for example, by Romanenko et al.[13] In this context, the following points of interest emerge from our results. (1) In the cases [R = $N(SiMe_3)_2$, Ph] where a single product was obtained from the Me_3SiN_3 reaction (eq 2), neither compound showed any tendency to rearrange either when heated to ca. 130 °C during distillation or when allowed to stand for several months at room temperature. (2) The product mixtures **6a**/**6b**

(11) Neilson, R. H.; Engenito, J. S. *Organometallics* **1982**, *1*, 1270.

(12) Scherer, O. J.; Gick, W. *Chem. Ber.* **1970**, *103*, 71.

(13) Romanenko, V. D.; Ruban, A. V.; Kalibabchuk, N. N.; Iksanova, S. V.; Markovski, L. N. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1981**, *51*, 1475.

Table I. NMR Spectroscopic Data[a]

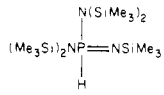
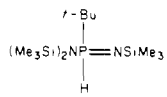
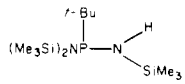
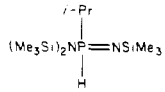
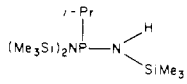
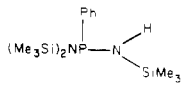
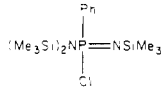
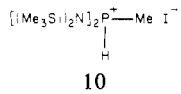
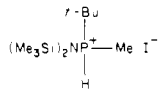
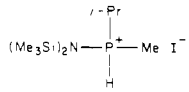
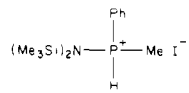
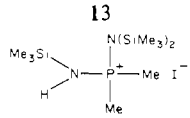
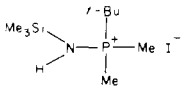
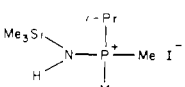
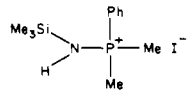
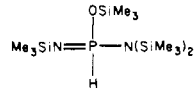
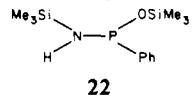
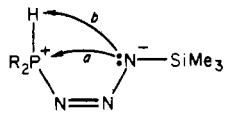
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
	Me_3Si[b]	0.28			5.02	3.1	−13.0
	PH	7.50	543				
5a							
	$(Me_3Si)_2N$	0.35			5.85		13.5
	Me_3SiN	0.45			3.56		
	Me_3C	1.20	18.0		26.54	4.0	
	Me_3C				34.28	94.0	
	PH	7.10	446				
6a							
	$(Me_3Si)_2N$	0.30			5.20		59.1
	Me_3SiN	0.29			3.56		
	Me_3C	1.20	12.0		27.13	18.3	
	Me_3C				34.11	23.2	
6b							
	$(Me_3Si)_2N$	0.50	0.8		5.18	7.9	9.9
	Me_3SiN	0.45	0.5		1.61	5.5	
	Me_2CH[c,d]	1.25			17.14		
		1.35			16.45		
	Me_2CH[c]	1.90		2.3	38.75	112.0	
	PH	6.90	444	2.3			
	$(Me_3Si)_2N$	0.45	0.5		4.21	2.4	84.0
	Me_3SiN	0.40			3 68	4.3	
	Me_2CH[c,d]	1.25			20.05	2.9	
		1.35			18.42	6.8	
7b	Me_2CH[c]	1.60			34.25	13.7	
	$(Me_3Si)_2N$	0.15	1.2		4.71	7.3	106.0
	Me_3SiN	0.20	0.8		1.71	6.1	
	Ph[c]	7.3			129		
8b							
	$(Me_3Si)_2N$	0.50			4.65	2.9	12.3
	Me_3SiN	0.10			2.50	4.9	
	Ph[c]	7.3			129		
9							
	Me_3Si	0.50	0.6		4.50	2.9	33.8
	Me	2.30	13.2	4.2	21.50	80.0	
	PH	9.25	606	4.2			
10							
	Me_3Si	0.45	0.6		3.76	2.8	43.4
	Me	2.10	13.2	5.4	9.23	53.7	
	Me_3C	1.25	19.5		25.2	2.9	
	Me_3C				32.80	52.7	
11	PH	8.30	512	5.4			
	Me_3Si	0.50	0.6		3.25	2.4	39.0
	Me	2.10	13.2	4.2	11.20	56.2	
	Me_2CH[c]	2.60			27.76	54.9	
	Me_2CH[d]	1.30	10.2	6.6	16.60	2.4	
12		1.35	7.8	6.6	16.40	4.3	
	PH	8.10	509	10.0			
				4.2			
	Me_3Si	0.35	1.2		3.00	3.1	18.7
	Me	2.50	13.5	5.1	18.82	64.1	
	Ph[c]	7.5			130		
	PH	8.50	521	5.1			
13							
	Me_3SiNH	0.52			5.65	1.9	51.0
	$(Me_3Si)_2N$	0.50	0.6		3.95	3.6	
	Me	2.15	12.9		21.99	79.9	
14							
	Me_3Si	0.29			1.70	1.2	61.5
	Me	1.75	12.6		9.42	61.0	
	Me_3C				31.47	61.1	
	Me_3C	1.15	16.5		23.88		
15							
	Me_3Si	0.20			1.62		57.5
	Me	1.90	13.5		10.79	62.5	
	Me_2CH[c]	2.55			22.37	61.5	
	Me_2CH	1.15	18.0	6.5	14.94		

Table I (*Continued*)

compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 17	Me_3Si	0.35			1.53	1.8	41.9
	Me	2.40	14.4		4.47	67.1	
	Ph[c]	7.6			130		
	Me_3SiO	0.30			1.62		−17.7
	Me_3SiN	0.32			3.83		
	$(Me_3Si)_2N$	0.41			4.03		
21	PH	7.32	596				
	Me_3SiO	0.20			1.38		13.4
	Me_3SiN	0.25			1.38		
	Ph[c]	7.5			130		
22	NH	2.60					

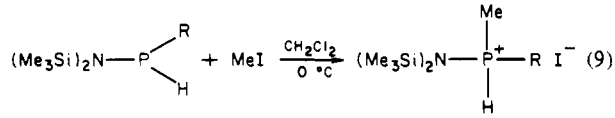
[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Equivalent Me_3Si groups due to rapid [1,3]-silyl exchange (see text and Table III). [c] Complex multiplet with unresolved coupling constants and/or overlapping signals. [d] Diastereotopic methyl groups observed in ^{1}H and ^{13}C spectra due to a chiral phosphorus.

and **7a/7b** obtained from the Me_3SiN_3 reactions of the alkylphosphines could be partially separated by fraction distillation. Moreover, the composition of the distilled samples did not revert back to that of the original mixture even after several weeks at room temperature. (3) The *tert*-butyl-substituted phosphoranimine **6a**, obtained pure via eq 5, was very thermally stable and could not be isomerized to the N–H form **6b** even when refluxed with excess Me_3SiN_3 at 95 °C for several hours. These observations do not eliminate the possibility of tautomerism (eq 8), but they do demonstrate that the *P–H and N–H isomers are not easily interconverted in the systems studied here*. This strongly suggests that the two types of products from the Me_3SiN_3 reactions are formed via independent reaction pathways (for example, **a** → P–H product and **b** → N–H product) rather than by isomerization of one form to the other.



A final noteworthy feature of the P–H phosphoranimines **5a–7a** concerns their dynamic stereochemistry. As is the case for many other (silylamino)phosphoranimines,[8,11,14] these compounds are fluxional on the NMR time scale due to intramolecular [1,3]-silyl exchange. Free energies of activation ($\Delta G_{1,3}^{\ddagger}$, Table III) indicate that the exchange barriers are within expected limits for this type of phosphoranimine. Not surprisingly, the most highly silylated compound **5a** exhibits the lowest energy barrier for this process.

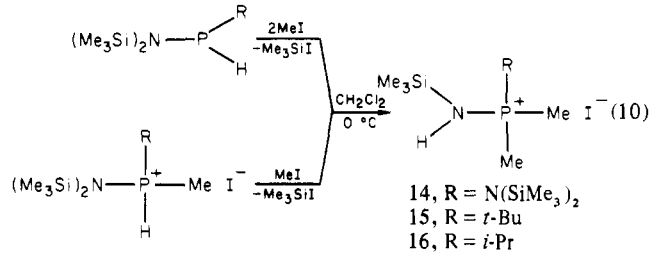
Reactions with MeI.[9] When the P–H phosphines **1–4** were allowed to react with *1 equiv* of methyl iodide, the corresponding >P(H)Me phosphonium salts **10–13** were obtained as the primary reaction products (eq 9). These reactions are



10, R = $N(SiMe_3)_2$
11, R = *t*-Bu
12, R = *i*-Pr
13, R = Ph

conveniently monitored by NMR spectroscopy (Table I) in which formation of the P–H phosphonium salt is readily indicated by the appearance of a doublet of doublets for the PMe protons, a downfield shift of ca. 10–25 ppm in the ^{31}P spectrum, and a large increase in the value of the $^1J_{PH}$ coupling constant.[7] Rather unexpectedly, however, we find that the salts **10–13** are prone to react further with MeI so that small amounts (ca. 5–10%) of secondary products (see below) are usually also observed.

If the phosphines **1–4** are treated with *2 equiv* of MeI, then the N–H-substituted *dimethyl*(silylamino)phosphonium iodides **14–17** are formed (eq 10). The same products result if the



14, R = $N(SiMe_3)_2$
15, R = *t*-Bu
16, R = *i*-Pr
17, R = Ph

reactions are done stepwise; that is, treatment of solutions of the P–H salts **10–13** with an additional equivalent of MeI causes rapid formation of the disubstituted products **14–17**.

Compounds **14–17** are characterized (Table I) by the disappearance of the P–H coupling in the ^{31}P NMR spectrum and by the increase in the intensity of the P–Me signals in the ^{1}H and ^{13}C NMR spectra. The chemical shifts (^{1}H and ^{13}C) and phosphorus coupling constants for the PMe_2 group are also in good agreement with data reported for similar phosphonium salts.[9,14] The formation of the Me_3SiI byproduct is clearly indicated by ^{1}H NMR spectroscopy.

All of the P–H and N–H phosphonium salts can be isolated as white solids by removal of solvent and other volatiles under reduced pressure. Analysis of these crude products by NMR generally shows the presence of slight impurities. Some attempts to purify these salts by recrystallization were unsuccessful, which, combined with their extreme sensitivity to atmospheric moisture, precluded satisfactory elemental analysis. The enhanced susceptibility to reaction with protic reagents of Si–N bonds in (silylamino)phosphonium salts, relative to the parent phosphines, has been noted elsewhere.[9,15]

In addition to NMR spectral data, the assigned structures of salts **10–17** are also consistent with their reactivity toward

(14) Li, B.-L.; Engenito, J. S.; Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1983**, *22*, 575.

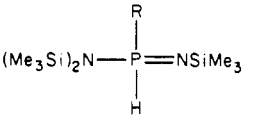
(15) Keat, R. *J. Chem. Soc. A* **1970**, 1795.

Table II. Preparative and Analytical Data

compd	preparative % yield	bp, °C (*P*, mm)	anal.[a] % C	% H
5a	71	74–77 (0.01)[b]	41.34 (40.95)	10.92 (10.54)
6a/6b[c]	86	55–59 (0.01)	46.19 (46.38)	11.02 (11.08)
7a/7b[c]	73	53–54 (0.9)	45.04 (44.67)	11.23 (10.93)
8b	52	73–76 (0.01)[d]	49.92 (50.19)	9.20 (9.27)
9	91	85–87 (0.02)	46.32 (46.26)	8.26 (8.28)
21	93	49–51 (0.02)	40.06 (39.90)	10.47 (10.11)
22[e]	85			

[a] Calculated values in parentheses. [b] Solid, mp 81–85 °C. [c] Data obtained on isomeric mixtures. [d] Solid, mp 30–31.5 °C. [e] Solid, mp 60–66 °C; decomposes on attempted distillation.

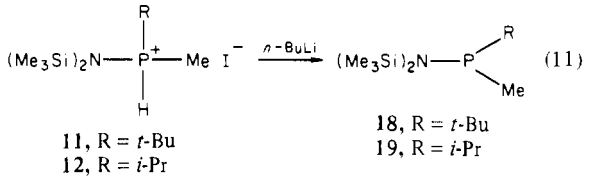
Table III. [1,3]-Silyl-Exchange Barriers[a]



compd	R	T_c, K	$\Delta G_{1,3}^{\ddagger}$ kcal/mol
5a	$(Me_3Si)_2N$	236	12.8
6a	*t*-Bu	359	18.2
7a	*i*-Pr	310	16.7
21	$OSiMe_3$	351	18.8

[a] Measured as described in ref 11.

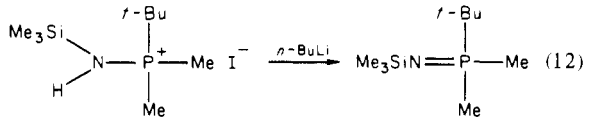
dehydrohalogenating agents. For example, treatment of the P–H compounds **11** and **12** with *n*-BuLi (eq 11) affords the



(11)

11, R = *t*-Bu
12, R = *i*-Pr

18, R = *t*-Bu
19, R = *i*-Pr

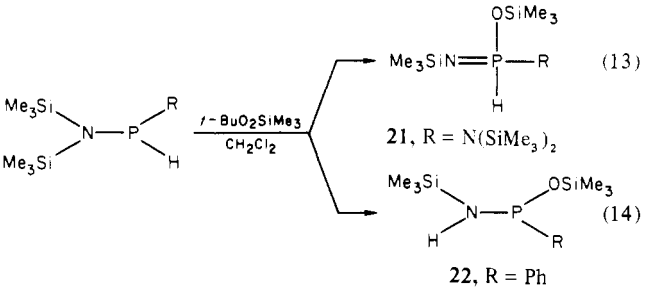


(12)

15 20

(silylamino)phosphines **18**[16] and **19**[17] in yields of ca. 80%. Similarly, dehydrohalogenation of the N–H phosphonium salt **15** with *n*-BuLi smoothly gives the *N*-silylphosphoranimine **20**[18] (eq 12). These reactions indicate that the P–H-substituted (silylamino)phosphines (e.g., **1–4**) may be useful precursors to other types of relatively inaccessible Si–N–P compounds.

Reactions with *t*-BuO_2SiMe_3.[10] We have shown earlier that (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ are conveniently oxidized by the silyl peroxide *t*-BuO_2SiMe_3 to yield *P*-siloxy-*N*-silylphosphoranimines in a process involving a [1,3]-silyl shift from nitrogen to oxygen.[10] In this study, however, somewhat less satisfactory results were obtained when similar oxidations were attempted with the P–H-substituted (silylamino)phosphines **1–4**. The reaction was straightforward only for the bis(silylamino)phosphine **1**, which underwent complete oxidation (eq 13) in 72 h to afford the P–H siloxyphosphoranimine **21** in 93% yield. Compound **21** shows the characteristically large $^1J_{PH}$ value (Table I) as noted above



(13)

21, R = $N(SiMe_3)_2$

(14)

22, R = Ph

for some of the Me_3SiN_3 reaction products. Moreover, three peaks in the intensity ratio 2:1:1 are observed in the Me_3Si region of the ^1H NMR spectrum of **21**. At higher temperatures two of the peaks coalesce to give a 3:1 intensity pattern, resulting from rapid silyl group exchange between the two nitrogen atoms ($\Delta G_{1,3}^{\ddagger}$ = 18.8 kcal/mol, Table III).

In the case of the phenylphosphine **4** (eq 14), the major oxidation product, obtained in ca. 85% yield, appears to be the rearranged N–H siloxyphosphine **22**. This structure is assigned on the basis of NMR spectroscopy (Table I), especially the lack of P–H coupling, and the strong N–H absorption observed in the IR spectrum of **22**. Attempted distillation, however, resulted in decomposition by elimination of $(Me_3Si)_2O$, which was identified by ^1H NMR. Partial purification of **22** was accomplished by crystallization from concentrated solutions in benzene, but small amounts (ca. 5%) of unidentified impurities could not be removed. A satisfactory elemental analysis was therefore not obtained.

Treatment of the alkylphosphines **2** and **3** with the silyl peroxide gave mixtures that by ^{31}P NMR appeared to contain both the P–H phosphoranimine and the N–H phosphine products. Unfortunately, no well-characterized compounds could be isolated by fractional distillation in either case.

General Conclusions. This study demonstrates that (silylamino)phosphines containing P–H bonds do, in fact, undergo the same types of oxidation and methylation reactions as their *P*-alkyl analogues. The P–H bonds, as well as the Si–N bonds, often come into play, however, leading to rearranged N–H phosphine products in some oxidations (e.g., **6b**, **7b**, **8b**, **22**) or to highly reactive phosphonium salts (e.g., **10–17**) with either P–H or N–H groups in the MeI reactions. Further study of the reactivity of these multifunctional phosphines, including their organic and organometallic derivative chemistry, is anticipated.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: Me_3SiN_3, *t*-BuO_2SiMe_3, MeI, CCl_4, and ether solutions of MeLi and $LiAlH_4$. Ether was distilled from CaH_2 prior to use; other solvents were dried over molecular sieves. The P–H phosphines[6] **1–4** and the P–I phosphoranimines[11] $(Me_3Si)_2NP(I)(R)=NSiMe_3$ (R = *t*-Bu, *i*-Pr) were prepared according to published procedures. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Routinely, the ^{31}P spectra were also recorded without ^1H decoupling so that the $^1J_{PH}$ values could be easily measured. Infrared spectra were recorded on a Beckman 4250 spectrophotometer using neat liquid samples. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

Reactions of P–H Phosphines with Me_3SiN_3. Generally, the phosphine (usually 20–50 mmol) and Me_3SiN_3 (ca. 10% molar excess) were combined in a 50-mL flask equipped with a magnetic stirrer and a reflux condenser. The mixture was then heated in an oil bath at 90–95 °C for 24 h with stirring. Nitrogen evolution was monitored

(16) Scherer, O. J.; Gick, W. *Chem. Ber.* **1971**, *104*, 1490.
(17) Neilson, R. H.; Roy, A. K., unpublished results.
(18) Buchner, W.; Wolfsberger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 967.

by means of an oil bubbler. After the mixture was cooled to room temperature, the products were isolated by the following individual procedures.

1, R = $N(SiMe_3)_2$. Distillation under reduced pressure (≤1 mm) through a short-path column gave the phosphoranimine **5a** as a colorless liquid that crystallized to a white solid (mp 81–85 °C) on standing. Redistillation through a 10-cm column afforded a pure sample of **5a** (71% yield, Table II).

2, R = *t*-Bu. The initial distillation gave a colorless liquid that was shown by NMR to be a mixture of **6a**/**6b** (Table II). Redistillation using the 10-cm column resulted in partial separation into **6a** (60% yield) and **6b** (26% yield). Proton NMR analysis indicated that each fraction was contaminated with approximately 10% of the other isomer.

4, R = *i*-Pr. Similarly, two distillations gave partial separation of the product mixture into **7a** (19% yield) and **7b** (54% yield). Each fraction contained about 10% of the other isomer as shown by ^1H NMR.

4, R = Ph. A single distillation through a 10-cm column afforded the N–H phosphine **8b** (Table II) as a colorless liquid (52% yield) that crystallized to a white solid (mp 30–31.5 °C) on standing.

Reaction of P–I Phosphoranimines with $LiAlH_4$. Typically, $LiAlH_4$ (4 mL, 1.0 M in ether) was added at 0 °C with stirring to a solution of the phosphoranimine $(Me_3Si)_2NP(I)(R)=NSiMe_3$ (16 mmol) in ether (15 mL). The reaction mixture was warmed to room temperature and stirred for 5 days. The solids were removed by filtration under N_2, and the solvent was removed under reduced pressure. Product isolation proceeded as follows.

R = *t*-Bu. A single distillation through a 10-cm column gave the pure P–H phosphinimine **6a** (80% yield).

R = *i*-Pr. An initial distillation gave a colorless liquid that was shown by NMR to be a mixture of **7a**/**7b**. Redistillation afforded partial separation into **7a** (55% yield) and **7b** (45% yield) with each fraction containing ca. 10% contamination of the other isomer.

Preparation of the Dialkylphosphoranimines, $(Me_3Si)_2NP(R)$-$Me=NSiMe_3$. R = *t*-Bu. A solution of the P–H phosphoranimine **6a** (1.5 g, 4.5 mmol) in Et_2O (10 mL) was treated, while stirring at 0 °C, with MeLi (2.3 mL of 2.0 M ether solution). The mixture was warmed to room temperature and stirred overnight (a preliminary experiment showed that the deprotonation of **6a** is a slow reaction). Methyl iodide (0.2 mL, 5 mmol) was then added, and a white solid formed immediately. After being stirred for 1 h, the mixture was filtered and solvent was removed from the filtrate under reduced pressure. Distillation afford the known P–Me phosphoranimine as a colorless liquid (1.1 g, 67% yield, bp 65–70 °C (0.1 mm)), which was identified by its NMR spectrum.[11]

R = *i*-Pr. When the same procedure was used, a mixture of the P–H phosphoranimine **7a** and the N–H phosphine **7b** was converted to the single phosphoranimine product $(Me_3Si)_2NP(i\text{-}Pr)Me=NSiMe_3$ (80% yield on 3 mmol scale reaction), which was identified by its NMR spectrum.[11]

Preparation of the *P*-Chlorophosphoranimine (9). Excess CCl_4 (ca. 3 mL) was added at 0 °C to a stirred sample of the N–H phosphine **8b** (4.2 g, 12 mmol). After the mixture was warmed to room temperature, excess CCl_4 was removed under vacuum. Distillation afforded the chlorophosphoranimine **9** (Tables I and II) as a colorless liquid (91% yield). Compound **9** was recovered unchanged in 70% yield after refluxing for 48 h in ether solution containing 1 equiv of $LiAlH_4$.

Reactions of P–H Phosphines with MeI. Typically, the phosphine (ca. 15 mmol), dissolved in CH_2Cl_2 (15 mL), was treated at 0 °C while stirring with a carefully measured *equimolar* quantity of MeI. The solution was then allowed to warm to room temperature. After the mixture was stirred for 1 h, the solvent was removed under vacuum, leaving the P–H phosphonium salts **10–13** as white solids. Generally, the products were contaminated by small amounts (ca. 5–10%) of the secondary products **14–17**. Recrystallization from cold (ca. −20 °C) CH_2Cl_2 did not significantly improve the purity of the products. NMR spectral data (Table I), however, are completely consistent with the assigned structures. By the same procedure, treatment of phosphines **1–4** with *2 equiv* of MeI resulted in the formation of the N–H phosphonium salts **14–17**, which were also isolated as white solids and identified by NMR spectroscopy (Table I). The byproduct Me_3SiI was identified in the solvent fraction by comparison of its ^1H NMR spectrum with that of an authentic sample. Alternatively, the preformed P–H salts **10–13** could be redissolved in CH_2Cl_2 and then treated with a second equivalent of MeI to yield compounds **14–17**.

Reactions of P–H Phosphonium Salts with *n*-BuLi. With use of the procedure described above, a solution of phosphonium salt **11** (6 mmol) in CH_2Cl_2 (10 mL) was prepared and cooled to −78 °C. While the solution was stirred, *n*-BuLi (2.4 mL, 6 mmol) was added slowly from a syringe. The mixture was then allowed to warm to room temperature. After ca. 30 min, the mixture was filtered and the solvent was removed under vacuum. Fractional distillation afforded the phosphine $(Me_3Si)_2NP(t\text{-}Bu)Me$ (**18**) as a colorless liquid (1.1 g, 70% yield, bp 55–58 °C (1.5mm)) that was identified by ^1H and ^{31}P NMR data.[16] Similarly, treatment of **12** with *n*-BuLi gave the analogous *i*-Pr-substituted phosphine **19** as a colorless, liquid (93% yield; bp 55–57 °C (1.0mm); ^{31}P, δ 83.5). Full details of the preparation and characterization of **19** by another method will be reported as part of another study.[17]

Reaction of N–H Phosphonium Salt with *n*-BuLi. A solution of phosphonium salt **15** (6 mmol) in CH_2Cl_2 (10 mL), prepared as described above, was treated at −78 °C with *n*-BuLi (3.75 mL, 6 mmol). After the mixture was stirred for 1 h at room temperature, filtration and solvent removal, followed by distillation, gave the phosphoranimine **20**[18] as a colorless liquid (0.63 g (51% yield); bp 48–49 °C (0.3mm); ^{31}P, δ 18.6).

Reactions of P–H Phosphines with *t*-BuO_2SiMe_3. 1, R = $N(SiMe_3)_2$. A solution of phosphine **1** (7.8 g, 22 mmol) in CH_2Cl_2 (15 mL) was treated with *t*-BuO_2SiMe_3 (4.4 mL, 22 mmol), and the mixture was stirred at room temperature for 72 h. Solvent removal and distillation gave the siloxyphosphoranimine **21** (Tables I and II).

4, R = Ph. A similar procedure afforded the N–H siloxyphosphine **22**, which decomposed on attempted distillation (see text) via elimination of $(Me_3Si)_2O$ (identified by ^1H NMR). Instead, recrystallization from benzene gave **22** as a slightly (ca. 5%) impure solid (Tables I and II).

Acknowledgment. We thank the Robert A. Welch Foundation and the U.S. Army Research Office for generous financial support of this research.