Contribution from the Paul M. Gross Chemical Laboratory,
Duke University, Durham, North Carolina 27706

Synthesis of (Silylmethyl)phosphinimines via Silyl Migration from Nitrogen to Carbon

JAMES C. WILBURN and ROBERT H. NEILSON*[1]

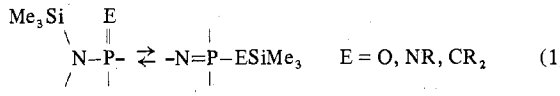
Received July 5, 1978

The *P*-methyl (silylamino)phosphines $Me_3Si(R)NPMe_2$ (**1**, R = Me_3Si; **2**, R = *t*-Bu; **3**, R = Me), $(Me_3Si)_2NP(Ph)Me$ (**4**), *t*-$BuMe_2Si(R)NPMe_2$ (**5**, R = Me_3Si; **6**, R = Me), and $Me_2SiCH_2CH_2SiMe_2NPMe_2$ (**7**) are conveniently prepared by treatment of lithium silylamides with PCl_3 or $PhPCl_2$ followed by MeMgBr. Phosphines **1**–**7** react with MeI to form the (silylamino)phosphonium iodides which, when allowed to react with *n*-BuLi, usually undergo dehydrohalogenation and N→C silyl migration to afford the (silylmethyl)phosphinimines $Me_3SiN{=}P(CH_2SiMe_3)RR'$ (**8**, R = R′ = Me; **9**, R = Me, R′ = Ph; **10**, R = R′ = Ph), $Me_2SiCH_2CH_2SiMe_2CH_2PMe_2{=}N$ (**11**), $RMe_2SiN{=}P(CH_2SiMe_2R')Me_2$ (**12a**, R = Me, R′ = *t*-Bu; **12b**, R = *t*-Bu, R′ = Me), and *t*-$BuN{=}P(CH_2SiMe_3)Me_2$ (**13**).

Introduction

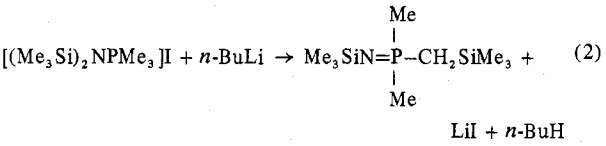
Compounds containing the silicon–nitrogen–phosphorus linkage have the interesting feature of combining the structural and stereochemical diversity of phosphorus with the reactivity of the silicon–nitrogen bond. The literature now includes examples of two-,[2] three-,[3-5] four-,[6-8] and five-coordinate[9,10] phosphorus compounds bearing silicon–nitrogen substituents. The effects of N-silylation on stereochemical processes such as P–N torsional barriers in (silylamino)phosphines[4] and axial–equatorial positional exchange in (silylamino)-phosphoranes[9,10] have been investigated.

From a synthetic viewpoint, suitably constructed *N*-silylphosphinimines offer considerable potential as phosphazene precursors via the thermally induced elimination of halo- or alkoxysilanes.[7,11] A closely related phenomenon (eq 1) is the



$$Me_3Si\text{–}N\text{–}P(E)\text{–} \rightleftarrows \text{–}N{=}P(\text{–}ESiMe_3)\text{–} \qquad E = O, NR, CR_2 \qquad (1)$$

lability of silyl substituents in four-coordinate, pentavalent phosphorus systems toward intramolecular migrations. While this type of rearrangement is fairly well documented for the (silylamino)phosphine oxides (E = O)[8,12-14] and imines (E = NR),[8,15] it has only recently been observed for the first time in ylidic systems (E = CR_2).[16] In a preliminary communication[16] we reported that, upon treatment with *n*-butyllithium, (bis(trimethylsilyl)amino)trimethylphosphonium iodide underwent dehydrohalogenation (eq 2) to afford the



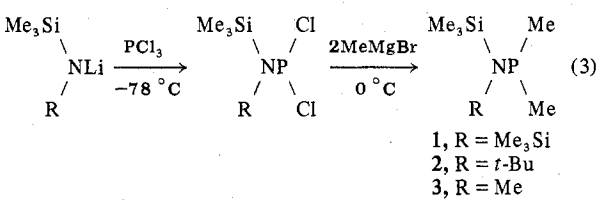
$$[(Me_3Si)_2NPMe_3]I + n\text{-BuLi} \rightarrow Me_3SiN{=}P(Me)(CH_2SiMe_3) + LiI + n\text{-BuH} \qquad (2)$$

rearranged *N*-silylphosphinimine rather than a phosphorus ylide. This paper describes the results of a more complete investigation of the scope of this novel reaction and also includes an improved synthetic route to some of the (silylamino)phosphine reagents.

Results and Discussion

(Silylamino)phosphines. Before the generality of the reaction shown in eq 2 could be assessed it was necessary to prepare a series of P-methylated (silylamino)phosphines. Only a few of these compounds such as $(Me_3Si)_2NPMe_2$ (**1**), prepared from $(Me_3Si)_2NLi$ and Me_2PCl, have been previously characterized.[8,17] This type of reaction is severely limited by the difficulty in preparing, storing and handling large quantities of Me_2PCl as well as by the sensitivity of the yield of the (silylamino)phosphines to slight changes in the reaction conditions.[8]

Alternatively, we have found a convenient, general, "one-pot" synthesis which requires only commercially available chlorophosphines. For example, addition of 1 molar equiv of PCl_3 to stirred solutions of various lithium silylamides in ether at low temperature affords the corresponding (silylamino)-dichlorophosphines[18,19] (eq 3) which are not isolated due to

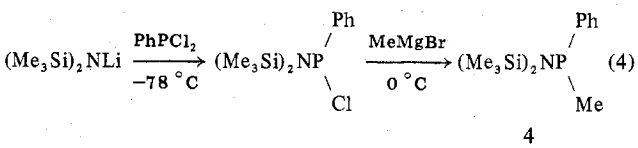


$$Me_3Si(R)NLi \xrightarrow[-78\ ^\circ C]{PCl_3} Me_3Si(Cl)NP(R)Cl \xrightarrow[0\ ^\circ C]{2MeMgBr} Me_3Si(Me)NP(R)Me \qquad (3)$$

1, R = Me_3Si
2, R = *t*-Bu
3, R = Me

their thermal instability. Subsequent addition of 2 equiv of a methyl Grignard reagent results in the formation of the (silylamino)dimethylphosphines (**1**–**3**).

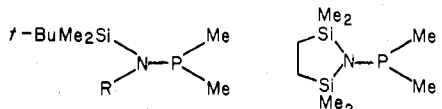
This approach appears to have broad applicability to the synthesis of (silylamino)phosphines with *P*-alkyl and/or -aryl substituents. Treatment of $(Me_3Si)_2NLi$ with $PhPCl_2$ followed by 1 equiv of MeMgBr (eq 4) yields the unsymmetrically



$$(Me_3Si)_2NLi \xrightarrow[-78\ ^\circ C]{PhPCl_2} (Me_3Si)_2NP(Ph)Cl \xrightarrow[0\ ^\circ C]{MeMgBr} (Me_3Si)_2NP(Ph)Me \qquad (4)$$

4

substituted methylphenylphosphine **4**. Moreover, the scope of this reaction is not limited to trimethylsilyl-substituted amines, and, in fact, we have used the method to prepare the *tert*-butyldimethylsilylated aminophosphines (**5** and **6**) as well as the novel cyclic compound **7**.



5, R = Me_3Si
6, R = Me

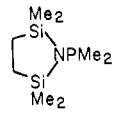
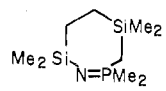
7

The (silylamino)phosphines (**1**–**7**) are all colorless, air-sensitive[20] liquids which were routinely isolated in good yields (Table I) by fractional distillation. In addition to elemental analysis and infrared spectroscopy (Table I), the phosphines were characterized by their ^1H and ^{13}C NMR spectra (Table II) which, in all cases, were consistent with the proposed structures. The values of the J_{PCH} (ca. 4–8 Hz) and J_{PC} (ca. 18–26 Hz) coupling constants are especially indicative of the P–C–H linkage in trivalent dimethylphosphorus compounds.[21]

The silyl substituents appear to play a key role in the success of this synthetic method since the reaction of (alkylamino)-halophosphines with Grignard or other organometallic reagents is generally not an effective synthetic route to the corre-

0020-1669/79/1318-0347$01.00/0

Table I. Physical, Analytical, and IR Spectroscopic Data[a] for (Silylamino)phosphines (2–7) and (Silylmethyl)phosphinimines (9–13)

compd	bp, °C (torr)	yield, %	anal.,[b] % C	anal.,[b] % H	IR spectrum,[c] cm^{-1}
$Me_3Si(t\text{-}Bu)NPMe_2$ **2**	56–59 (2.0)	64	52.94 (52.64)	11.99 (11.78)	2960 s, 2905 m, 1470 w, 1420 w, 1390 w, 1360 m, 1250 s, 1220 w, 1190 s, 1040 m, 1000 m, 960 s, 870 vs, 760 w, 685 m, 640 w
$Me_3Si(Me)NPMe_2$ **3**	42.5–43 (13)	46	44.21 (44.14)	11.08 (11.11)	2950 s, 2900 m, 2810 w, 1420 m, 1250 s, 1180 w, 1080 s, 930 w, 905 s, 855 s, 750 m, 685 m, 635 w
$(Me_3Si)_2NP(Ph)Me$ **4**	90–94 (0.05)	65	55.37 (55.08)	9.50 (9.24)	2940 s, 2880 s, 1425 m, 1240 vs, 925 vs, 880 vs, 830 vs, 750 m, 730 m, 685 s, 670 s
$t\text{-}BuMe_2Si(Me_3Si)NPMe_2$ **5**	67–71 (0.5)	76	50.41 (50.14)	11.68 (11.48)	2950 vs, 2860 m, 1460 w, 1400 w, 1360 w, 1250 s, 940 s, 855 vs, 760 m, 690 w, 675 m
$t\text{-}BuMe_2Si(Me)NPMe_2$ **6**	36–40 (0.8)	75	52.76 (52.64)	12.01 (11.78)	2930 s, 2890 s, 2860 s, 1420 w, 1255 s, 1180 w, 1070 m, 930 m, 900 s, 830 vs, 770 m, 680 m, 665 m
 **7**	27–28 (0.1)	68	43.63 (43.79)	10.41 (10.11)	2935 s, 2880 s, 2790 w, 1410 m, 1280 m, 1265 m, 1245 s, 1210 w, 1065 m, 1020 m, 940 vs, 830 vs, 805 s, 775 s, 690 m, 665 m, 620 m
$Me_3SiN{=}P(Ph)Me$ (CH_2SiMe_3) **9**	109–114 (0.2)	80	56.27 (56.52)	9.47 (9.49)	2950 m, 2900 m, 1410 m, 1300 s, 1280 s, 1240 s, 1090 m, 830 vs, 770 m, 690 m, 670 w, 640 w
$Me_3SiN{=}PPh_2$ (CH_2SiMe_3) **10**	107 (0.01)		63.17 (63.46)	8.29 (8.41)	
 **11**	67–70 (0.05) mp 52–53	63	46.33 (46.31)	10.65 (10.36)	2950 s, 2890 s, 2810 w, 1415 m, 1305 s, 1285 s, 1255 vs, 1125 w, 1105 m, 1090 m, 1060 m, 1045 m, 1000 w, 915 s, 835 vs, 770 s, 735 s, 680 m, 660 w, 630 w, 610 m
$RMe_2SiN{=}PMe_2$ (CH_2SiMe_2R'[d]) **12a**, R = Me, R′ = *t*-Bu · **b**, R = *t*-Bu, R′ = Me	55–59 (0.02)	56	52.28 (51.93)	11.82 (11.62)	2950 m, 2850 w, 1460 w, 1300 m, 1280 m, 1250 s, 1100 w, 930 m, 910 m, 855 s, 820 s, 760 m, 730 s
$t\text{-}BuN{=}PMe_2$ (CH_2SiMe_3) **13**	51–51.5 (1.0)	42	54.73 (54.75)	12.10 (11.95)	2910 s, 1420 w, 1355 m, 1310 s, 1270 vs, 1165 w, 1060 s, 960 m, 930 s, 840 s, 760 m, 700 s

[a] For compounds **1** and **8** see ref 8 and 16. [b] Calculated values in parentheses. [c] Neat liquids. [d] Data given for mixture of **12a** and **12b**.

Table II. Proton and $^{13}C\{^1H\}$NMR Data[a] for (Silylamino)phosphines (1–7) and Their Methylphosphonium Iodide Salts

compd	signal obsd	phosphine ^1H δ (J_{PH})	phosphine ^{13}C δ (J_{PC})	phosphonium iodide ^1H δ (J_{PH})	phosphonium iodide ^{13}C δ (J_{PC})
$(Me_3Si)_2NPMe_2$[b] (**1**)	Me_3Si	0.24 (1.0)	4.51 (7.9)	0.48	5.21 (1.8)
	MeP	1.34 (6.6)	19.27 (22.0)	2.31 (13.0)	18.96 (64.1)
2	Me_3Si	0.24	6.95 (7.3)	0.60	6.13
	Me_3C	1.31	33.14 (11.0)	1.63	32.10 (4.3)
	Me_3C		58.40 (13.4)		59.90 (2.4)
	MeP	1.32 (8.5)	19.25 (20.8)	2.43 (13.0)	19.05 (63.5)
3	Me_3Si	−0.02 (0.8)	0.35 (9.2)	0.36	1.26
	MeN	2.37 (5.5)	26.31 (8.6)	2.80 (14.0)	32.89
	MeP	0.97 (5.0)	14.80 (17.7)	2.23 (13.0)	14.54 (64.7)
4	Me_3Si	0.16	4.35 (7.3)	0.29	4.21 (2.3)
	MeP	1.65 (6.2)	17.08 (26.3)	2.44 (12.8)	18.14 (64.1)
5	Me_3Si	0.16	6.45 (1.2)	0.38	6.09 (2.4)
	Me_2Si	0.15 (1.5)	0.26 (18.9)	0.35	2.86 (3.1)
	Me_3C	0.86	28.08 (5.5)	0.86	27.61
	Me_3C		20.02		19.57
	MeP	1.29 (7.0)	19.41 (23.2)	2.25 (13.0)	19.57 (63.5)
6	Me_2Si	0.04 (2.0)	−4.06 (13.4)	0.25	−3.85
	Me_3C	0.82	26.93 (2.4)	0.87	25.18
	Me_3C		20.02		17.95
	MeN	2.44 (6.0)	27.54 (8.5)	2.80 (14.4)	33.06
	MeP	1.03 (5.0)	14.62 (18.3)	2.18 (13.4)	13.36 (64.7)
7	Me_2Si	0.27	2.05 (5.5)	0.38	1.38 (0.2)
	CH_2Si	0.80	8.78 (1.8)	0.84	7.41 (6.4)
	MeP	1.31 (4.2)	20.67 (18.3)	2.13 (13.5)	16.63 (64.1)

[a] Chemical shifts in ppm downfield from external Me_4Si; coupling constants in Hz. Solvents (concentration): ^1H, CH_2Cl_2 (20%); ^{13}C, $CDCl_3$ (50%). [b] Data taken from ref 8.

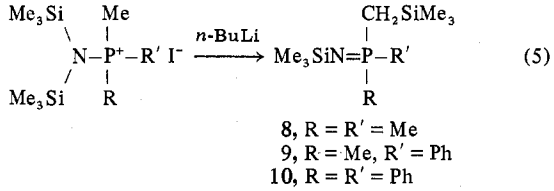
sponding (alkylamino)organophosphines. For instance, Me_2NPMe_2 is prepared only with difficulty and in low yield from Me_2NPCl_2 presumably because of a competitive reaction involving N–P bond cleavage.[22] It seems likely that this side reaction would be inhibited by sterically bulky groups (e.g., Me_3Si), and it is noted that the lowest yield obtained in this study was for compound **3** which contains the least sterically hindered amino group.

While our work was in progress, Scherer[23] reported that $Me_3SiN(Me)PCl_2$ (as prepared in eq 3) reacts with various lithium amides to afford bis(amino)phosphines. This further suggests that the chloro(silylamino)phosphines have considerable potential as synthetic reagents in spite of their relative instability.

(Silylamino)phosphonium Salts. Compounds **1–7** reacted smoothly and exothermically with iodomethane to form the corresponding (silylamino)phosphonium iodides. Generally the reaction was carried out in CH_2Cl_2 or $CHCl_3$ in which the phosphonium salts are readily soluble. Although the compounds were usually manipulated in solution because of their extreme sensitivity to atmospheric moisture, solvent removal left the pure salts as white crystalline solids.

Formation of the phosphonium salts was conveniently monitored by ^1H and ^{13}C NMR spectroscopy (Table II). After the addition of 1 equiv of MeI to a solution of the phosphine, the NMR spectra consisted solely of signals assignable to the phosphonium species. Large downfield shifts (ca. 0.8–1.2 ppm) and substantial increases in the P–C–H couplings were observed for the PMe protons. The most obvious difference in the ^{13}C NMR spectra after salt formation had occurred was the greatly increased magnitude of the P–C coupling (ca. 64 Hz). Spectroscopic changes of this nature are clearly consistent with the formation of the four-coordinate, positively charged phosphorus center.[21] The ^{13}C NMR data in Table II also reveal an interesting sterically related trend in the SiMe and PMe chemical shifts for both the phosphines and the phosphonium salts. These signals for compounds **1**, **2**, **4**, and **5** are shifted downfield by 4–6 ppm relative to those of the less sterically hindered N–Me compounds **3** and **6**.

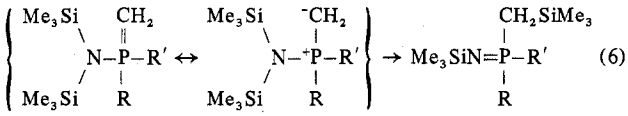
(Silylmethyl)phosphinimines. Treatment of organophosphonium salts with bases such as *n*-butyllithium is a very useful preparative route to phosphorus ylides (e.g., $R_3P{=}CH_2$).[24] When P-methylated (bis(trimethylsilyl)amino)phosphonium iodides are allowed to react (eq 5) with an



(5)

8, R = R′ = Me
9, R = Me, R′ = Ph
10, R = R′ = Ph

equimolar amount of *n*-BuLi, however, the isolated products are the rearranged *N*-(trimethylsilyl)-*P*-((trimethylsilyl)-methyl)phosphinimines (**8–10**). Although not experimentally verified, it is speculated that the reaction proceeds through an ylide intermediate (eq 6) which readily undergoes a



(6)

[1,3]-silyl shift from nitrogen to carbon as suggested in our preliminary communication.[16] The occurrence of this type of rearrangement is consistent with the behavior of (bis(trimethylsilyl)amino)phosphine oxides and imines (eq 1) as well as with the nucleophilic character of phosphorus ylides.[24]

The (silylmethyl)phosphinimines **8–10** are colorless, moisture-sensitive liquids which were fully characterized (Tables I and III). The observation of two Me_3Si resonances in both the ^1H and ^{13}C NMR spectra is entirely consistent with the rearranged imine structure. It is conceivable that the ylide isomer could also give two Me_3Si signals if N–P bond rotation was slow on the NMR time scale; however, this possibility has been discounted for similar compounds.[8,14] Moreover, chemical shifts (^1H and ^{13}C) of the CH_2 group are in good agreement with data reported for other (trimethylsilyl)methyl-substituted phosphorus compounds.[25] The upfield ^1H (ca. −0.8 ppm) and ^{13}C (ca. −7.0 ppm) chemical shifts[26] which are typical of an ylidic CH_2 group were not observed.

While the phosphinimines **8** and **9** were obtained in good yield and purity after a single distillation, synthesis of the diphenyl analogue **10** was somewhat less straightforward. An analytically pure sample of **10** was obtained, although several redistillations were required to remove an unidentified impurity. Nevertheless, the successful preparation of compounds **8–10** illustrates the broad scope of the rearrangement reaction (eq 5) with regard to changes in substitution at phosphorus.

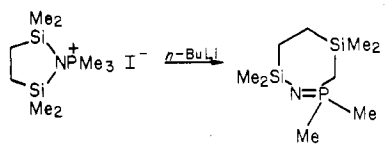
It was also of interest to investigate the influence which silyl groups other than Me_3Si might have on the course of this reaction. An amine which is electronically similar to, but less sterically hindered than, bis(trimethylsilyl)amine is $Me_2SiCH_2CH_2SiMe_2NH$ which, although it is easily prepared,[27] does not appear to have any previously reported derivative chemistry. As in the case of $(Me_3Si)_2NH$, we have found that this cyclic analogue is readily converted to its dimethylphosphino and trimethylphosphonium derivatives.

Table III. Proton and $^{13}C\{^1H\}$NMR Data[a] for (Silylmethyl)phosphinimines (8–13)

compd	signal obsd	^1H NMR δ	^1H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}
$Me_3SiN{=}PMe_2$ (8)	CH_2SiMe_3[b]				
	Me_3SiC	−0.21		0.47	2.9
	Me_3SiN	0.02		4.17	4.2
	CH_2P	0.91	17.0	23.44	69.9
	Me_2P	1.25	13.0	22.18	64.7
9	Me_3SiC	0.02		0.33	2.9
	Me_3SiN	0.05		4.30	3.5
	CH_2P	1.33	15.5	22.89	69.0
	MeP	1.64	13.0	21.71	61.7
10	Me_3SiC	0.17[c]		0.63	2.9
	Me_3SiN	0.17		4.33	2.9
	CH_2P	1.87	15.0	20.38	69.3
11	Me_2Si	0.00		−1.72	4.27
		0.20		1.22	6.10
	CH_2Si	0.80		9.26	
				12.43	
	CH_2P	1.31	16.0	23.70	47.00
	Me_2P	1.41	12.6	21.40	73.24
12a,b[d]	Me_2Si	0.07		−4.59	
		−0.16		−0.87	2.8
		−0.24		0.45	2.9
				4.14	4.1
	CH_2Si	0.93	15.5	17.38	28.6
				17.7	26.1
	Me_3C	0.74		26.07	
		0.79		26.72	
	Me_3C			20.94	7.6
				25.81	
	Me_2P	1.27	12.0	22.26	64.9
		1.30	12.5	22.52	64.3
13	Me_3Si	0.09		0.65	2.5
	CH_2Si	1.98	12.0	22.76	76.3
	Me_3C	1.09		35.48	11.6
	Me_3C			51.54	6.1
	Me_2P	1.33	12.0	22.01	53.7

[a] Chemical shifts in ppm downfield from external Me_4Si; coupling constants in Hz. Solvents (concentration): ^1H, CH_2Cl_2 (20%); ^{13}C, $CDCl_3$ (50%). [b] Data taken from ref 16. [c] In benzene solution nonequivalence of the Me_3SiC (δ 0.37) and Me_3SiN (δ 0.63) is observed. [d] Data given for mixture of **12a** and **12b**.

Somewhat surprisingly, the latter compound reacted (eq 7)



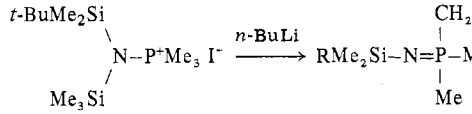
(7)

11

smoothly with *n*-BuLi to yield the seven-membered cyclic phosphinimine **11** as a low-melting, white solid in 63% yield. The unsymmetrical ring-expanded structure of **11** is confirmed by its ^{13}C NMR spectrum (Figure 1) which shows nonequivalence of the C- and N-bonded Me_2SiCH_2 groupings as well as the expected PMe_2 and PCH_2 doublets. The ^1H NMR spectrum also reveals two Me_2Si environments and consequently a complex multiplet for the $SiCH_2CH_2Si$ ring protons.

It is significant that the iodomethane derivative of the cyclic (disilylamino)phosphine **7** undergoes dehydrohalogenation and structural rearrangement (eq 7) in the same manner as that of its acylic counterpart **1** (eq 5). The isolation of the cyclic phosphinimine **11** in high yield is taken as strong evidence that the silyl shift from nitrogen to carbon is an intramolecular process. If such were not the case, then the logically expected product would have been the acyclic oligomer $(-N{=}PMe_2CH_2SiMe_2CH_2CH_2SiMe_2-)_n$. The intramolecularity of the rearrangement is certainly consistent with, but is not required by, the earlier postulation of a phosphorus ylide intermediate (eq 6).

As part of this study we have also explored the possibility of N→C silyl migrations in one system where two different silyl substituents are present. Upon treatment with MeI and *n*-BuLi, the unsymmetrical (disilylamino)phosphine **5** affords approximately equal amounts of the *N*-trimethylsilyl- and *N*-(*tert*-butyldimethylsilyl)-substituted phosphinimines (eq 8).

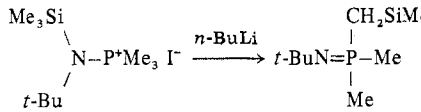


(8)

12a, R = Me, R′ = *t*-Bu
b, R = *t*-Bu, R′ = Me

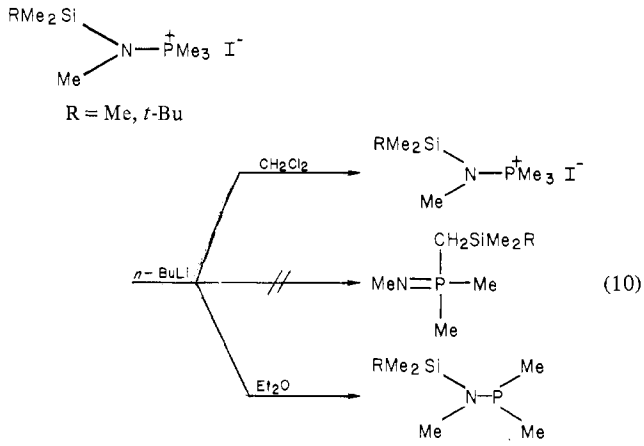
Compounds **12a** and **12b** apparently have virtually identical boiling points and were not separated, but NMR spectroscopy (Table III) clearly demonstrates the presence of both isomers. Although precise peak assignments are not possible due to the scarcity of similar compounds for comparison, the ^{13}C NMR spectrum (Figure 2) consists of two $(H_3C)_3C$ singlets, two $(H_3C)_3C$ signals, two $P(CH_3)_2$ doublets, two PCH_2 doublets, and four signals in the H_3CSi region. Proton NMR spectra obtained on the crude reaction products also show that both isomers are present indicating that a thermally induced redistribution process during distillation is not responsible for the final mixture. The fact that **12a** and **12b** are formed in such nearly equal proportions may have mechanistic implications, but further experiments with mixed silyl substituents are required before any definitive conclusions can be drawn.

In view of the generality of the silyl shift from nitrogen to carbon in the disilylated phosphorus ylides derived from compounds **1**, **4**, **5**, and **7** it seemed likely that a similar rearrangement would occur in monosilyl-substituted compounds as well. Indeed, (*tert*-butyl(trimethylsilyl)amino)trimethylphosphonium iodide does dehydrohalogenate to give the N-alkylated phosphinimine **13** (eq 9), but reactions (eq 10)



(9)

13

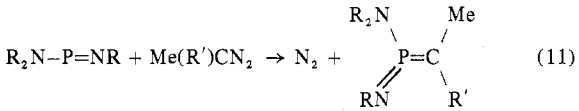


R = Me, *t*-Bu

(10)

with the MeI salts of the N–Me compounds **3** and **6** did not yield similar rearranged products. In these cases the nature of the solvent medium strongly affected the course of the reactions. In CH_2Cl_2, which had been used successfully for the other reactions (eq 5, 7–9), treatment of the phosphonium salt with *n*-BuLi gave an unidentified white precipitate and a gas (presumably butane). Filtration and solvent removal left only the (silylamino)phosphonium salt possibly formed via proton abstraction from the solvent by the intermediate ylide. On the other hand, when Et_2O was used as the solvent, the reaction (eq 10) gave the (silylamino)phosphine in high yield. This indicates that in Et_2O the enhanced nucleophilicity of the butyl anion leads to attack at the carbon adjacent to the phosphonium center to give pentane and the phosphine rather than dehydrohalogenation to give the ylide. The difference in the products obtained from these reactions (eq 9 and 10) clearly demonstrates that sterically bulky substituents (e.g., *t*-Bu or Me_3Si) at nitrogen favor the N→C silyl shift. Again this observation seems to be most consistent with an intramolecular pathway for the rearrangement.

The results described herein are also of interest in relation to a recent paper by Niecke and Wildbredt[28] in which the synthesis (eq 11) of some novel three-coordinate silyl-



(11)

R = Me_3Si
R′ = Me, Et, *i*-Pr, *t*-Bu

amino-substituted phosphorus ylides is reported. Proton, ^{31}P, and ^{13}C NMR spectra confirm the structure, and it seems likely that steric crowding at the ylide carbon is responsible for the apparent failure of these compounds to rearrange via the type of silyl shift which we have observed.

Experimental Section

Materials. Iodomethane, bis(trimethylsilyl)amine, *n*-butyllithium, methylmagnesium bromide, and the chlorophosphines (PCl_3, $PhPCl_2$) were obtained from commercial sources. The alkyl(trimethylsilyl)amines[29] $Me_3SiN(H)R$ (R = Me, *t*-Bu) were prepared by addition of Me_3SiCl to an excess of the amine in an inert solvent. The cyclic disilazane[27] $Me_2SiCH_2CH_2SiMe_2NH$, the (*tert*-butyldimethylsilyl)amines[30] *t*-$BuMe_2SiN(H)R$ (R = Me, Me_3Si), and (bis(trimethylsilyl)amino)diphenylphosphine[31] were prepared according to published procedures.

General Procedures. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. Ethyl ether was distilled from calcium hydride prior to use. Other solvents were dried over molecular sieves. Proton NMR spectra were recorded on JEOL MH-100 and Varian T-60 spectrometers and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL FX-60 spectrometer. Infrared spectra were

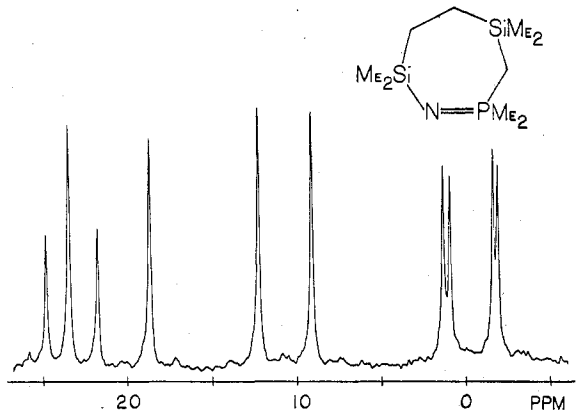


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of compound **11**.

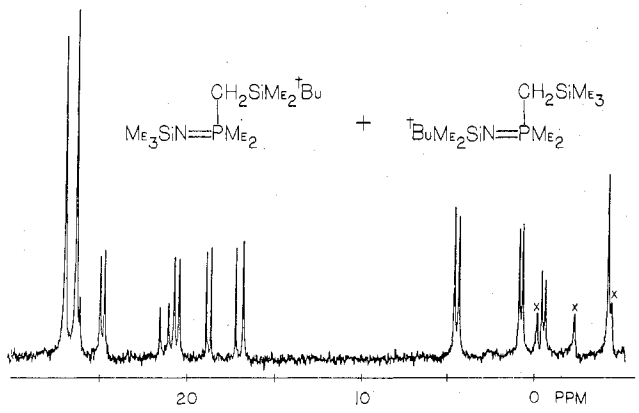


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of a mixture of compounds **12a** and **12b**. Peaks marked × are alias signals from $CDCl_3$.

recorded on a Perkin-Elmer 297 spectrophotometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

The following procedures are typical of those used for the synthesis of the (silylamino)phosphines, their phosphonium iodide salts, and their (silylmethyl)phosphinimine derivatives. Physical, analytical, and spectroscopic data for all of the new compounds are summarized in Tables I–III.

Preparation of (Bis(trimethylsilyl)amino)methylphenylphosphine (4). Dichlorophenylphosphine (7.34 mL, 50 mmol) was added from a syringe to a stirred solution of lithium bis(trimethylsilyl)amide (prepared from 50 mmol of $(Me_3Si)_2NH$ and 23.4 mL of a 2.22 M hexane solution of *n*-BuLi) in ether (150 mL) at −78 °C. The mixture was then allowed to warm to 0 °C and was stirred for ca. 1 h. Methylmagnesium bromide (52 mmol, 18.6 mL of a 2.8 M ether solution) was added from a dropping funnel to this *vigorously stirred* suspension of $(Me_3Si)_2NP(Cl)Ph$. After warming to room temperature and being stirred for ca. 1 h, the mixture was filtered (*Caution*: The residual solids react exothermically with water and must be disposed of carefully.) and the solvents were removed under reduced pressure. Distillation afforded compound **4** as a colorless liquid (9.16 g, 65% yield, bp 90–94 °C (0.05 torr)).

Preparation of *P*-Methyl-*P*-phenyl-*P*-((trimethylsilyl)methyl)-*N*-(trimethylsilyl)phosphinimine (9). Iodomethane (1.21 mL, 19.5 mmol) was added to a stirred solution of the phosphine **4** (5.45 g, 19.2 mmol) in CH_2Cl_2 (25 mL) at 0 °C. After the solution was warmed to room temperature and was stirred for 15 min, NMR spectroscopy (Table II) showed complete formation of the phosphonium iodide salt. The solution was cooled to 0 °C,[32] and *n*-butyllithium (20 mmol, 9.01 mL of a 2.22 M hexane solution) was added slowly from a dropping funnel over a period of ca. 15 min. (*Caution*: The reaction is very exothermic and potentially hazardous. Slow addition of *n*-BuLi is imperative.) The solid byproduct (presumably LiI) was not easily removed by filtration, so the solvents were removed under reduced pressure. From the gummy white residue, compound **9** was distilled as a colorless liquid (4.57 g, 80% yield, bp 109–114 °C (0.20 torr)). Alternatively, the product could be separated from the solid by extraction with pentane and isolated by fractional distillation.

Acknowledgment. The authors thank the United States Army Research Office, the Duke University Research Council, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

Registry No. **1**, 63744-11-6; **1**(Me)I, 63744-08-1; **1**$(Me)^+\cdot I^-$, 63744-09-2; **2**, 68437-82-1; **2**(Me)I, 68437-83-2; **2**$(Me)^+\cdot I^-$, 68474-68-0; **3**, 68437-84-3; **3**(Me)I, 68437-85-4; **3**$(Me)^+\cdot I^-$, 68437-86-5; **4**, 68437-87-6; **4**(Me)I, 68437-88-7; **4**$(Me)^+\cdot I^-$, 68437-89-8; **5**, 68437-90-1; **5**(Me)I, 68437-91-2; **5**$(Me)^+\cdot I^-$, 68437-92-3; **6**, 68437-93-4; **6**(Me)I, 68437-94-5; **6**$(Me)^+\cdot I^-$, 68437-95-6; **7**, 68437-96-7; **7**(Me)I, 68437-97-8; **7**$(Me)^+\cdot I^-$, 68437-98-9; **8**, 13916-37-5; **9**, 68437-99-0; **10**, 68438-00-6; **11**, 68438-01-7; **12a**, 68438-02-8; **12b**, 68438-03-9; **13**, 68438-04-0; PCl_3, 7719-12-2; $PhPCl_2$, 644-97-3; $(Me_3Si)_2NH$, 999-97-3; $Me_3SiN(H)Me$, 16513-17-0; $Me_3SiN(H)$-*t*-Bu, 5577-67-3; *t*-$BuMe_2SiN(H)Me$, 61012-64-4; *t*-$BuMe_2SiN(H)SiMe_3$, 66417-55-8; $Me_2SiCH_2CH_2SiMe_2NH$, 7418-19-1; $(Me_3Si)_2NPPh_2$, 13685-61-5; MeMgBr, 74-83-9; MeI, 74-88-4.

References and Notes

(1) To whom correspondence should be addressed at the Department of Chemistry, Texas Christian University, Fort Worth, TX 76129.
(2) (a) E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.*, **12**, 585 (1973); (b) O. J. Scherer and N. Kuhn, *ibid.*, **13**, 811 (1974).
(3) R. Keat, *J. Chem. Soc. A*, 1795 (1970).
(4) R. H. Neilson, R. C.-Y. Lee, and A. H. Cowley, *Inorg. Chem.*, **16**, 1455 (1977).
(5) E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.*, **13**, 134 (1974).
(6) H. Schmidbaur, *Adv. Organomet. Chem.*, **9**, 259 (1970).
(7) P. Wisian-Neilson, R. H. Neilson, and A. H. Cowley, *Inorg. Chem.*, **16**, 1460 (1977).
(8) J. C. Wilburn and R. H. Neilson, *Inorg. Chem.*, **16**, 2519 (1977).
(9) J. A. Gibson and G.-V. Röschenthaler, *J. Chem. Soc., Dalton Trans.*, 1440 (1976).
(10) A. H. Cowley and R. C.-Y. Lee, *J. Chem. Soc., Chem. Commun.*, 111 (1977).
(11) E.-P. Flindt and H. Rose, *Z. Anorg. Allg. Chem.*, **428**, 204 (1977).
(12) P. K. G. Hodgson, R. Katz, and G. Zon, *J. Organomet. Chem.*, **117**, C63 (1976).
(13) O. J. Scherer and W. Gick, *Chem. Ber.*, **104**, 1490 (1971).
(14) R. H. Neilson, R. D. Jacobs, R. W. Scheirman, and J. C. Wilburn, *Inorg. Chem.*, **17**, 1880 (1978).
(15) O. J. Scherer, *Angew. Chem., Int. Ed. Engl.*, **8**, 861 (1969).
(16) J. C. Wilburn and R. H. Neilson, *J. Chem. Soc., Chem. Commun.*, 308 (1977).
(17) W. Zeiss, C. Feldt, J. Weis, and G. Dunkel, *Chem. Ber.*, **111**, 1180 (1978).
(18) R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat, and L. Stobbs, *J. Chem. Soc., Dalton Trans.*, 1414 (1973).
(19) O. J. Scherer and N. Kuhn, *J. Organomet. Chem.*, **82**, C3 (1974).
(20) The oxidation reactions of some of the (silylamino)phosphines will be reported separately.
(21) G. Mavel, *Annu. Rep. NMR Spectrosc.*, **5B**, 1 (1973).
(22) E. A. Dietz and D. R. Martin, *Inorg. Chem.*, **12**, 241 (1973).
(23) O. J. Scherer and W. Glässel, *Chem. Ber.*, **110**, 3874 (1977).
(24) H. J. Bestman and R. Zimmermann, *Org. Phosphorus Compd.*, **3**, 1 (1972).
(25) H. Schmidbaur and W. Malisch, *Chem. Ber.*, **102**, 83 (1969).
(26) H. Schmidbaur, W. Buchner, and D. Scheutzow, *Chem. Ber.*, **106**, 1251 (1973).
(27) R. H. Baney and G. G. Haberland, *J. Organomet. Chem.*, **5**, 320 (1966).
(28) E. Niecke and D. A. Wildbredt, *Angew. Chem., Int. Ed. Engl.*, **17**, 199 (1978).
(29) R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).
(30) J. R. Bowser, R. H. Neilson, and R. L. Wells, *Inorg. Chem.*, **17**, 1882 (1978).
(31) H. Nöth and L. Meinel, *Z. Anorg. Allg. Chem.*, **349**, 225 (1967).
(32) In the synthesis of **12**, however, the *n*-BuLi addition was done at −78 °C.