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SYNTHESIS OF SILICON—NITROGEN—PHOSPHORUS HALIDES STABILIZED BY THE t-BUTYLDIMETHYLSILYL GROUP

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Summary

The reactions of phosphorus halides with lithium t-butyldimethylsilyl(methyl)-amide were used to prepare the new Si—N—P derivatives t-$BuMe_2SiN(Me)X$ (I, X = PF_4; II, X = PF_2; III, X = PCl_2). The dichlorophosphine (III) is readily oxidized by Me_2SO to the phosphoryl compound t-$BuMe_2SiN(Me)P(O)Cl_2$ (IV) whereas the difluorophosphine (II) does not react with Me_2SO. Treatment of t-$BuMe_2$-$SiN(SiMe_3)Li$ with PCl_5 gave the trichlorophosphinimine t-$BuMe_2SiN{=}PCl_3$ (V). Steric crowding at silicon enhances the thermal stability of these compounds relative to their Me_3Si analogues.

Introduction

The reaction of alkali metal derivatives of silylamines with phosphorus halides is a general preparative route to the stereochemically interesting [1—5] and synthetically useful [6—7] class of compounds with the Si—N—P linkage. When highly halogenated phosphorus centers are present, however, the ease of halosilane elimination often prevents the isolation of the desired products leading instead to the production of novel cyclic [8] or acylic [6,9,10] phosphorus—nitrogen compounds.

Recently it has been shown that similar Si—N bond cleavage reactions in silicon—nitrogen—boron systems can be suppressed by the use of sterically hindered silyl substituents [11]. We report here the synthesis and characterization of a series of stabilized silicon—nitrogen—phosphorus—halogen compounds which contain the t-butyldimethylsilyl group.

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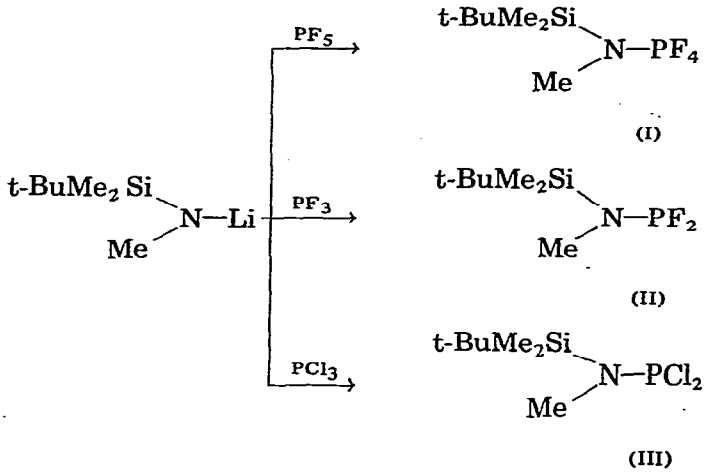
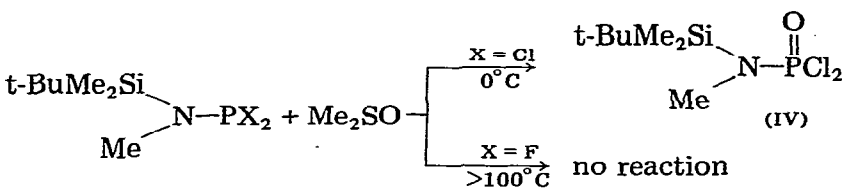
Results

Treatment of ether solutions of lithium t-butyldimethylsilyl(methyl)amide [11] (eq. 1) with PF_5, PF_3, or PCl_3 afforded good yields of the corresponding tetrafluorophosphorane (I) and dihalophosphines (II, III).



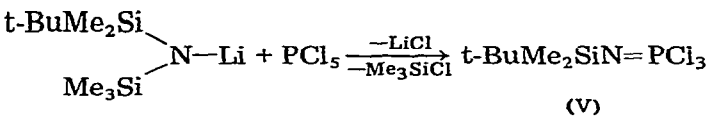
(1)

The dichlorophosphine (III) was readily oxidized by dimethyl sulfoxide (eq. 2) to its oxide derivative (IV) but the difluoro analogue (II) did not react even under more severe conditions.



(2)

The reaction (eq. 3) of PCl_5 with lithium t-butyldimethylsilyl(trimethylsilyl)-amide [11] gave moderate yields of *N*-(t-butyldimethylsilyl)trichlorophosphinimine (V).



(3)

(V)

Compounds I—V are colorless, moisture-sensitive liquids which were characterized by elemental analysis, infrared spectroscopy, and NMR (^1H and ^{13}C) spectroscopy. Some of these data are presented in Table 1.

Discussion

Of the systems reported here, the stabilizing influence of the t-$BuMe_2Si$ group is best illustrated by the successful isolation of compound I which appears to be the first example of a stable, acyclic phosphorane containing a silylamino sub-

TABLE 1

ANALYTICAL AND NMR SPECTROSCOPIC DATA FOR *N*-*t*-BUTYLDIMETHYLSILYL SUBSTITUTED PHOSPHORUS HALIDES

Compound R = t-BuMe$_2$Si	Analysis (Found (calcd.) (%))		NMR spectra [a]				
			Signal	$\delta(^1H)$	J(P—H)	$\delta(^{13}C)$	J(P—C)
	C	H					
R \N—PF_4 / Me (I)	33.52 (33.46)	7.17 (7.22)	Me_2Si $\underline{Me_3C}$ $Me_3\underline{C}$ MeN	0.32 0.98 2.77	 16.8 [b]	—1.9 26.8 18.5 35.1	
R \N—PF_2 / Me (II)	39.77 (39.42)	8.71 (8.51)	Me_2Si $\underline{Me_3C}$ $Me_3\underline{C}$ MeN	0.25 0.92 2.63	4.5 7.0 [d]	—4.5 26.5 19.21 [e]	15.4 [c] 2.0
R \N—PCl_2 / Me (III)	33.97 (34.15)	7.24 (7.36)	Me_2Si $\underline{Me_3C}$ $Me_3\underline{C}$ MeN	0.21 0.87 2.87	4.2 6.6	—4.4 26.4 19.5 31.9	17.7
R O \ ‖ N—PCl_2 / Me (IV)	31.72 (32.07)	6.71 (6.92)	Me_2Si $\underline{Me_3C}$ $Me_3\underline{C}$ MeN	0.26 0.89 2.76	 21.0	—3.3 24.5 20.0 34.4	
R—N=PCl_3 [f]	27.26 (27.03)	5.97 (5.67)	Me_2Si $\underline{Me_3C}$ $Me_3\underline{C}$	0.10 0.92 	 	—2.7 26.2 18.4	4.9 6.8

[a] Chemical shifts in ppm downfield from external Me_4Si; coupling constants in Hz. Solvent (solute concentration): ^1H, CH_2Cl_2 (20%); ^{13}C, $CDCl_3$ (50%). [b] J(F—H) 2.0 Hz. [c] J(F—C) 1.6 Hz. [d] J(F—H) 2.5 Hz, [e] Low intensity, not observed. [f] Cl, found: 39.03; calcd. 39.89.

stituent. The pentacoordinate structure of I, with rapid intramolecular exchange rendering the axial and equatorial fluorines equivalent on the NMR time scale, was confirmed by the doublet of quintets (J(PNCH) 16.8 Hz, J(FPNCH) 2.0 Hz) observed in the *N*-methyl region of the ^1H NMR spectrum. Moreover, the proton-coupled ^{31}P spectrum consisted of a quintet of quartets (J(PF) 855 Hz, J(PNCH) ~ 16 Hz) with the value of J(PF) being typical [5,12] for a fluxional aminotetrafluorophosphorane.

The silylaminophosphorane (I) could be distilled at moderate temperatures (~50°C) with no evidence of thermal decomposition. When a neat sample was heated in a sealed tube at 100°C, however, decomposition proceeded smoothly according to eq. 4 producing the expected fluorosilane [13] and diazadiphosphetidine [14].

$$\text{t-BuMe}_2\text{Si}\diagdown\!\!\diagup\text{N—PF}_4\ (\text{Me}) \xrightarrow{100^\circ\text{C}} \text{t-BuMe}_2\text{SiF} + \tfrac{1}{2}\,(\text{MeNPF}_3)_2 \qquad (4)$$

There have been few previous attempts to synthesize phosphoranes containing silylamino substituents. Gibson and Röschenthaler [15] have obtained a stable compound, $(Me_3Si)_2NPF_2OC(CF_3)_2C(CF_3)_2O$, by incorporating phosphorus into the perfluoropinacol ring system. Our efforts to prepare related acyclic [bis(trimethylsilyl)amino]fluorophosphoranes were unsuccessful due to their

facile elimination of Me_3SiF and formation of *N*-trimethylsilyl-*P*-fluorophosphinimines [6]. More recently, Cowley and Lee [5] have isolated [trimethylsilyl(methyl)amino]tetrafluorophosphorane in low yield from the oxidative fluorination of $Me_3SiN(Me)PF_2$. This trimethylsilyl analogue of I, however, decomposes rapidly above 0°C and its characterization was based mainly on low temperature ^{19}F NMR data.

Clearly, a significant property of the phosphorane I is its markedly increased stability toward fluorosilane elimination relative to similar *N*-trimethylsilyl compounds. It is presumed that the bulky t-butyl group hinders fluorine attack at silicon, thus preventing cleavage of the Si—N bond.

The chloro compounds III—V also appear to be more stable than their *N*-trimethylsilyl counterparts. Both the dichlorophosphine III and its oxide IV could be distilled without decomposition but heating above 100°C brought about t-$BuMe_2SiCl$ elimination and formation of as yet unidentified solids. By contrast, $Me_3SiN(Me)PCl_2$ evolves Me_3SiCl at room temperature [16] although it is still a useful synthetic intermediate when prepared in solution [17].

Further evidence for the diminished reactivity of the t-$BuMe_2Si$ group toward Si—N bond cleavage is found in the reaction of PCl_5 with the unsymmetrical disilylamide (eq. 3). Initially the reaction must involve cleavage of the Me_3Si—N bond since Me_3SiCl but not t-$BuMe_2SiCl$ was identified in the solvent fraction. Nevertheless, the t-butyldimethylsilylphosphinimine (V) appears to be only marginally more stable than $Me_3SiN{=}PCl_3$ [18]. The distillation of V was sometimes accompanied by decomposition and samples kept at room temperature slowly evolved t-$BuMe_2SiCl$. The thermal decomposition of *N*-silylphosphinimines is presently under investigation in our laboratory as a synthetic route to phosphazenes.

Experimental

Materials and general procedures

Dimethylsulfoxide, n-BuLi, and the phosphorus halides PX_n (n = 3, 5; X = F, Cl) were obtained from commercial sources. The silylamines t-$BuMe_2SiN(H)R$ (R = Me, Me_3Si) were prepared according to published procedures [11].

Standard inert-atmosphere techniques were employed for all reactions and other manipulations. Ethyl ether was distilled from calcium hydride prior to use. Other solvents were dried over molecular sieves.

Proton, ^{31}P, and $^{13}C\{^1H\}$ NMR spectra were obtained on JEOL MH-100, Bruker HX-90, and JEOL FX-60 spectrometers, respectively, with the latter two operating in the Fourier transform mode. Infrared spectra of the samples as neat liquids were recorded on a Perkin—Elmer 297 spectrophotometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of [(t-butyldimethylsilyl)methylamino]tetrafluorophosphorane (I)

In a 250 ml flask equipped with a magnetic stirrer, a reflux condenser, and an atmosphere of dry nitrogen, n-BuLi (18.4 ml of 2.4 *M* hexane solution, 0.044 mol) was added with stirring to a solution of t-$BuMe_2SiN(Me)H$ (5.91 g, 0.040 mol) in ethyl ether (100 ml) which was cooled to 0°C. The solution was allowed

to warm to room temperature and stirring was continued for an additional 30 min. The reaction flask was then attached to a standard glass vacuum system, cooled to —78° C, and evacuated. Phosphorus pentafluoride (0.045 mol) was allowed to condense slowly into the stirred solution at —78° C. The mixture was then allowed to warm to room temperature during which time the formation of a white solid was observed. After stirring for 30 min, the bulk of the solvent was removed under vacuum and the remaining volatile material was distilled through a U-trap cooled to —30° C which retained I as a colorless liquid (4.96 g, 49% yield). The product was pure as determined by its NMR spectra but could be distilled (b.p. 50° C/6 Torr) without decomposition to afford analytically pure material. The ^{31}P NMR spectrum consisted of a quintet (J(PF) 855 Hz) of quartets (J(PNCH) ~ 16 Hz) centered at +62.8 ppm (upfield from external H_3PO_4). Infrared spectrum: 2960s, 2935s, 2910m, 2870s, 1478s, 1470s, 1445w, 1412w, 1399w, 1370m, 1342m, 1265s, 1205s, 1115s, 1082m, 1060w, 1010w, 940vs, 895s, 850vs, 825s, 810s, 790s, 695m, 684w, 600w cm^{-1}.

Thermal decomposition of phosphorane I

A neat sample (0.664 g) of compound I, sealed under vacuum in a small ampoule, was heated in an oven at 100° C for 18 h. The ampoule was opened on the vacuum line and the contents were distilled through traps held at —45, —78, and —196° C. The —45 and —196° C traps were empty and a small amount of nonvolatile white solid remaining in the ampoule was discarded. The —78° C trap retained a colorless liquid (0.565 g, 85% yield) which was confirmed by IR spectroscopy to be a mixture of the known compounds, t-BuMe$_2$SiF [13] and $(F_3PNMe)_2$ [14], whose similar vapor pressures prohibited their separation. The ^{1}H NMR spectrum of the mixture consisted of a Me$_2$Si doublet (δ 0.25 ppm, J(FH) 7.0 Hz) and a t-Bu singlet (δ 1.03 ppm), characteristic of the fluorosilane; in addition to an NMe triplet (δ 2.68 ppm, J(PH) 13.2 Hz), characteristic of the diazadiphosphetidine. The intensity ratio of the t-Bu and NMe signals was 3/1, indicating that the stoichiometry of the decomposition reaction was that given by eq. 4.

Preparation of [(t-butyldimethylsilyl)methylamino]difluorophosphine (II)

A solution of t-BuMe$_2$SiN(Me)Li (0.040 mol) was prepared as described above in a 1-liter bulb equipped with a Teflon stopcock. The solution was degassed by the freeze-thaw method and PF_3 (0.045 mol) was condensed into the bulb at —196° C. The mixture was allowed to warm first to —78° C and then to room temperature with occasional shaking. As described for compound I, the product was retained in a U-trap at —30° C as a colorless liquid (6.95 g, 82% yield, b.p. 43—44° C/6 Torr). Infrared spectrum: 2940s, 2900s, 2800s, 2750s, 1470s, 1415w, 1395m, 1365m, 1260s, 1195s, 1080vs, 1010w, 900vs, 820vs, 800vs, 790s, 750vs, 690s, 630s cm^{-1}.

Preparation of [(t-butyldimethylsilyl)methylamino]dichlorophosphine (III)

Phosphorus trichloride (0.075 mol) was added via syringe to a stirred solution of t-BuMe$_2$SiN(Me)Li (0.075 mol) in Et$_2$O (200 ml) at —78° C. The mixture was allowed to warm slowly to room temperature and was stirred for 30 min. After filtration and solvent removal under reduced pressure, distillation afforded III

as a colorless liquid (15.8 g, 80% yield, b.p. 47—50°C/0.02 Torr). Infrared spectrum: 2960s, 2940s, 2900m, 2870s, 1470m, 1425w, 1410w, 1395w, 1365w, 1260s, 1170m, 1080s, 1010w, 875vs, 840s, 820s, 810s, 790s, 740w, 685m, 615w cm^{-1}.

Preparation of [(t-butyldimethylsilyl)methylamino]dichlorophosphine oxide (IV)

In a 100 ml flask equipped with a reflux condenser, Me_2SO (0.063 mol) was added at 0°C to a stirred solution of compound III (0.0613 mol) in CH_2Cl_2 (50 ml). Shortly after all of the Me_2SO was added an exothermic reaction occurred and the solvent refluxed. After stirring for 1 h solvent and Me_2S were removed under vacuum and distillation gave IV as a colorless liquid (8.63 g, 54% yield, b.p. 62°C/0.02 Torr). Infrared spectrum: 2955s, 2930s, 2900m, 2880m, 2860s, 1465m, 1365w, 1290vs, 1265s, 1195m, 1075s, 910vs, 870m, 845s, 825s, 690m, 600m cm^{-1}.

In a similar manner the reaction of Me_2SO with the difluorophosphine (II) was attempted. No reaction took place at room temperature so the solvent was removed and the neat mixture of Me_2SO and II was heated at the reflux point for 1 h. Proton NMR spectroscopic analysis still showed only unreacted starting materials.

Preparation of N-(t-butyldimethylsilyl)trichlorophosphinimine (V)

Under a purge of dry nitrogen, PCl_5 (0.70 mol) was added quickly to a stirred solution of t-$BuMe_2SiN(SiMe_3)Li$ (0.070 mol) in Et_2O (200 ml) at 0°C. Upon warming to room temperature an exothermic reaction occurred. After stirring 30 min the mixture was filtered and solvents were removed under reduced pressure. NMR analysis of the solvent showed that it contained Me_3SiCl. From the viscous yellow residue compound V was distilled as a colorless liquid (6.75 g, 36% yield, b.p. 57°C/0.5 Torr). At this stage the product was sometimes contaminated with small amounts of t-$BuMe_2SiCl$. Redistillation (b.p. 30°C/0.01 Torr) gave the purified product which slowly evolved t-$BuMe_2SiCl$ on standing for several days at room temperature.

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References

1 O.J. Scherer, Angew. Chem. Int. Ed. Engl., 8 (1969) 861.
2 R.H. Neilson, R.C.-Y. Lee, and A.H. Cowley, Inorg. Chem., 16 (1977) 1455.
3 J.C. Wilburn and R.H. Neilson, J. Chem. Soc. Chem. Commun., (1977) 308.
4 J.C. Wilburn and R.H. Neilson, Inorg. Chem., 16 (1977) 2519.
5 A.H. Cowley and R.C.-Y. Lee, J. Chem. Soc. Chem. Commun., (1977) 111.
6 P. Wisian-Neilson, R.H. Neilson and A.H. Cowley, Inorg. Chem., 16 (1977) 1460.
7 Von E.-P. Flindt and H. Rose, Z. Anorg. Allg. Chem., 428 (1977) 204.
8 O.J. Scherer and P. Klusmann, Angew. Chem. Int. Ed. Engl., 8 (1969) 752.
9 E. Niecke and W. Flick, Angew. Chem. Int. Ed. Engl., 12 (1973) 585.

10 O.J. Scherer and N. Kuhn, Angew. Chem. Int. Ed. Engl., 13 (1974) 811.
11 J.R. Bowser, R.H. Neilson and R.L. Wells, Inorg. Chem., 17 (1978) 1882.
12 V. Mark, C.H. Dungan, M.M. Crutchfield and J.R. Van Wazer, Topics in Phosphorus Chem., 5 (1967) 227.
13 M. Kumada, M. Ishikawa, S. Maeda, and K. Ikura, J. Organometal. Chem., 2 (1964) 146.
14 R. Schmutzler, J. Chem. Soc. Dalton Trans., (1973) 2687.
15 J.A. Gibson and G.-V. Röschenthaler, J. Chem. Soc. Dalton Trans., (1976) 1440.
16 R. Jefferson, J.F. Nixon, T.M. Painter, R. Keat and L. Stobbs, J. Chem. Soc. Dalton Trans., (1973) 1414.
17 O.J. Scherer and W. Glässel, Chem. Ber., 110 (1977) 3874.
18 E. Niecke and W. Bitter, Inorg. Nucl. Chem. Lett., 9 (1973) 127.