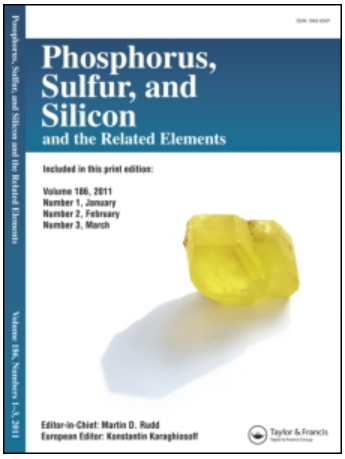

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REACTIONS OF A PHOSPHORANIMINE ANION WITH SOME ORGANIC ELECTROPHILES

Aroop K. Roy[ab]; Urszula G. Wettermark[a]; Gary M. Scheide[a]; Patty Wisian-neilson[ac]; Robert H. Neilson[a]
[a] Department of Chemistry, Texas Christian University, Fort Worth, Texas [b] Michigan Molecular Institute, Midland, Michigan [c] Department of Chemistry, Southern Methodist University, Dallas, Texas

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REACTIONS OF A PHOSPHORANIMINE ANION WITH SOME ORGANIC ELECTROPHILES[1]

AROOP K. ROY,[2a] URSZULA G. WETTERMARK, GARY M. SCHEIDE, PATTY WISIAN-NEILSON,[2b] and ROBERT H. NEILSON*
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

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The reactions of a variety of electrophiles with the *N*-silyl-P-trifluoroethoxyphosphoranimine anion $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2^-$ (**1a**), prepared by the deprotonation of the dimethyl precursor $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (**1**) with *n*-BuLi in Et_2O at −78°C, were studied. Thus, treatment of **1a** with alkyl halides, ethyl chloroformate, or bromine afforded the new *N*-silylphosphoranimine derivatives $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2R$ [**2**: $R = Me$, **3**: $R = CH_2Ph$, **4**: $R = CH{=}CH_2$, **5**: $R = C(O)OEt$, and **6**: $R = Br$]. In another series, when **1a** was allowed to react with various carbonyl compounds, 1,2-addition of the anion to the carbonyl group was observed. Quenching with Me_3SiCl gave the O-silylated products $Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2{-}C(OSiMe_3)R^1R^2$ [**7**: $R^1 = R^2 = Me$; **8**: $R^1 = Me$, $R^2 = Ph$; **9**: $R^1 = Me$, $R^2 = CH{=}CH_2$; and **10**: $R^1 = H$, $R^2 = Ph$]. Compounds **2–10** were obtained as distillable, thermally stable liquids and were characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and elemental analysis.

INTRODUCTION

The condensation-polymerization of *N*-silyl-P-trifluoroethoxyphosphoranimines such as $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (**1**) is an important preparative route to poly(alkyl/arylphosphazenes).[3] Recently, the scope and utility of this method has been extended by our finding that these polymer precursors (e.g., **1**) can be deprotonated by *n*-BuLi to yield the corresponding anions (e.g., **1a**) as reactive intermediates (Equation 1). Subsequent treatment of the anion with P–Cl or Si–Cl reagents affords phosphoranimines bearing pendant phosphinyl [$-PPh_2$, $-P(NMe_2)_2$][1a,4] or silyl [$-SiMe_2R$; $R = Me$, Ph, H, $CH{=}CH_2$, $(CH_2)_3CN$][1b,5]

$$\underset{\textbf{1}}{Me_3SiN{=}P(Me)(OCH_2CF_3)} \xrightarrow[-78°C,Et_2O]{n\text{-BuLi}} \underset{\textbf{1a}}{Me_3SiN{=}P(Me)(OCH_2CF_3)CH_2^-Li^+} \qquad (1)$$

substituents. Some analogous deprotonation/substitution reactions have been carried out on the phosphazene polymer $[Ph(Me)PN]_n$ to yield a series of silylated polymers.[6] Work in other laboratories[7,8] has shown that the permethylated phosphoranimine $Me_3SiN{=}PMe_3$ as well as the cyclic methylphosphazenes, e.g., $[Me_2PN]_n$, can be derivatized in a similar manner.

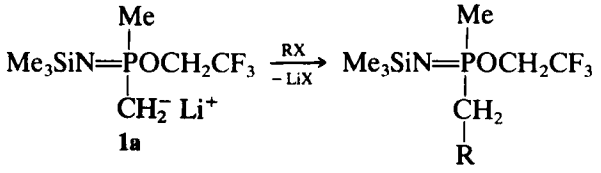
In this paper, we report some further derivative chemistry of the phosphoranimine anion **1a**. Specifically, the reactions of **1a** with various organic halides, bromine, and carbonyl compounds are described. In addition to providing several new, functionalized phosphoranimine "monomers", these

reactions serve as models for similar derivative chemistry of the preformed poly(alkyl/arylphosphazenes).

RESULTS AND DISCUSSION

Our recent studies[4,5] show that, although the phosphoranimine anion **1a** is easily prepared in Et_2O solution at −78°C, it is unstable at temperatures above ca. −50°C. Thus, while highly electrophilic reagents such as Me_3SiCl and Ph_2PCl react smoothly with **1a** to give good yields of substitution products, simple alkyl halides initially gave less satisfactory results. In the latter cases, the reaction rates are slow enough that thermal decomposition of the anion **1a**, as indicated by the partial regeneration of **1**, becomes a competing reaction. We find that this problem is alleviated to some extent by the addition of one equivalent of tetramethylethylenediamine (TMEDA) to the anion solution prior to addition of the alkyl halide. Presumably, TMEDA enhances the reactivity of **1a** so that nucleophilic substitution on RX becomes the kinetically favored process.

In this manner, the alkyl derivatives **2**, **3**, and **4** were produced in moderate yields when the anion was treated with MeI, $PhCH_2Br$, and $CH_2{=}CHCH_2Br$, respectively (Equation 2). These new derivatives were separated from small amounts of the starting material **1** by careful fractional distillation and were fully characterized by elemental analysis and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy (Tables I and II). The thermal decomposition reactions of **2**–**4** and their co-thermolyses with **1** lead to some new poly(alkyl/arylphosphazenes).[1b]



(2)

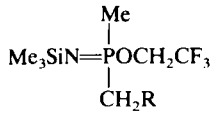
1a

2: R = Me, X = I
3: R = CH_2Ph, X = Br
4: R = $CH{=}CH_2$, X = Br
5: R = C(O)OEt, X = Cl
6: R = X = Br

The reactions of **1a** with a variety of other organic halides [e.g., $BrCH_2C{\equiv}CH$, $BrCH_2CH_2CH{=}CH_2$, $BrCH_2C(O)OEt$, and PhC(O)Cl] were also attempted. None of the desired substitution products were obtained; typically, only a low yield (ca. 10–30%) of **1** was isolated upon distillation of the volatile reaction products. The reason for the failure of these reactions is not readily apparent, although, in some cases, the presence of acidic protons in the organic reactant probably accounts for the formation of compound **1**. Treatment of **1a** with ethyl chloroformate, however, did result in the formation of the carboethoxy derivative **5** (Equation 2), isolated in 36% yield. Likewise, the direct bromination of the anion afforded the P-(bromomethyl)phosphoranimine **6** (Equation 2) in a comparable yield. A similar bromination has been successfully applied to the polymeric anion derived from $[Ph(Me)P{=}N]_n$.[9]

TABLE I

NMR spectroscopic data[a] for new *N*-silylphosphoranimines,



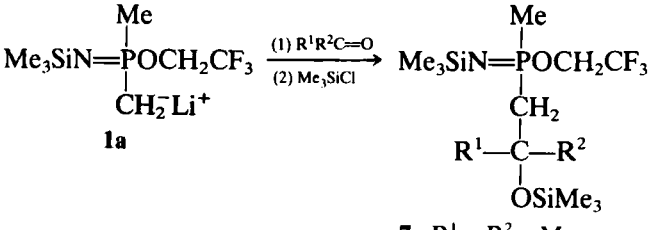
No.	R	Signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
2	Me	Me_3Si	0.15		3.70	5.0	37.17
		PMe	1.39	13.0	16.01	87.4	
		PCH_2	1.67	14.8 (7.4)[b]	25.71	95.5	
		$CH_2\underline{C}H_3$	1.09	19.5 (7.4)[b]	6.78	3.8	
		OCH_2[c]	4.18	9.2 (9.2)[d]	59.56	4.8 (37.7)[d]	
		CF_3[c]			124.20	7.3 (277.6)[d]	
3	CH_2Ph	Me_3Si	0.13		3.72	2.8	33.76
		PMe	1.35	14.0	17.11	87.7	
		PCH_2	2.0–2.1[e]		34.56	93.7	
		$\underline{C}H_2Ph$	2.85–2.95[e]		28.97	3.2	
		Ph	7.2–7.4[e]	C_1	141.17	15.2	
				C_{2-6}	126–129		
4	$CH_2CH{=}CH_2$	Me_3Si	−0.02		3.56	2.9	35.38
		PMe	1.40	13.0	16.88	87.8	
		PCH_2	1.74	13.5	31.88	94.7	
		$\underline{C}H_2CH$	2.2–2.3[e]		26.86	3.4	
		$\underline{C}H{=}CH_2$	5.7–5.9[e]		137.46	16.2	
		$CH{=}\underline{C}H_2$	4.9–5.1[e]		115.33		
5	C(O)OEt	Me_3Si	−0.09		3.15	6.8	22.72
		PMe	1.48	15.0	17.77	96.7	
		PCH_2	2.76	18.0	41.00	82.0	
		$O\underline{C}H_2CH_3$	4.07	(7.2)[b]	61.34		
		$OCH_2\underline{C}H_3$	1.15	(7.2)[b]	13.90		
6	Br	Me_3Si	−0.05		3.29	3.7	23.96
		PMe	1.53	15.0	15.13	100.7	
		PCH_2	3.15	7.8	24.75	94.6	
7	$\underline{C}Me_2$	Me_3SiO	0.03		2.39		33.52
	|	Me_3SiN	0.12		3.31	4.1	
	$OSiMe_3$	PMe	1.48	13.8	19.28	83.6	
		PCH_2	1.8–2.0[e]		47.53	99.8	
		$C\underline{Me}_2$	1.31		32.40	11.0	
			1.43		30.30	4.1	
		$\underline{C}Me_2$			72.90	4.0	
8[f]	C(Ph)Me	Me_3SiO	0.03		2.35		31.49
	|	Me_3SiN	0.14		3.68	4.1	
	$OSiMe_3$	PMe	1.50	14.2	19.68	84.6	
		PCH_2	2.0–2.4[e]		50.12	97.7	
		$C\underline{Me}$	1.97		28.09	4.0	
		$\underline{C}Me$			75.99	3.1	
		Ph	7.2–7.5[e]	C_1	148.23	9.1	
				C_{2-6}	127–128		
9[g]	Me	Me_3SiO	0.03		2.64		31.24[g]
	|	Me_3SiN	0.11		3.65	3.0	31.09
	$\underline{C}{-}CH{=}CH_2$				3.61	3.0	
	|	PMe	1.50	14.2	19.73	84.6	
	$OSiMe_3$		1.52	14.6	19.63	84.6	
		PCH_2	1.8–1.9[e]		46.90	97.7	
					47.89	97.7	

TABLE I (*Continued*)

			^{1}H NMR		^{13}C NMR		^{31}P NMR
No.	R	Signal	δ	J_{PH}	δ	J_{PC}	δ
		C<u>Me</u>	1.46	2.0	27.05	4.0	
			1.57		28.78	9.1	
		<u>C</u>Me			74.63	4.0	
					74.55	4.0	
		<u>CH</u>=CH$_2$	5.97	(17.1)[b] (10.8)[b]	146.08	10.1	
			6.11	(17.1)[b] (10.8)[b]	144.95	5.1	
		CH=<u>CH$_2$</u>	4.9–5.2[e]		112.20	9.0	
10[g]	C(Ph)H	Me_3SiO	0.02		0.25		32.93[g]
	|		0.03		0.40		30.53
	OSiMe$_3$	Me_3SiN	0.08		3.73	4.1	
			0.12		3.87	4.1	
		PMe	1.26	13.8	18.45	87.6	
			1.55	13.8	18.95	87.6	
		PCH_2	1.9–2.1[e]		43.53	95.7	
			2.2–2.4[e]		44.43	92.6	
		CH	5.0–5.2[e]		71.34		
					71.66	3.0	
		Ph	7.2–7.4[e]	C_1	144.76	13.1	
				C_{2-6}	126–128		

[a] Chemical shifts relative to Me_4Si for ^{1}H and ^{13}C spectra and to H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: $CDCl_3$ and/or CH_2Cl_2.
[b] J_{HH} values in parentheses.
[c] The ^{1}H and ^{13}C NMR spectral data for the OCH_2CF_3 group showed very little variation throughout the series **2–10**. The complete data is given for **2** as a representative example.
[d] J_{FH} and J_{FC} values in parentheses.
[e] Complex multiplet.
[f] Data given only for major diastereomer (see text).
[g] Data given for mixture of diastereomers.

In related experiments, solutions of the anion **1a** were treated with some representative carbonyl compounds. These reactions occurred smoothly at −78°C (TMEDA was not required) via 1,2-addition of **1a** to the C=O bond. Subsequent addition of Me_3SiCl (protic quenching agents were avoided due to the sensitivity of the Si—N=P linkage) afforded the silyl ether derivatives **7–10** in ca. 40–70% yields (Equation 3). The lower yields observed for the reactions involving acetone (**7**) and acetophenone (**8**) can be attributed, in part, to protonation of the anion



(3)

7: $R^1 = R^2 = Me$
8: $R^1 = Me$, $R^2 = Ph$
9: $R^1 = Me$, $R^2 = CH{=}CH_2$
10: $R^1 = H$, $R^2 = Ph$

TABLE II

Preparative and analytical data

Compound	Yield %	bp °C/mm Hg	Analysis[a] %C	%H
2	61	80/15.0	36.74 (36.74)	7.34 (7.27)
3	38	70/2.5	50.50 (50.25)	6.99 (6.87)
4	40	56–58/2.7	41.98 (41.80)	7.54 (7.37)
5	36	46–49/0.1	37.92 (37.61)	6.76 (6.63)
6	33	62/3.0	26.09 (25.78)	5.18 (4.95)
7	40	60/0.02	41.85 (41.36)	8.41 (8.28)
8	39	110/0.02	49.94 (49.18)	7.67 (7.57)
9	68	70/0.1	43.38 (43.17)	8.06 (8.02)
10	61	92/0.1	47.85 (47.98)	7.29 (7.34)

[a] Calculated values in parentheses.

by the relatively acidic —C(O)CH_3 protons. In these cases, significant amounts of **1** were seen in the ^{31}P NMR spectra of the crude reaction mixtures. Furthermore, GC—MS analysis of the undistilled product mixture from the acetophenone reaction showed the presence of an elimination byproduct, most likely $Me_3SiN{=}P(OCH_2CF_3)(Me){-}C(Ph)(OSiMe_3){=}CH_2$. Such side reactions occurred to a much smaller extent when methyl vinyl ketone (**9**) or benzaldehyde (**10**) were used and, consequently, higher product yields were obtained.

Some noteworthy observations can be made from the NMR spectra of these silyl ethers. First, as is the case for all of the compounds reported here, phosphoranimines **7–10** contain asymmetric centers at phosphorus. This feature is clearly reflected, for example, by the nonequivalence of the —CMe_2— methyl groups of **7** in both the ^1H and ^{13}C NMR spectra. Second, compounds **8–10** also contain chiral centers at carbon in the —$C(OSiMe_3)R^1R^2$ substituents, giving rise to the formation of diastereomers. Thus, two ^{31}P NMR signals are observed for each of these compounds and many of the ^1H and ^{13}C NMR resonances are also found in pairs, corresponding to a mixture of diastereomers. Based on NMR integrations, the isomer ratios are ca. 5:1, 1:1, and 2:1 for **8**, **9**, and **10**, respectively. Third, the ^1H and ^{13}C NMR spectra of **9** confirms that the anion **1a** reacts with methyl vinyl ketone in a 1, 2 rather than a 1, 4 fashion. Signals for a terminal $CH{=}CH_2$ group, integrating as three vinyl protons, are readily apparent. By contrast, the product of 1,4-addition, $Me_3SiN{=}P(OCH_2CF_3)(Me)$-$CH_2CH_2$—$CH{=}C(OSiMe_3)Me$, would exhibit signals for only one vinyl proton as well as other major differences in both the ^1H and the ^{13}C NMR spectra. For instance, the ^{13}C NMR spectra of compounds **7–10** all contain similar chemical

shifts and coupling constants (J_{PC}) for the methylene and the quaternary carbons of the P—CH_2—$C(OSiMe_3)R^1R^2$ moiety.

EXPERIMENTAL

Materials and general procedures. The following reagents were obtained from commercial sources and used without further purification: bromine, *n*-BuLi (hexane solution), and Me_3SiCl. The organic reagents [MeI, $PHCH_2Br$, $CH_2{=}CHCH_2Br$, EtOC(O)Cl, acetone, PhC(O)Me, MeC(O)CH=CH_2, and PhC(O)H] were distilled and stored over molecular sieves prior to use. Ether, hexane, and TMEDA were distilled from CaH_2 prior to use. The starting phosphoranimine **1** was prepared according to the published procedure.[10] Some ^1H NMR spectra (**5** and **6**) were obtained on a Varian EM-390 spectrometer; some ^{13}C (**5** and **6**) and all ^{31}P NMR spectra, with ^1H decoupling, were recorded on a JEOL FX-60 instrument. Other ^1H and ^{13}C NMR spectra (**2–4** and **7–10**) were obtained on a Varian XL-300 spectrometer. Mass spectra were obtained on a Finnigan OWA GCMS instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. The following procedures are typical of those used for the preparation of the new compounds in this study. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum.

Preparation of Phosphoranimines **2–6**. In a typical experiment, a 250-mL, 3-necked flask, equipped with a magnetic stirrer, N_2 inlet, and a septum, was charged with $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (**1**) (6.18 g, 25 mmol), Et_2O (40 mL), and TMEDA (3.3 mL, 25 mmol). The mixture was cooled to −78°C and *n*-BuLi (26.3 mmol, 10.1 mL, 2.6 M in hexane) was added slowly via syringe. After the solution was stirred for ca. 30 min, MeI (1.6 mL, 25 mmol) was added via syringe. The mixture was allowed to warm slowly to room temperature while being stirred overnight. Hexane (50 mL) was added and the mixture was filtered under nitrogen. After solvent removal under reduced pressure, distillation through a 10-cm column afforded **2** as a colorless liquid (4.0 g, 61% yield). In some instances, redistillation was necessary to remove small amounts of the starting phosphoranimine **1** and/or TMEDA from the product. Compounds **3** and **4** were prepared according to the same procedure by using benzyl and allyl bromide, respectively, in place of MeI. For the preparations of **5** [from EtOC(O)Cl] and **6** (from Br_2), the same procedure was followed except that the use of TMEDA was unnecessary.

Preparation of Phosphoranimines **7–10**. Generally, a solution of the phosphoranimine anion **1a** (ca. 40 mmol) in Et_2O (50 mL) was prepared as described above. After the solution was stirred at −78°C for 30 min, acetone (3.0 mL, 41 mmol) was added via syringe and the mixture was stirred for an additional 3 h without warming. The mixture was then treated with Me_3SiCl (5.2 mL, 41 mmol) and was allowed to warm to room temperature overnight. Product isolation as described above and distillation through a 10-cm column afforded **7** as a colorless liquid (5.87 g, 40% yield). Compounds **8–10** were prepared according to the same procedure by using acetophenone, methyl vinyl ketone, and benzaldehyde, respectively, in place of acetone.

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