Reactions of (Silylamino)phosphines with Ketones and Aldehydes[1,2]

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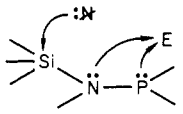
(Silylamino)phosphines including $(Me_3Si)_2NPMe_2$ (1), $Me_2SiCH_2CH_2SiMe_2NPMe_2$ (2), and $Me_3SiN(R)PMe_2$ (3, R = *t*-Bu; 4, R = Me) react smoothly with carbonyl compounds in dichloromethane via nucleophilic attack by phosphorus and [1,4]-silyl migration from nitrogen to oxygen. Thus, treatment of phosphine 1 with saturated ketones and aldehydes affords high yields of the new *N*-silylphosphinimines $Me_3SiN{=}PMe_2{-}CRR'{-}OSiMe_3$ (**5a–h**). Similarly, 2 reacts with acetone to form the 8-membered ring product $Me_2SiCH_2CH_2SiMe_2N{=}PMe_2CMe_2{-}O$ (**6**). With α,β-unsaturated carbonyl compounds, 1,4 addition occurs to yield the acyclic (from 1) or 10-membered cyclic (from 2) silyl enol ethers $Me_3SiN{=}PMe_2CHRCH{=}CR'OSiMe_3$ [7, R = R′ = H; 8, R = R′ = Me; 9, R, R′ = $(-CH_2-)_3$] and $Me_2SiCH_2CH_2SiMe_2N{=}PMe_2CH_2CH{=}CMeO$ (**10**). The (*N*-alkyl-*N*-silylamino)phosphines 3 and 4 also react with carbonyl compounds, but, except for $t\text{-}BuN{=}PMe_2C(CF_3)_2OSiMe_3$ (**11**), the products are phosphine oxides $O{=}PMe_2{-}CRR'{-}OSiMe_3$ (**13**, R = H, R′ = Me; **14**, R = R′ = Me; **15**, R = H, R′ = Ph). Phosphine 3 reacts with methyl vinyl ketone to afford the unstable phosphinimine $t\text{-}BuN{=}PMe_2CH_2CH{=}CMeOSiMe_3$ (**16**). Proton, ^{13}C, and ^{31}P NMR spectroscopic data for this new series of compounds are reported.

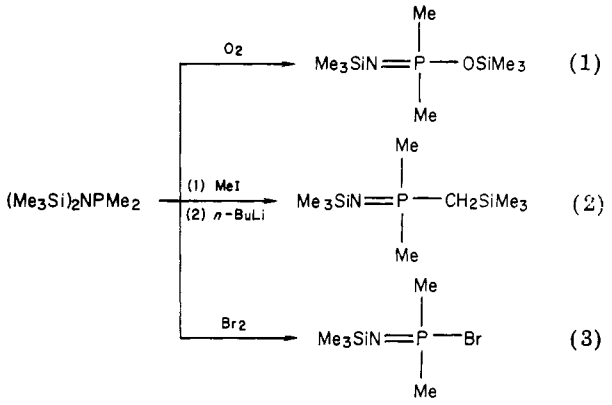
Introduction

Recent studies of (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ have shown them to be easily prepared reagents which exhibit a rich and interesting derivative chemistry. Specifically there are three potential modes of reactivity in such systems: (a) nucleophilic attack by phosphorus; (b) nucleophilic attack by nitrogen; (c) electrophilic attack by silicon.

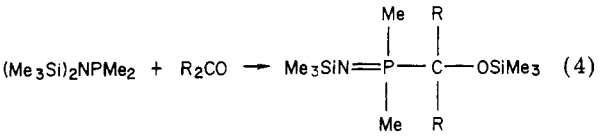


:N = nucleophile; E = electrophile

We have previously observed that a combination of pathways a and c is operative in the attempted synthesis of oxide (eq 1)[3] or ylide (eq 2)[4] derivatives. In both cases, the isolated products are the isomeric *N*-silylphosphinimines resulting from [1,3]-silyl migrations. Similarly, the bromination of (silylamino)phosphines (eq 3)[5] involves reaction at both phosphorus and silicon to afford the *P*-bromophosphinimines which are important intermediates in the synthesis of alkyl-substituted phosphazene polymers.[6,7]

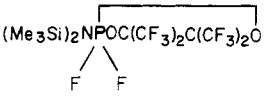


The findings have led us into a more extensive investigation of the reactivity of (silylamino)phosphines especially toward electrophilic organic substrates. A preliminary study[8] has shown that treatment of $(Me_3Si)_2NPMe_2$ with either acetone or hexafluoroacetone gives high yields of novel phosphinimines (eq 4). These observations were



R = Me, CF_3

contrasted with the general lack of reactivity of phosphines with ketones[9] and with the oxidative reaction of $(CF_3)_2CO$ with $(Me_3Si)_2NPF_2$ to give the cyclic phosphorane[10]



We report here some results of a more detailed study in which a representative series of (silylamino)phosphines were treated with a variety of aldehydes and ketones including α,β-unsaturated systems. The reactions of (silylamino)phosphines with other types of organic compounds will be reported in subsequent papers.

(1) Presented in part at the International Conference on Phosphorus Chemistry, Durham, NC, June 1981; Abstr. 176.
(2) Taken in part from the Ph.D. Dissertation of D. W. Morton, Texas Christian University, Fort Worth, TX, 1981.
(3) Neilson, R. H.; Wisian-Neilson, P.; Wilburn, J. C. *Inorg. Chem.* **1980**, *19*, 413.
(4) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347.
(5) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.
(6) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.
(7) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425.
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(9) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Halsted Press: New York, 1976; Chapter 4.
(10) Gibson, J. A.; Röschenthaler, G.-V.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1975**, 918.

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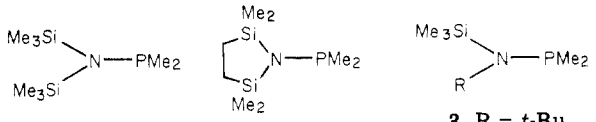
Table I. Preparative and Analytical Data for New *N*-Silylphosphinimines

compd	preparative			analytical[a]	
	rx time	% yield	bp, °C (mm)	% C	% H
5a	<1 min	89	39-40 (0.2)	33.97 (34.10)	6.40 (6.24)
5b	42 h	88	51-53 (1.2)	47.18 (47.27)	11.05 (10.82)
5c	1.5 h	91	50 (0.3)	45.25 (45.24)	10.60 (10.63)
5d	6 h	69	80-82 (0.01)	54.94 (55.00)	9.47 (9.23)
5e[b]	2 h	72	62 (0.07) (mp 48-51)		
5f	4.3 h	66	57 (0.01)	42.35 (42.08)	9.41 (9.31)
5g[c]	1 h				
5h	48 h	67	56-57 (0.01)	52.90 (52.62)	10.96 (10.72)
6[c]	2 h				
7	<1 min	61	57-58 (0.01)	47.72 (47.61)	10.37 (10.17)
8	<1 min	91	45 (0.01)	49.28 (49.44)	10.47 (10.37)
9	36 h	69	79 (0.02)	52.82 (52.95)	10.14 (10.16)
10[c]	<1 min				
11	<1 min	81	43-45 (0.3)	38.86 (38.81)	6.49 (6.51)
13	4 h	69	54-56 (0.02) (mp 43-44)	43.01 (43.27)	9.66 (9.86)
14	65 h	76	46-47 (0.01)	46.37 (46.13)	10.40 (10.16)
15	1 h	66	99-101 (0.02) (mp 73-74)	56.47 (56.22)	8.30 (8.26)
16[c]	<1 min	42	60 (0.02)		

[a] Calculated values in parentheses. [b] Insufficient purity for elemental analysis. [c] Elemental analysis prevented by thermal instability.

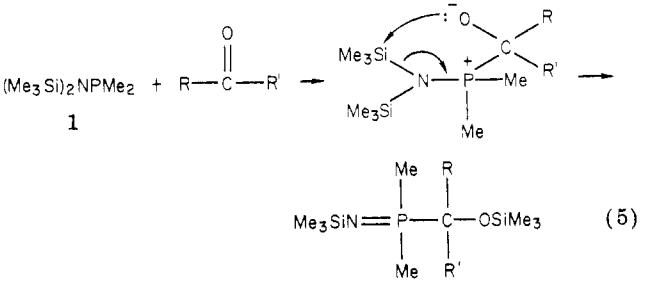
Results and Discussion

The reactions of carbonyl compounds with [bis(trimethylsilyl)amino]dimethylphosphine (**1**), its cyclic analogue **2**, and the (*N*-alkyl-*N*-silylamino)phosphines **3** and **4** were studied in this work.



1 **2** **3**, R = *t*-Bu; **4**, R = Me

(Disilylamino)phosphines. When 1 equiv of the aldehyde or ketone was added to a dichloromethane solution of the phosphine **1** at 0 °C (or room temperature in some cases), a spontaneous, sometimes very exothermic, reaction ensued (eq 5). Solvent removal and fractional distillation



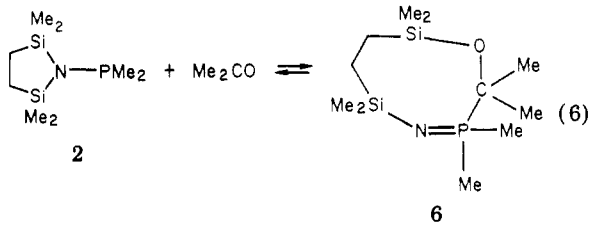
(5)

5a, R = CF_3, R′ = CF_3
b, R = R′ = Me
c, R = Me, R′ = H
d, R = Ph, R′ = H
e, R = Me, R′ = C(O)Me
f, R = Me, R′ = CH_2Cl
g, R = R′ = CH_2Cl
h, R = R′ = $-CH_2(CH_2)_3CH_2-$

generally afforded high yields of the novel *N*-silylphosphinimines **5** which apparently result from nucleophilic attack by phosphorus on the carbonyl carbon followed by a [1,4]-silyl migration from nitrogen to oxygen.

The reaction conditions, yields, and physical properties of these phosphinimines are summarized in Table I. Structural characterization of the products was readily accomplished by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and these data are collected in Table II. The progress of the reaction was conveniently monitored by ^{1}H NMR spectroscopy which clearly showed the formation of nonequivalent Me_3Si groups as well as the characteristic increase of the P–C–H coupling constant for the PMe_2 protons.[3-5]

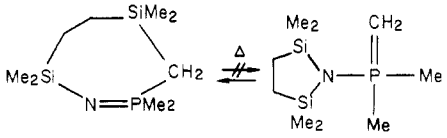
Upon treatment of the (disilylamino)phosphine **2** with acetone, ring expansion to the 8-membered cyclic phosphinimine **6** occurred (eq 6). Compound **6** is a white, waxy



(6)

solid which, on heating above ca. 65 °C, decomposed cleanly to the starting phosphine **2** and acetone. Due to this thermal instability, it was not possible to obtain an analytically pure sample of **6**. Nevertheless, its formation as virtually the only reaction product is clearly shown by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (Table II).

The reasons for the reversibility of eq 6 are not clear although it is possible that the 8-membered ring may adopt a conformation which places the siloxy silicon atom in close proximity to the nitrogen, thus facilitating Si–N bond formation. In this context, it is interesting to note that the more rigid 7-membered cyclic phosphinimine[4] (eq 7) is a stable compound which shows no tendency to revert back to its precursor.



(7)

In spite of its thermal instability, the exclusive formation of the ring-expanded product **6** (eq 6) does have mechanistic implications. In this case certainly, and perhaps in the others (eq 5), the silyl shift from nitrogen to oxygen must occur by an *intramolecular* pathway. Otherwise, acyclic oligomers would have been produced.

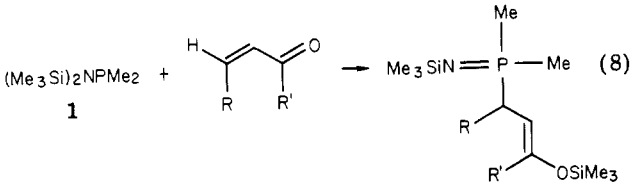
The reaction times in Table I show the expected trends in reactivity of aldehydes and ketones. For example, the reaction with acetaldehyde is much faster than the reaction with acetone. The fluoro- and chloro-substituted acetones

also react substantially faster than acetone itself, undoubtedly due to the enhanced electrophilicity of the haloacetones. These qualitative observations are consistent with a mechanism in which attack by phosphorus on the carbonyl carbon is the rate-determining step.

A few other features of this general reaction (eq 5) are worthy of note. First, another possible mode of reactivity for the chloroacetones might have been attack by phosphorus on the CH_2Cl carbon to give a phosphonium salt; however, products resulting from this pathway were not observed. Second, in the case of biacetyl, reaction with phosphine **1** occurred at only one of the carbonyl groups to yield **5e** even if an excess of **1** was employed.

Third, the compounds **5f** and **5g** derived from chloroacetone and 1,3-dichloroacetone, respectively, are an interesting pair with regard to their spectral and physical properties. As indicated in Table I, compound **5f** is distillable and can be purified by careful fractionation to remove any unreacted chloroacetone. The diastereotopic protons of the chloromethyl group give rise to an ABX pattern (X = ^{31}P) in which the upfield half is clearly split into quartets with a coupling constant of 0.4 Hz. This coupling is assigned as a ^4J between one of the CH_2 protons and those of the CH_3 group attached to the chiral carbon. Compound **5g** was prepared in order to observe the ABX pattern without this long-range coupling. Indeed, spectra of the crude product **5g** were obtained with the desired result. Attempted distillation of **5g**, however, brought about elimination of Me_3SiCl and the bulk of the material solidified into a white mass. Complete characterization of the solid was not accomplished, but the NMR data are consistent with the formation of oligomers of the type $[-N{=}PMe_2{-}C(OSiMe_3)(CH_2Cl)CH_2-]_x$.

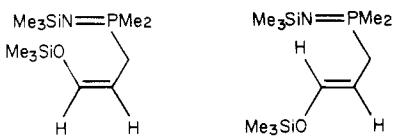
Similar reactions of α,β-unsaturated carbonyl compounds with (silylamino)phosphines were studied to determine whether the addition would proceed in a 1,2 or 1,4 manner. The carbonyl compounds investigated were methyl vinyl ketone, acrolein, and 2-cyclohexen-1-one. In each case, 1,4 addition was the observed result (eq 8), leading to the formation of *N*-silylphosphinimines **7–9** containing silyl enol ether functional groups.



(8)

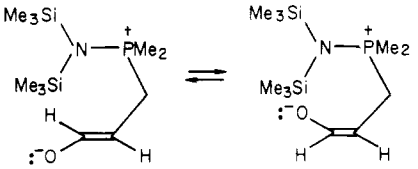
7, R = R′ = H
8, R = H, R′ = Me
9, R = R′ = $-CH_2CH_2CH_2-$

The product of the acrolein reaction **7** is obtained as a mixture of isomers in a ratio of approximately 80% *Z* and 20% *E*. These two configurations were distinguished in the ^1H NMR spectrum by the magnitudes of the vinylic coupling constants: 5.75 Hz for the cis protons of **7**(*Z*) and 11.91 Hz for the trans protons of **7**(*E*). The product ratio was estimated from the ^{13}C NMR spectrum by using the relative intensities of the corresponding vinylic and allylic carbon signals.



7 (*Z*) **7** (*E*)

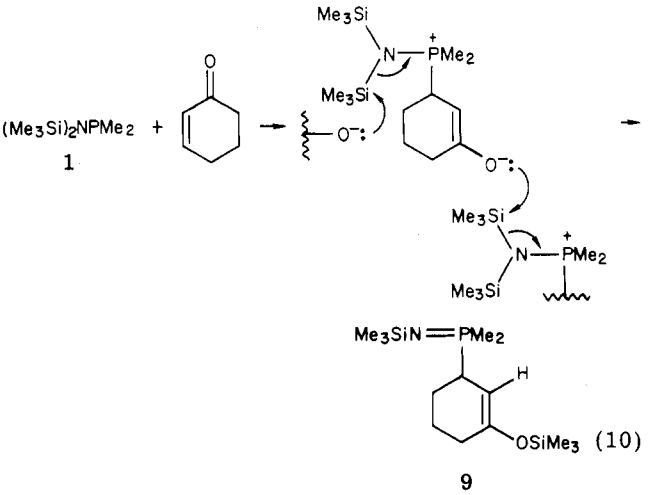
Molecular models of the intermediate enolates (eq 9)



(9)

E *Z*

show that an intramolecular [1,6]-silyl migration is more easily accomplished when the configuration is *Z*, thus giving rise to the more abundant product **7**(*Z*). The *E* isomer may be formed by an intramolecular silyl migration in the enolate with *E* configuration, although the transition state for such a process has a rather strained geometry. Alternatively, it is possible that **7**(*E*) is formed by an *intermolecular* silyl shift, as in the case of the reaction of **1** with 2-cyclohexen-1-one (eq 10).

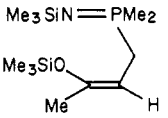


(10)

9

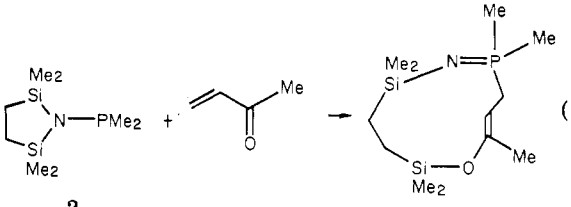
It is interesting to note that the reaction of **1** with acrolein (and with methyl vinyl ketone) occurs almost instanteously, but the reaction with 2-cyanohexen-1-one requires about 38 h for completion. This marked contrast in reaction times (and molecular models) strongly suggests that the formation of **9** occurs via an *intermolecular* silyl migration as shown in eq 10.

Methyl vinyl ketone reacts (eq 8) as rapidly with phosphine **1** as does acrolein. In this case, however, only a single silyl enol ether **8** is obtained. Although the actual configuration is uncertain, the rapidity of the reaction suggests an intramolecular silyl shift which would favor formation of the *Z* isomer.



8 (*Z*)

The cyclic (silylamino)phosphine **2** also reacted with methyl vinyl ketone (eq 11), and the reaction progress was



(11)

2 **10**

monitored by NMR spectroscopy. If methyl vinyl ketone

Table II. NMR Spectroscopic Data[a]

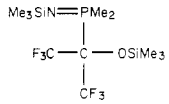
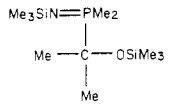
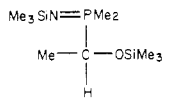
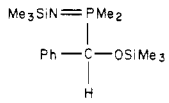
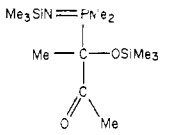
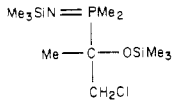
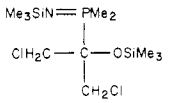
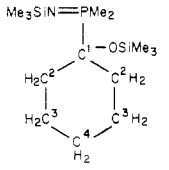
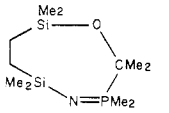
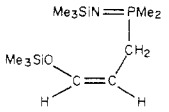
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 **5a**	Me_3SiN	0.07	0.4		3.51	3.1	7.76
	Me_3SiO	0.34			1.14		
	Me_2P	1.60	12.6		17.77	72.6	
	$(F_3C)_2C$				79.84[b]	70.8	
	F_3C				123.10[b]		
 **5b**	Me_3SiN	−0.02	0.4		4.16	3.1	20.93
	Me_3SiO	0.17			2.40		
	Me_2P	1.30	12.6		12.97	65.3	
	Me_2C	1.41	12.6		24.02	5.5	
	Me_2C				73.54	96.4	
 **5c**	Me_3SiN	−0.03	0.4		3.96	3.1	17.41
	Me_3SiO	0.28			−0.08		
	MeP	1.39	12.3		11.67	64.1	
	MeP	1.45	12.3		15.57	66.5	
	*Me*C	1.49	15.0	6.8	16.41	2.4	
	HC	3.94	4.8	6.8	68.24	93.4	
 **5d**	Me_3SiN	−0.04	0.4		3.86	3.7	15.06
	Me_3SiO	0.15			−0.12		
	MeP	1.17	12.6		12.26	61.0	
	MeP	1.45	12.6		16.08	69.6	
	HC	4.73	10.7		75.90	87.9	
	Ph	7.18–7.44			126.82	3.7	
					127.45	5.5	
					127.47		
					137.34	0.6	
 **5e**	Me_3SiN	0.03	0.4		3.84	3.1	15.62
	Me_3SiO	0.21			2.14		
	MeP	1.27	12.6	0.6	13.90	66.5	
	MeP	1.39	12.2	0.6	14.23	62.9	
	P*C*Me	1.69	14.3		20.21		
	P*C*Me				84.54	83.6	
	PCC*Me*	2.35			28.34		
	PC*C*Me				207.85	3.9	
 **5f**	Me_3SiN	0.00[c]	0.4		3.96	3.1	18.73
	Me_3SiO	0.24			2.27		
	MeP	1.32	12.2	0.5	14.01	64.7	
	MeP	1.35	12.3	0.5	14.42	63.5	
	P*C*Me	1.59	13.3	0.4	19.35	4.3	
	P*C*Me				75.71	93.4	
	C*H*Cl	3.91	4.8	11.5			
				0.4			
	C*H*Cl	4.06	6.4	11.5			
	CH_2Cl				51.15	16.5	
 **5g**	Me_3SiN	0.03	0.4		3.96	3.1	15.44
	Me_3SiO	0.29			2.27		
	Me_2P	1.47	12.0		16.81	63.5	
	P*C*H_2	3.9	9.0	11.6	46.74	11.0	
	P*C*H_2	4.10	9.4	11.6			
	P*C*CH_2				78.17	91.6	
 **5h**	Me_3SiN	−0.03	0.4		4.32	2.9	17.84
	Me_3SiO	0.20			2.79		
	Me_2P	1.27	12.0		13.61	61.5	
	C^1				76.64	96.7	
	C^2H_2	1.60–1.83			30.93	5.9	
	C^3H_2	1.60–1.83			21.18	9.8	
	C^4H_2	1.60–1.83			25.40		
 **6**	Me_2SiN	−0.09	0.4		1.97	5.5	20.50
	Me_2SiO	0.07			0.49		
	$SiCH_2$	0.61[d]			11.09		
	Me_2P	1.29	12.0		13.26	65.3	
	Me$_2$C	1.34	13.4		25.30	8.5	
	Me_2C				73.62	83.0	
 **7 (*Z*)**	Me_3SiN	0.03	0.4		3.61	3.7	8.16
	Me_3SiO	0.20			−1.10		
	Me_2P	1.35	12.8		16.91	67.8	
	P*C*H_2	2.50	16.1	7.9	29.73	65.9	
				1.2			
	PC*CH*	4.47	4.8	7.9	100.59	8.6	
				5.7			
	PCC*CH*	6.25	4.9	5.7	139.69	11.0	
				1.2			

Table II (*Continued*)

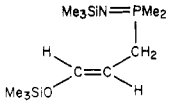
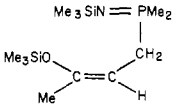
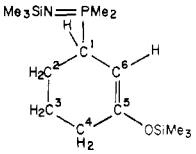
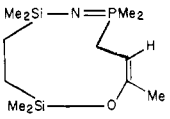
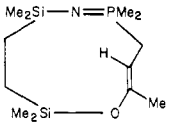
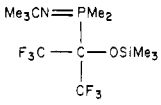
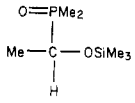
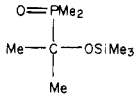
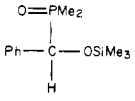
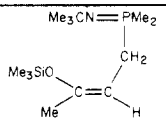
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 7(*E*)	Me_3SiN	0.03	0.4		3.61	3.7	5.84
	Me_3SiO	0.20			−1.10		
	Me_2P	1.35	12.8		16.91	67.8	
	PCH_2	2.29	14.9	8.1	32.91	67.8	
				1.2			
	PC*CH*	4.92	5.5	11.9	101.78	7.9	
				8.1			
	PCC*CH*	6.20	4.8	11.9	142.09	13.4	
				1.2			
 8	Me_3SiN	−0.03	0.4		4.00	4.3	12.13
	Me_3SiO	0.21			0.71		
	Me_2P	1.24	12.3		17.38	68.4	
	PCH_2	2.30	15.6	7.5	31.54	65.31	
	PC*CH*	4.32	5.4	7.5	98.50	8.6	
				<0.4			
	PCCC*Me*	1.78	5.4	<0.4	22.32	2.9	
	PCC*C*Me				149.24	11.6	
 9	Me_3SiN	0.04[e]	0.4		3.84	3.1	12.33
	Me_3SiO	0.21			−0.12		
	Me_2P	1.28	11.4		15.15	67.1	
	HC^1	2.2–2.7			38.94	71.4	
	H_2C^2	1.2–2.1			22.13	<0.6	
	H_2C^3	1.2–2.1			21.77	10.4	
	H_2C^4	1.2–2.1			29.16	2.4	
	C^5				152.67	11.6	
	HC^6	4.90	8.7	5.6	99.43	5.5	
 10(*Z*)	Me_2SiN	0.03[e]	0.4		1.67	4.9	11.17
	Me_2SiO	0.26			−0.73		
	CH_2SiN	0.39–0.90			11.05	4.3	
	CH_2SiO	0.39–0.90			7.51		
	Me_2P	1.40	12.0		18.13	70.2	
	PCH_2	2.42	12.3	7.9	31.09	62.9	
	PC*CH*	4.35	4.9	7.9	96.77	9.8	
				1.0			
	PCCC*Me*	1.88	5.4	1.0	22.15	3.1	
	PCC*C*Me				150.17	11.0	
 10(*E*)	Me_2SiN	0.04[e]	0.4		1.01	3.1	5.84
	Me_2SiO	0.20			−1.95		
	CH_2SiN	0.39–0.90			11.05	4.3	
	CH_2SiO	0.39–0.90			9.26		
	Me_2P	1.34	12.0		17.16	67.8	
	PCH_2	2.42	12.3	7.9	31.09	66.5	
	PC*CH*	4.44	4.9	7.9	97.42	8.6	
				1.0			
	PCCC*Me*	1.83	5.7	1.0	22.15	2.4	
	PCC*C*Me				148.97	11.6	
 11	Me_3Si	0.34			0.90		−4.90
	Me_3C	1.18			34.74	10.4	
	Me_3C				51.52	5.5	
	Me_2P	1.60	11.5		17.30	72.0	
	$(F_3C)_2C$				79.49[f]	67.8	
	F_3C				123.03[f]		
 13	Me_3Si	0.03			−1.42		47.49
	MeP	1.23	12.4	0.4	8.75	66.5	
	MeP	1.28	12.8	0.4	11.66	67.1	
	*Me*C	1.25	14.5	6.9	15.13	1.8	
	HC	3.83	5.5	6.9	65.22	91.6	
 14	Me_3Si	0.04			1.01		52.16
	Me_2P	1.24	12.6		9.34	65.9	
	Me_2C	1.34	13.2		22.52	5.5	
	Me_2C				70.84	95.8	
 15	Me_3Si	0.06			−1.18		46.02
	MeP	1.11	12.8		9.71	67.1	
	MeP	1.40	12.8		12.26	67.1	
	HC	4.93	10.2		72.91	86.1	
	Ph	7.10–7.43			125.22	4.3	
					126.64	3.1	
					127.00	1.8	
					135.63	1.6	

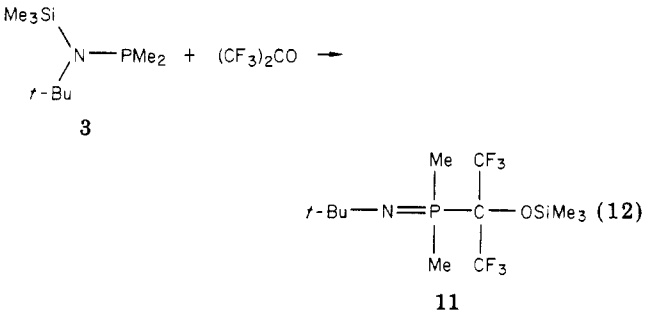
Table II (*Continued*)

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
 16	Me_3Si	0.16			1.42[g]		ca. 12[g,h]
	Me_3C	1.10			36.73	11.6	
	Me_3C				52.06	6.1	
	Me_2P	1.22	12.0		18.33	64.1	
	PCH_2	2.32	14.9	7.8	32.97	62.3	
	PC*CH*	4.35	5.4	7.8	101.07	7.3	
				0.6			
	PCCC*Me*	1.74	4.5	0.6	23.13	1.8	
	PCC*C*Me				149.05	10.4	

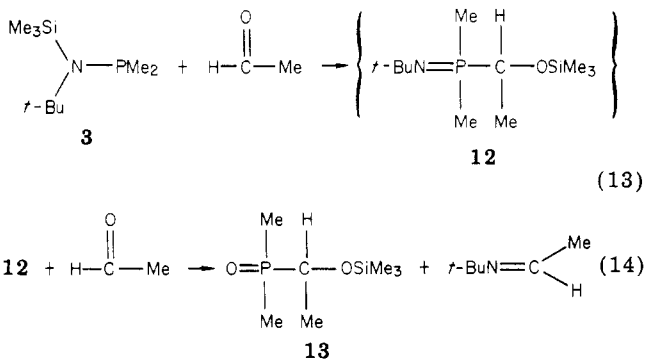
[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] J_{CF} = 289.9 Hz, J_{CCF} = 28.5 Hz. [c] Benzene solution used for ^{1}H NMR. [d] $\bar{\nu}$ for AA'BB' pattern. [e] Benzene/$CDCl_3$ solution used for ^{1}H NMR. [f] J_{CF} = 289.5 Hz, J_{CCF} = 28.1 Hz. [g] Benzene-d_6 solution used for ^{13}C and ^{31}P NMR. [h] Spectrum recorded on partially decomposed sample.

was slowly added to a dichloromethane solution of **2** at either −78 or 0 °C and if the ^{1}H NMR spectrum was obtained immediately, then the PMe_2 group appears as a doublet at δ 1.33. As several hours pass, however, a new doublet at δ 1.27 begins to appear, eventually replacing the one at δ 1.33. A similar phenomenon occurs in the ^{31}P NMR spectra: an initial signal at δ 11.17 being slowly replaced by one at δ 5.84. Comparison of these ^{31}P chemical shifts with those of **7** (*Z*, δ 8.16, and *E*, δ 5.84) suggests that, in the reaction of **2** with methyl vinyl ketone, initially a product with *Z* configuration was formed, which slowly converted to the *E* isomer. Unfortunately, it was not possible to distill either of these compounds without substantial decomposition to unidentified products. Consequently their characterization is based upon NMR spectral data (Table II).

(*N*-Alkyl-*N*-silylamino)phosphines. The *tert*-butyl derivative **3** reacted spontaneously with hexafluoroacetone as expected to form the phosphinimine **11** (eq 12), but it

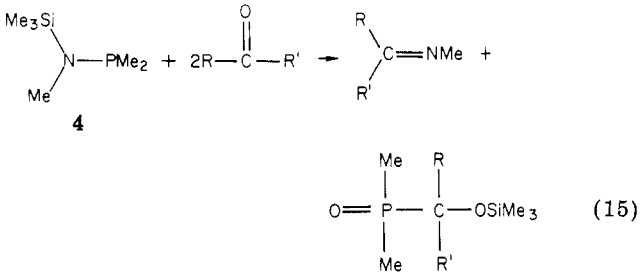


was unreactive toward acetone even after several months. Phosphine **3** does, however, react with acetaldehyde to form phosphine oxide **13** in high yield (eq 13, 14) rather



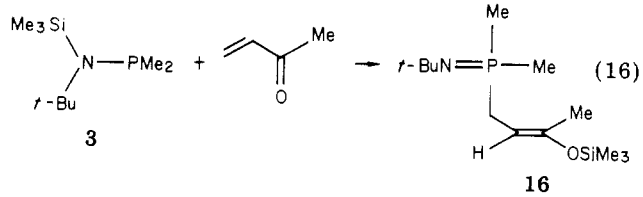
than the phosphinimine **12**. If only 1 equiv of acetaldehyde was added to **3**, only the phosphine oxide **13**, the imine *t*-BuN=CHMe, and unreacted phosphine **3** could be detected by ^{1}H NMR. It is concluded that the *N*-*tert*-butylphosphinimine **12**, which was never observed by ^{1}H NMR, reacts faster with the aldehyde than does the phosphine **3**. Similar reactivity trends have been observed by Pudovik and co-workers for some related Si–N–P systems.[11-13]

In contrast to **3**, the *N*-methyl analogue **4** does react with acetone to form the phosphine oxide **14**. Phosphine **4** also reacts with benzaldehyde to yield **15** (eq 15).



14, R = R' = Me
15, R = H, R' = Ph

Generally, the reactions of the *N*-alkyl phosphines **3** and **4** with α,β-unsaturated carbonyl compounds gave somewhat less straightforward results. Phosphine **3** reacted with 1 equiv of methyl vinyl ketone to yield the 1,4-addition product **16** (eq 16), a compound which is stable in



the reaction mixture and for a short time after distillation. A freshly distilled sample of **16**, however, decomposed on standing for several hours to an unidentified dark brown substance.

Phosphine **4** also reacts vigorously with methyl vinyl ketone, but, unlike **3**, the products are unidentifiable. Presumably, the *N*-methyl analogue of **16** is formed initially, but this compound must be even less stable than **16**. Due to these instability problems, the reactions of **3** and **4** with other α,β-unsaturated carbonyl compounds were not investigated.

(11) Pudovik, M. A.; Medevdeva, M. D.; Kibardina, L. K.; Pudovik, A. N. *J. Gen. Chem. USSR (Engl. Trnsl.)* **1975**, *45*, 924.
(12) Pudovik, M. A.; Kibardina, L. K.; Medvedeva, M. D.; Pestova, T. A.; Kharlampidi, Kh. E.; Pudovik, A. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1976**, *46*, 1878.
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Conclusion

(Silylamino)phosphines generally react smoothly with carbonyl compounds via nucleophilic attack by phosphorus with subsequent silyl migration to oxygen. This process is a convenient synthetic route to new *N*-silylphosphinimines or phosphine oxides which contain Me_3SiO-functionalized organic substituents.

Experimental Section

Materials and General Procedures. The (silylamino)phosphines were prepared according to the published procedures.[4,14] Acetone, acetaldehyde, benzaldehyde, cyclohexanone, and dichloromethane were obtained from commerical sources, distilled, and stored over molecular sieves prior to use. Acrolein was distilled and used immediately. Other reagents were used as obtained without further purification. All reactions were performed under an atmosphere of dry nitrogen with reagents being transferred by syringe. Proton NMR spectra were obtained on Varian EM390 or JEOL MH-100 spectrometers. Carbon-13 and ^{31}P NMR spectra were obtained on a JEOL FX-60 spectrometer operating in the FT mode. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Reactions of (Silylamino)phosphines with Aldehydes and Ketones. Typically, the phosphine (ca. 10–20 mmol) was dissolved in CH_2Cl_2 (ca. 10–15 mL) in a 25-mL flask equipped with a magnetic stirrer and an adapter with a gas-inlet side arm and a rubber septum. The carbonyl compound was then added via syringe to the stirred phosphine solution. Some reagents (see below) required addition at 0 °C to moderate the exothermic reaction. The progress of the reactions was monitored by ^1H NMR spectroscopy, and Table I lists the times by which disappearance of the starting phosphine was observed to be complete. Reaction times of <1 min indicate that the reaction is very rapid at 0 °C. Upon completion of the reaction, solvent was removed under reduced pressure, and the product was purified by fractional distillation (Table I).

In the above procedure, the reagents added at room temperature were acetone, cyclohexanone, and 2-cyclohexen-1-one. Those added at 0 °C were acetaldehyde, benzaldehyde, chloroacetone, dichloroacetone (as a CH_2Cl_2 solution), acrolein, and methyl vinyl ketone.

In the synthesis of the 10-membered ring **10**, the *Z* isomer was favored if methyl vinyl ketone was slowly swept into the reaction mixture at 0 °C under a stream of nitrogen.

In the syntheses of **5a** and **11**, hexafluoroacetone was introduced as a gas into an evacuated flask containing the phosphine, without solvent, which was being stirred at 0 °C. An exothermic reaction ensued in which only 1 equiv of hexafluoroacetone was consumed. Products were then purified by fractional distillation (Table I).

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

Registry No. **1**, 63744-11-6; **2**, 68437-96-7; **3**, 68437-82-1; **4**, 68437-84-3; **5a**, 72805-01-7; **5b**, 72805-03-9; **5c**, 79200-64-9; **5d**, 79200-65-0; **5e**, 79200-66-1; **5f**, 79200-67-2; **5g**, 79200-68-3; **5h**, 79200-69-4; **6**, 79200-70-7; **7**(*Z*), 79200-71-8; **7**(*E*), 79200-72-9; **8**, 79200-73-0; **9**, 79200-74-1; **10**(*Z*), 79200-75-2; **10**(*E*), 79200-76-3; **11**, 72805-02-8; **13**, 79215-35-3; **14**, 79200-77-4; **15**, 79200-78-5; **16**, 79200-79-6; hexafluoroacetone, 684-16-2; acetone, 67-64-1; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; biacetyl, 431-03-8; chloroacetone, 78-95-5; dichloroacetone, 534-07-6; cyclohexanone, 108-94-1; methyl vinyl ketone, 78-94-4; acrolein, 107-02-8; 2-cyclohexen-1-one, 930-68-7.

(14) Wilburn, J. C. Ph.D. Dissertation, Duke University, Durham, NC, 1978.

A Double Michaelis–Arbuzov Rearrangement Involving $(\eta^5\text{-}C_5H_5)CoI_2(CO)$ and $P(OCH_3)_3$. Formation of the Cobalt "Supersandwich" Complex

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Received July 15, 1981

The reaction of $(\eta^5\text{-}C_5H_5)CoI_2(CO)$ with $P(OR)_3$, R = CH_3 and C_2H_5, yields different products depending on the amount of phosphite and on conditions employed. By stoichiometric ligand substitution, $(\eta^5\text{-}C_5H_5)CoI_2[P(OCH_3)_3]$ is produced. However, with excess $P(OCH_3)_3$ a double Michaelis–Arbuzov reaction occurs to yield $(\eta^5\text{-}C_5H_5)Co[P(O)(OCH_3)_2]_2[P(OCH_3)_3]$ (**3**) with formation of CH_3I. Complex **3**, isolatable in both the anhydrous and monohydrated form, is converted to the cobalt supersandwich $(\eta^5\text{-}C_5H_5)_2Co_3[P(O)(OCH_3)_2]_6$ by pyrolysis or by the addition of anhydrous $CoCl_2$. The nature of **3** has been verified by a single-crystal X-ray diffraction study at −100 °C. It crystallizes as a monohydrate in space group C_{2h}^5—$P2_1/c$ with four formula units in a cell of dimensions a = 7.872 (1) Å, b = 15.105 (2) Å, c = 16.517 (2) Å, and β = 91.819 (1)°. Least-squares refinement of a data set containing 3238 reflections having $F_o^2 > 3\sigma(F_o^2)$ converged to conventional agreement indices (on F) of R = 0.031 and R_w = 0.034. The spectral, structural, and reactivity details of the complex, apparently unique in its formation via a double Michaelis–Arbuzov reaction, are discussed.

Introduction

The Michaelis–Arbuzov rearrangement, as illustrated in reaction 1, results in the production of a phosphonate

$$RX + P(OR')_3 \rightarrow P(O)R(OR')_2 + R'X \qquad (1)$$

species by alkyl transfer to phosphorus in a reaction between an alkyl halide and a trialkyl phosphite.[2–4] Analogous transformations which occur when certain organotransition-metal halides such as $CpFeX(CO)_2$,[5,6] CpNiX-

(1) (a) University of Delaware. (b) E. I. du Pont de Nemours and Co., Contribution No. 2952.

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