Reactions of (Silylamino)phosphines with Some Organic Halides[1,2]

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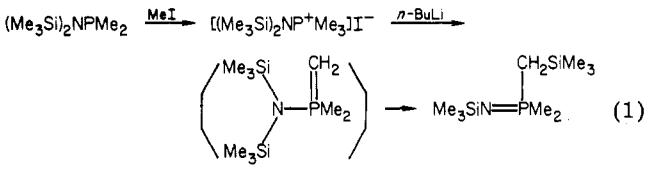
(Silylamino)phosphines including $(Me_3Si)_2NPR_2$ (**1a**, R = Me; **1b**, R = Et), $Me_2SiCH_2CH_2SiMe_2NPMe_2$ (**2**), and $Me_3SiN(R)PMe_2$ (**3a**, R = *t*-Bu; **3b**, R = Me) react readily with organic halides to give a variety of products. Treatment of **1a**, **1b**, or **3a** with ethyl bromoacetate yields the structurally rearranged phosphonium salts $[R'N(H)-P^+R_2-CHSiMe_3-CO_2Et]Br^-$ (**4a**, R = Me, R′ = $SiMe_3$; **4b**, R = Et, R′ = $SiMe_3$; **10**, R = Me, R′ = *t*-Bu) while the cyclic compound **2** gives the simple phosphonium salt $[Me_2SiCH_2CH_2SiMe_2N-P^+Me_2-CH_2CO_2Et]Br^-$ (**9**). The salts **4a** and **4b** react with alkyl lithium reagents to give the *N*-silylphosphinimines $Me_3SiN{=}PR_2{-}CH_2CO_2Et$ (**8a**, R = Me; **8b**, R = Et). With allyl bromide phosphine **1a** reacts to form a mixture of the isomeric phosphonium salts $[(Me_3Si)_2N-P^+Me_2R]Br^-$ (**11**, R = $CH_2CH{=}CH_2$; **12**, R = $CH{=}CHCH_3$) which readily eliminate Me_3SiBr, yielding the phosphinimines $Me_3SiN{=}PMe_2R$ (**13**, R = $CH_2CH{=}CH_2$; **14**, R = $CH{=}CHCH_3$). Traces of atmospheric moisture catalyze the isomerizations of **11** to **12** and **13** to **14**. Phosphine **2** again affords a simple phosphonium salt **15** with allyl bromide. Phosphine **1a** reacts smoothly with chloroformates to give the alkoxycarbonyl-substituted phosphinimines $Me_3SiN{=}PMe_2{-}C(O)OR$ (**16a**, R = Me; **16b**, R = Et). The *N-tert*-butyl analogue (**18**), from **3a** and methyl chloroformate, was obtained as a mixture with other unidentified products, and the cyclic compound **2** gave only a low yield of the P–N cleavage product **17**. The *N*-methyl phosphine **3b**, however, reacts cleanly via Si–N bond cleavage to afford the aminophosphine $MeOC(O)N(Me)-PMe_2$ (**19**) in high yield. Proton, ^{13}C, and ^{31}P NMR spectroscopic data for this new series of compounds are reported.

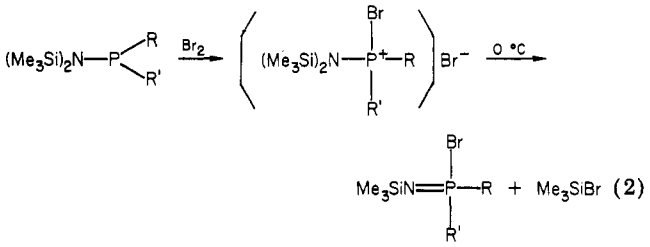
Introduction

As reported in earlier papers,[3–5] the chemistry of (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ usually involves participation of both phosphorus and silicon as reactive sites. For example, while salt formation occurs readily with MeI, subsequent dehydrohalogenation (eq 1) results in a



(1)

[1,3]-silyl shift rather than simple ylide formation.[3] Elimination of silyl halides from (silylamino)phosphonium salts is another mode of reactivity as illustrated by the bromination reaction (eq 2) which yields the synthetically important *P*-bromophosphinimines.[4]

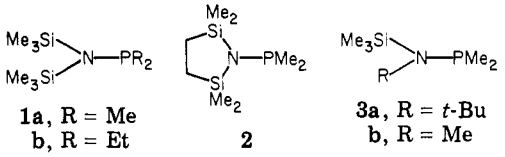


(2)

We report here the reactions of some (silylamino)phosphines with a representative group of reactive organic halides: ethyl bromoacetate, allyl bromide, and chloroformates. Silyl halide elimination from the resulting phosphonium salts yields phosphinimines bearing organic functional groups on phosphorus.

Results and Discussion

As in the related study,[5] the (silylamino)phosphines used in this work included the [bis(trimethylsilyl)amino]dialkylphosphines **1**, the cyclic analogue **2**, and the (*N*-alkyl-*N*-silylamino)phosphines **3**.

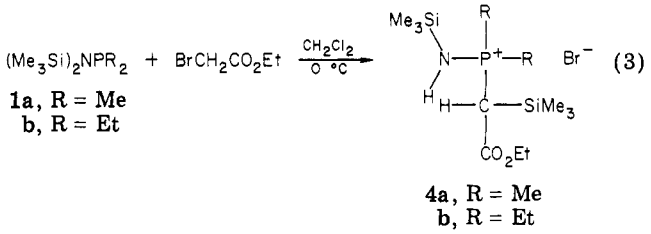


1a, R = Me
b, R = Et

2

3a, R = *t*-Bu
b, R = Me

Reactions with Ethyl Bromoacetate. Treatment of phosphine **1a** or **1b** with 1 equiv of ethyl bromoacetate in dichloromethane solution yields, quite surprisingly, the structurally rearranged phosphonium salts **4a** and **4b**, respectively (eq 3). The structure of **4**, in which a proton



(3)

1a, R = Me
b, R = Et

4a, R = Me
b, R = Et

and a $SiMe_3$ group have exchanged positions, was confirmed by ^{13}C and ^1H NMR spectroscopy. Most notably, the carbon to which both phosphorus and silicon are bonded appears as a doublet of doublets in the off-resonance decoupled ^{13}C spectrum. Furthermore, the Me_3Si groups are nonequivalent in both the ^{13}C and ^1H NMR spectra, and the N–H proton is clearly visible in the ^1H spectrum (Table I).

A possible pathway for the formation of these phosphonium salts is proposed in eq 4. Phosphonium salt **5** is assumed to be the initial product; however, it could not be observed in the reaction mixture by NMR spectroscopy. It seems reasonable to suggest that the N–H proton in **4**

(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) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347.
(4) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.
(5) Morton, D. W.; Neilson, R. H. *Organometallics*, in press. For a preliminary report see: Neilson, R. H.; Goebel, D. W. *J. Chem. Soc., Chem. Commun.* **1979**, 769.

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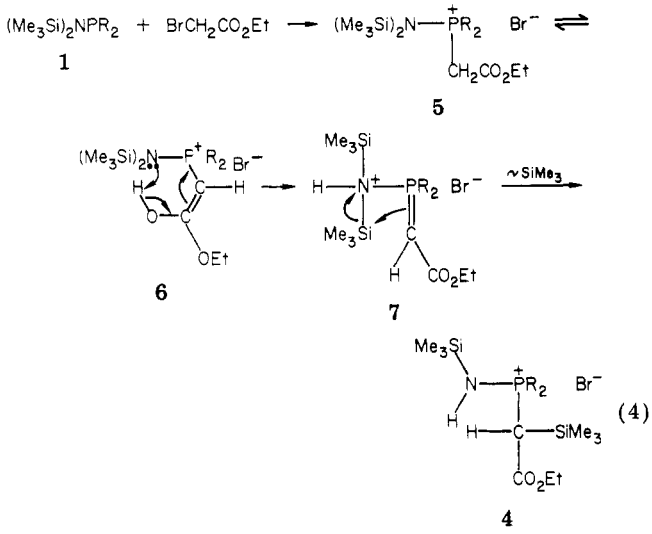
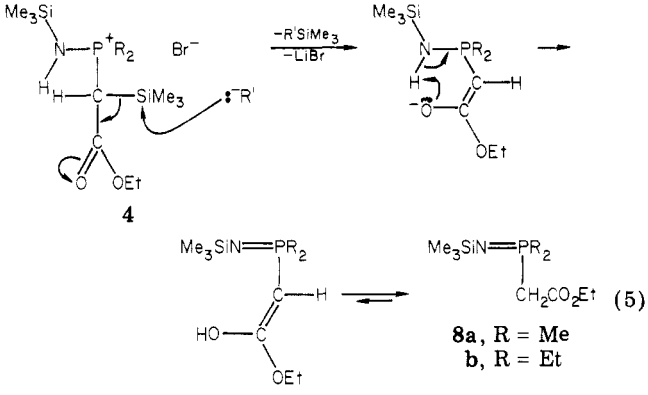


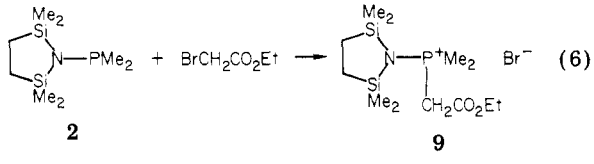
may be transferred via the enol 6 to give 7. The formation of 4 from 7 could then occur by a [1,3]-silyl migration from nitrogen to carbon.[3]

Another rather unexpected result was obtained when the phosphonium salts 4 were treated with either *n*-butyl- or *tert*-butyllithium (eq 5). Instead of removing an N–H or

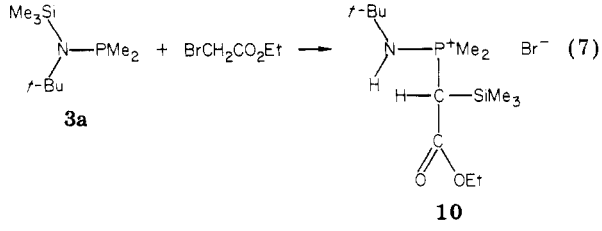


C–H proton, the alkyl anion apparently attacks the C-bonded silyl group to afford, after proton transfer back to carbon, the *N*-silylphosphinimines 8.

The cyclic (disilylamino)phosphine 2 also forms a salt (9) with ethyl bromoacetate, but no silyl migration to carbon occurs (eq 6). The (*N*-*tert*-butyl-*N*-silylamino)-

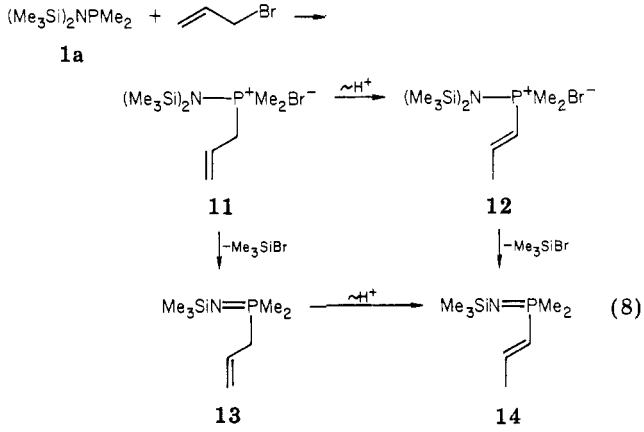


phosphine 3a, however, reacts in the same manner as 1 to yield 10 (eq 7). The phosphonium salts 9 and 10 both



react vigorously with *n*-butyllithium but none of the reaction products could be identified by NMR spectroscopy.

Reactions with Allyl Bromide. Phosphine 1a reacts exothermically with allyl bromide to produce a mixture of compounds 11–14 (eq 8). When the reactants were

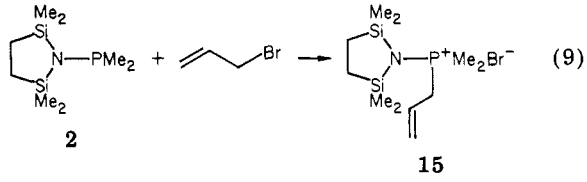


combined under rigorously anhydrous conditions in dichloromethane at −78 °C in an NMR tube and the probe temperature was raised gradually, the following observations were made. At −78 °C, much of 1a remained unreacted, but signals due to 11 and 13 could be discerned. By −40 °C, practically all of 1a had reacted, and by +2 °C the mixture consisted of about 50% of 11 and 50% of 13. At +30 °C the spectrum showed that all of 11 had decomposed to 13.

If a trace amount of water is introduced by briefly opening the reaction vessel to air, however, 13 is observed to slowly convert into 14. This is probably an acid-catalyzed isomerization caused by HBr from the hydrolysis of Me_3SiBr. If moisture is introduced before the salt 11 has completely decomposed to 13, then the isomeric phosphonium salt 12 can be observed by ^1H NMR. Compound 12 can, of course, eliminate Me_3SiBr directly to form 14.

On a preparative scale, mixtures of 13 and 14 are usually observed, but nearly pure 13 is obtained if moisture is carefully excluded. When left standing for several days, 13 gradually rearranges to the conjugated isomer 14 which, based on the large vinylic coupling of 16.5 Hz, is assigned the *E* configuration.

Phosphine 2 also reacts with allyl bromide to form the stable phosphonium salt 15 (eq 9) which does not give a

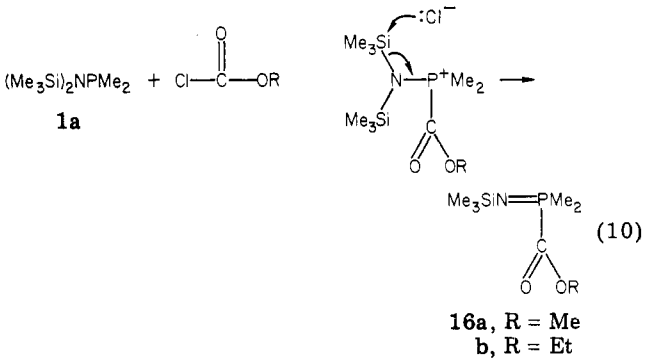


phosphinimine at room temperature. Compound 15 exhibits no tendency toward double-bond migration, which is most likely a result of the fact that there is no halosilane formation (and no acid catalyst) as in eq 8.

Reactions with Chloroformates. The course of the reaction of (silylamino)phosphines with methyl or ethyl chloroformate was found to vary markedly depending upon the electronic and steric effects of the nitrogen substituents in the starting phosphine. Thus, different types of products were obtained from similar reactions of phosphines 1, 2, or 3 with the chloroformates.

Phosphine 1a reacts via nucleophilic attack by phosphorus on the carbonyl carbon followed by loss of Me_3SiCl (eq 10) to give the alkoxycarbonyl-substituted phosphinimines 16 in ca. 70% yields. In contrast, however, to the reactions with ethyl bromoacetate (eq 4) or allyl bromide (eq 8), the intermediate phosphonium salt could not be observed by NMR spectroscopy.

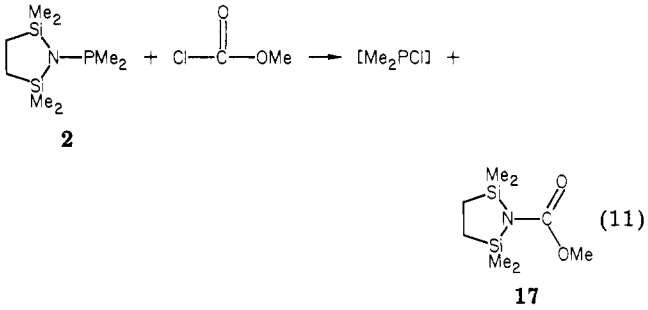
The cyclic analogue 2 reacted quite differently with methyl chloroformate. In this case, only a P–N cleavage



(10)

16a, R = Me
b, R = Et

product, **17**, (eq 11) was obtained in low yield (ca. 15%).

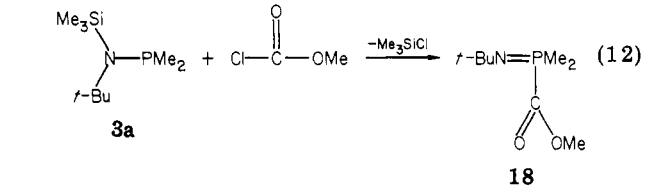


(11)

17

Although it was not identified in the product mixture, the other initial product was probably Me_2PCl which could have reacted[6,7] with **2** to form other unidentified products, thus accounting for the low yield of **17**.

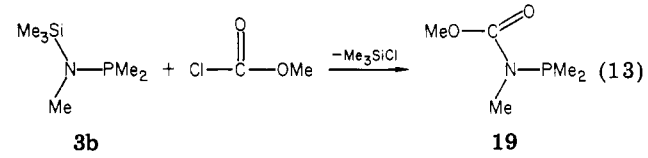
When phosphine **3a** was treated with methyl chloroformate (eq 12), a mixture of products was formed, being



(12)

comprised of about 50% of **18**. The other components of the mixture could not be identified and **18** was not obtained in sufficient purity for elemental analysis.

The (*N*-methyl-*N*-silylamino)phosphine **3b**, in which nitrogen is less sterically crowded, reacts in yet a different manner with methyl chloroformate. In this case, simple Si–N bond cleavage occurs, leading to formation of the *N*-methoxycarbonyl-substituted aminophosphine **19** in 76% yield (eq 13). Although it is an unusual mode of



(13)

reactivity for (silylamino)phosphines, nucleophilic attack by nitrogen in compounds bearing the $Me_3SiN(Me)$– group has been previously observed when strong electrophiles such as acid halides are involved.[6-8]

Conclusion

The results reported here and in the related paper[5] demonstrate that the reactions of (silylamino)phosphines with electrophilic organic substrates are useful for the preparation of a variety of new functionalized phosphinimines. In addition, some consistent reactivity trends in these systems are apparent: (1) (disilylamino)phosphines such as **1** react via nucleophilic attack by phosphorus followed by silyl group migration[5] or silyl halide elimination; (2) the cyclic compound **2** reacts similarly although Si–N bond cleavage is much less likely to occur in the initially formed products (see, for example, phosphonium salts **9** and **15**); (3) the *N-tert*-butyl derivative **3a** usually reacts like the (disilylamino)phosphines **1** but, quite often, side reactions and/or unstable products are obtained; and (4) when relatively strong electrophiles (e.g., methyl chloroformate) are used, the (*N*-methyl-*N*-silylamino)phosphine **3b** can react via nucleophilic attack by nitrogen rather than phosphorus.

Experimental Section

Materials and General Procedures. The (silylamino)phosphines were prepared according to the published procedures.[3,9] Dichloromethane was distilled and stored over molecular sieves prior to use. Ethyl bromoacetate, allyl bromide, and the chloroformates were obtained from commercial sources and used 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 a Varian EM390 or JEOL MH-100 spectrometer. 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.

Reaction of 1 with Ethyl Bromoacetate. Typically, phosphine **1a** (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. One equivalent of ethyl bromoacetate was then added via syringe to the stirred phosphine solution at 0 °C. The reaction was complete instantaneously. Evaporation of solvent left the phosphonium salt **4a** as a white, hygroscopic solid (mp 56–58 °C dec) which was identified by NMR spectroscopy (Table I). Anal. Calcd: C, 37.11; H, 8.04. Found: C, 37.10; H, 7.87. The salt **4b** was prepared from phosphine **1b** by using the same procedure.

Preparation of Phosphinimines 8. One equivalent of *n*-butyllithium or *tert*-butyllithium (1.6 M in hexane or 2.1 M in pentane, respectively) was added via syringe to a stirred CH_2Cl_2 solution of freshly prepared phosphonium salt **4a** (ca. 15 mmol) at 0 °C. The mixture was allowed to warm to room temperature while stirring for ca. 20 min. Filtration, solvent removal, and distillation afforded **8a** as a colorless liquid (50% yield, bp 42.5–44.5 °C (0.02 mm)). Anal. Calcd: C, 45.93; H, 9.42. Found: C, 46.17; H, 9.61. With use of the same procedure, the phosphinimine **8b** was prepared from **4b** (65% yield, bp 50.5 °C (0.02 mm)). Anal. Calcd: C, 50.16; H, 9.95. Found: C, 50.40; H, 9.98.

Reactions of 2 or 3a with Ethyl Bromoacetate. With use of the procedure described above for compound **1**, treatment of phosphines **2** or **3a** with ethyl bromoacetate gave the phosphonium salts **9** and **10**, respectively, which were identified by NMR spectroscopy (Table I). Anal. Calcd for compound **9**: C, 37.30; H, 7.56. Found: C, 37.02; H, 7.85 (mp 127–130 °C dec).

Reaction of 1a with Allyl Bromide. With use of the same procedure, phosphine **1a** was treated with 1 equiv of allyl bromide. If ice bath cooling is used and moisture is rigorously excluded, then only phosphonium salt **11** is observed. However, if allyl bromide is added at room temperature, causing the solvent to reflux, and a trace amount of moisture is introduced by briefly exposing the mixture to air, then some of the isomeric salt **12** can be observed by ^1H NMR.

Preparation of Phosphinimines 13 and 14. The solvent was removed from the reaction mixture in the preparation of salts **11** and **12** described above. The flask containing the remaining white solid was attached to a fractional distillation assembly. A vacuum of about 4 mm was applied and the flask was heated to ca. 70 °C at which point the solid liquefied and the products distilled. This procedure gave a mixture (84% yield, bp 54.5–55

(6) Nöth, H.; Storch, W. *Chem. Ber.* **1977**, *110*, 2607.
(7) Keat, R. *J. Chem. Soc. A* **1970**, 1795.
(8) Pudovik, M. A.; Kibardina, L. K.; Medvedeva, M. D.; Pudovik, A. N. *J. Gen. Chem. USSR (Engl. Trans.)* **1979**, *49*, 855.
(9) Wilburn, J. C. Ph.D. Dissertation, Duke University, Durham, NC, 1978.

Table I. NMR Spectroscopic Data[a]

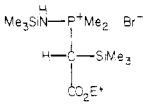
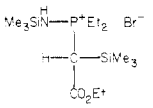
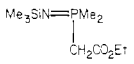
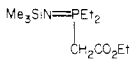
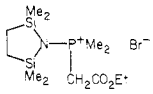
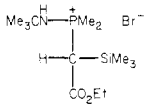
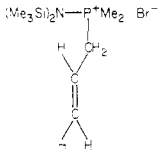
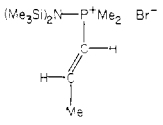
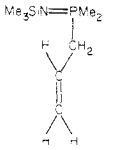
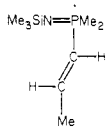
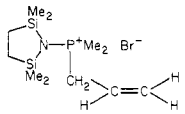
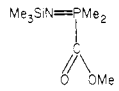
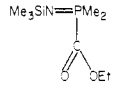
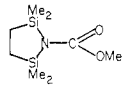
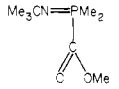
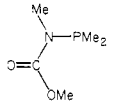
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 **4a**	Me_3SiN	0.09			−0.45		35.89
	Me_3SiC	0.01			−1.56		
	Me_2P	1.75	14.0		14.62	72.3	
	PCH	3.94	11.4		56.11	120.1	
	NH	5.59					
	OCH_2CH_3	1.12		6.9	11.95		
	OCH_2CH_3	3.89		6.9	64.91		
	C=O				164.90	5.9	
 **4b**	Me_3SiN	0.45[b]			0.43	1.8	47.96
	Me_3SiC	0.42			−0.93		
	PCH_2CH_3	1.27	19.2	7.3	4.47	4.9	
	PCH_2CH_3	2.36	12.8	7.3	18.60	50.1	
	PCH	3.55	8.3		51.80	115.4	
	NH	5.63					
	OCH_2CH_3	1.50		7.0	12.70		
	OCH_2CH_3	4.18		7.0	65.70		
	C=O				167.62	6.7	
 **8a**	Me_3SiN	−0.06	0.4		3.31	3.9	2.35
	Me_2P	1.46	12.6		18.49	71.3	
	PCH_2	2.78	14.4		41.32	52.7	
	OCH_2CH_3	1.21		7.0	13.58		
	OCH_2CH_3	4.09		7.0	60.36		
	C=O				166.76	4.9	
 **8b**	Me_3SiN	−0.06	0.4		3.61	2.9	11.78
	PCH_2CH_3	0.9–1.3[c]			5.43	4.9	
	PCH_2CH_3	1.4–1.8[c]			22.42	70.3	
	PCH_2CO_2	2.70	13.5		36.74	47.9	
	OCH_2CH_3	1.22		7.4	13.64		
	OCH_2CH_3	4.07		7.4	60.36		
	C=O				167.05	3.9	
 **9**	Me_2Si	0.46[b]			1.18		48.25
	$SiCH_2$	0.91			7.57	6.7	
	PMe_2	2.44	13.5		14.88	65.3	
	PCH_2	4.12	14.1		36.02	63.5	
	OCH_2CH_3	1.29		7.0	13.28		
	OCH_2CH_3	4.16		7.0	61.48		
	C=O				162.53	5.5	
 **10**	Me_3Si	0.32			−2.01		31.04
	Me_3C	1.28			29.04	3.9	
	Me_3C				50.74	3.9	
	PMe_2	1.91	13.0		13.51	72.3	
	PCH	3.87	12.0		56.37	116.2	
	NH	5.62					
	OCH_2CH_3	1.29		7.6	11.44		
	OCH_2CH_3	3.97		7.6	64.32		
	C=O				164.06	5.9	
 **11**	Me_3Si	0.44[b]					30.73
	Me_2P	2.35	12.6				
	PCH_2	3.54	13.4	5.9			
	PCCH	~5.8[d]		5.9			
	$PCCCH_2$	~5.0					
		~5.2					
 **12**	Me_3Si	0.44[b]					
	Me_2P	2.35	12.6				
	PCH	~5.7	*e*	16.7			
				1.4			
	PCCH	~6.7	*e*	16.7			
				6.3			
	PCCMe	2.03	2.6	6.1			
				1.4			
 **13**	Me_3Si	0.04[b]	0.4		3.51	4.3	7.08
	Me_2P	1.34	12.0		17.01	68.4	
	PCH_2	2.49	15.0	7.1	39.57	64.1	
	PCCH	5.5–6.0[d]		7.1	128.89	8.5	
	$PCCCH_2$	4.9–5.1		1.4	118.35	11.6	
		5.1–5.2		1.3			

Table I (*Continued*)

compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
	Me_3Si	0.04 [b]	0.4		3.51	4.3	0.08
	Me_2P	1.38	12.3		19.00	70.8	
	PCH	5.74	24.6	16.5	127.63	96.4	
				1.5			
	PC*CH*	6.46	20.0	16.5	141.74	1.8	
14				6.3			
	PCC*Me*	1.86	1.6	6.3	19.00	18.3	
				1.5			
	Me_2Si	0.44			1.22		50.09
	$SiCH_2$	0.90			7.17	6.7	
	Me_2P	2.22	13.2		13.26	64.1	
	PCH_2	3.42	15.4	6.1	33.42	59.8	
	PC*CH*	5.3-6.0 [d]		6.1	123.57	9.8	
15	PCC*CH*$_2$	5.3-6.0			123.25	13.4	
	Me_3Si	−0.13	0.4		2.34	3.9	−3.41
	Me_2P	1.47	13.5		16.93	73.2	
	OMe	3.67	0.8		51.00	2.0	
16a	C=O				172.37	117.2	
	Me_3Si	−0.07	0.4		2.60	3.9	−3.41
	Me_2P	1.50	13.3		16.99	73.2	
	OCH_2*CH_3*	1.06	1.0	7.1	13.32		
	O*CH_2*CH_3	4.16	0.7	7.1	60.56	2.0	
16b	C=O				172.18	117.2	
	Me_2Si	0.18					
	$SiCH_2$	0.71					
	OMe	3.54					
17							
	*Me_3*C	1.28	0.9		26.76	30.94	
	Me_3*C*				49.79	4.9	
	PMe_2	1.55	13.6		14.17	69.6	
	OMe	3.68	0.8		51.31	3.1	
18	C=O				170.88	134.8	
	Me_2P	1.15	7.8		13.95	17.7	38.06
	NMe	2.72	3.9		29.99	3.1	
	OMe	3.53			51.67	1.8	
19	C=O				157.44	12.2	

[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] Benzene/$CDCl_3$ solution used for ^{1}H NMR. [c] PEt_2 protons give a complex ABC_3X pattern. [d] Protons of allyl group give a complex $ABCM_2X$ pattern. [e] J_{PH} values could not be extracted from complex signals.

°C (2.1 mm)) of phosphinimines **13** and **14** consisting mainly of **14**. In order to obtain nearly pure **13**, we conducted the preparation of the salt **11** in a flask already attached to a distillation assembly and cooled to −78 °C. The reaction mixture was warmed to 0 °C, volatiles were removed at 0.2 mm, and almost pure **13** was distilled at 30–31 °C (0.2 mm). A gradual isomerization to **14** occurred over a period of several days. Anal. Calcd: C, 50.76; H, 10.65. Found: C, 50.79; H, 10.80.

Reaction of 2 with Allyl Bromide. Addition of 1 equiv of allyl bromide to a stirred solution of phosphine **2** (ca. 15 mmol) in CH_2Cl_2 (ca. 10 mL) at 0 °C gave phosphonium salt **15** which was identified by NMR spectroscopy (Table I). Anal. Calcd: C, 38.81; H, 7.99. Found: C, 37.72; H, 7.51 (mp 80–83 °C dec).

Preparation of Phosphinimines 16. In the same manner, a solution of phosphine **1a** in CH_2Cl_2 was treated with methyl chloroformate at 0 °C. Solvent was removed after a few minutes and distillation gave phosphinimine **16a** as a colorless liquid (67% yield, bp 54.5 °C (0.5 mm)). Anal. Calcd: C, 40.56; H, 8.75. Found: C, 40.78; H, 8.73. With use of the same procedure, **1a** and ethyl chloroformate gave phosphinimine **16b** (72% yield, bp 54.5 °C (0.3 mm)). Anal. Calcd: C, 43.42; H, 9.11. Found: C, 43.22; H, 9.04.

Reaction of 2 with Methyl Chloroformate. Phosphine **2** was treated with 1 equiv of methyl chloroformate in CH_2Cl_2 at 0 °C. Solvent was removed after 1 h. From the residual mixture, compound **17** was distilled as a colorless liquid (15% yield, bp 42–45 °C (0.7 mm)) which was identified by ^{1}H NMR spectroscopy. No phosphorus-containing products could be identified.

Reaction of 3a with Methyl Chloroformate. Similarly, phosphine **3a** was treated with methyl chloroformate. Solvent was removed after 30 min. Distillation gave a fraction (bp 50 °C (0.4 mm)) which contained about 50% of **18** as evidenced by ^{1}H NMR spectroscopy. Other products could not be identified. Approximate yield of **18**: 25%.

Preparation of Phosphine 19. Similarly, phosphine **3b** was treated with methyl chloroformate. Solvent was removed after a few minutes and distillation gave phosphine **19** as a colorless liquid (76% yield, bp 51.5 °C (3.3 mm)). Anal. Calcd: C, 40.27; H, 8.11. Found: C, 40.28; H, 8.04.

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Registry No. 1a, 63744-11-6; **1b**, 73270-05-0; **2**, 68437-96-7; **3a**, 68437-82-1; **3b**, 68437-84-3; **4a**, 80448-20-0; **4b**, 80448-21-1; **8a**, 80448-22-2; **8b**, 80448-23-3; **9**, 80448-24-4; **10**, 80448-25-5; **11**, 80448-26-6; **12**, 80448-27-7; **13**, 80448-28-8; **14**, 80448-29-9; **15**, 80448-30-2; **16a**, 80448-31-3; **16b**, 80448-32-4; **17**, 80448-33-5; **18**, 80448-34-6; **19**, 80448-35-7.