

Reaction of Silylaminophosphines with Acid Anhydrides

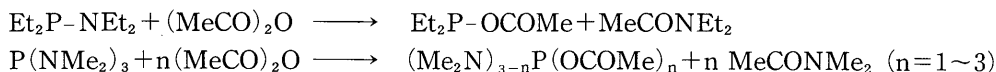
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(Received April 15, 1988)

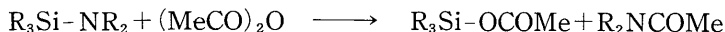
Reaction of [methyl(trimethylsilyl)amino] dialkylphosphines with acetic anhydride yields *N*-methyl-*N*-(dialkylphosphino)acetamides and trimethylsilyl acetate. The structures of the *N*-phosphinoacetamides were determined by the ^1H , ^{13}C and ^{31}P NMR and IR spectroscopy, and by their derivative chemistry. The unusual large $^4J_{\text{PNCCH}}$ or $^3J_{\text{PNCC}}$ and small $^3J_{\text{PNCH}}$ or $^2J_{\text{PNC}}$ coupling constants of the phosphinoacetamides are explained on the basis of their conformation and the dihedral angle dependence of the coupling constants. The phosphinoacetamide reacts with sulfur, iodomethane and $\text{Fe}_2(\text{CO})_9$ to yield the corresponding phosphine sulfide, phosphonium salt and phosphine iron carbonyl complex. Propionic anhydride, succinic anhydride and phthalic anhydride also react with [methyl(trimethylsilyl)amino] dialkylphosphines to give the corresponding *N*-methyl-*N*-(dialkylphosphino)carboxamides.

1. Introduction

Reaction of non-silylated aminophosphines such as $\text{Et}_2\text{P}-\text{NEt}_2^{1)}$ or $\text{P}(\text{NMe}_2)_3^{2)}$ with acetic anhydride proceeds with the phosphorus–nitrogen bond cleavage to yield acetoxyated phosphines and *N,N*-dialkylacetamides.



The Si–N bond of silylamines is cleaved by acetic anhydride to give trialkylsilyl acetates and *N,N*-dialkylacetamides.³⁾



However, there is no report concerning the reaction of silylaminophosphines with acid anhydrides. The chemistry of silylaminophosphines is often different from that of simple dialkylaminophosphines or trialkylsilylamines due to the combination of three characteristic hetero atoms, namely, phosphorus, nitrogen and silicon. They are known to react with

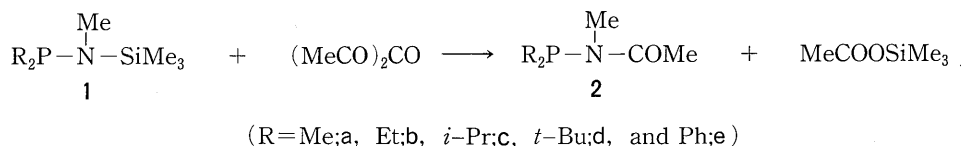
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carbonyl compounds such as ketones and aldehydes⁴⁾ to give addition and subsequent rearrangement products. This paper describes the silicon–nitrogen bond cleavage reaction of silylaminophosphines with acid anhydrides.

2. Results and Discussion

When $\text{Me}_2\text{PN}(\text{Me})\text{SiMe}_3$ (1a) was treated with acetic anhydride in ether at room temperature, a slow reaction took place to give *N*-methyl-*N*-(dimethylphosphino)acetamide (2a) and trimethylsilyl acetate. Other *N*-monosilylated aminodialkylphosphines (1b-e) also reacted with acetic anhydride to afford the corresponding *N*-(dialkylphosphino)-acetamides (2 b-e) along with trimethylsilyl acetate.



These products were characterized by ^1H , ^{13}C and ^{31}P NMR and IR spectra (Table 1). The ^1H NMR (60 MHz) spectrum of 2 a consists of three resonances as shown in Fig. 1; $\delta=2.85$ (3 H, s), 2.30 (3 H, d, $J_{\text{PH}}=5.0$ Hz), and 1.28 (6 H, d, $J_{\text{PH}}=6.3$ Hz). The singlet peak at $\delta=2.85$ is assigned to NMe protons because the reaction products of 1 with propionic anhydride give a singlet peak in this region and the ^1H NMR chemical shifts of NCH_3 and COCH_3 of

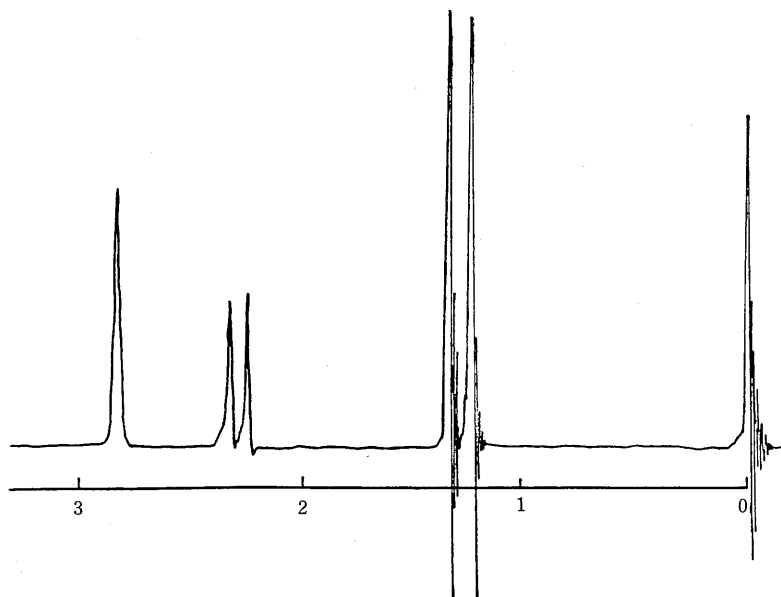


Figure 1. ^1H NMR Spectrum of $\text{Me}_2\text{PN}(\text{Me})\text{COMe}$ 2 a.

2 are similar values of *N*-methylacetamide. The other resonances at $\delta=1.28$ and 2.30 are assigned to PMe_2 and COMe groups, respectively, on the basis of their chemical shifts, coupling constants and relative intensities. The ^1H NMR spectra of 2 a and 2 e did not change

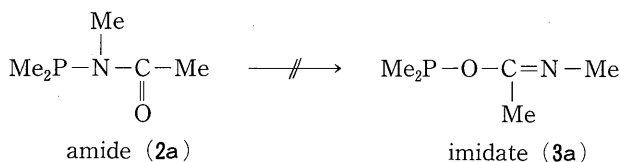
Table 1. Bp, Yield, NMR and IR Data for *N*-Methyl-*N*-(dialkylphosphino)acetamides (2 a-e)

R	Preparative data		NMR Spectra				IR, cm ⁻¹ ν (C=O)
	bp, °C/mmHg	yield, %	signal	¹ H δ (<i>J</i> _{PH})	¹³ C δ (<i>J</i> _{PC})	³¹ P δ	
Me	77–79/12	86	Me ₂ P	1.28(6.3)	14.87(17.6)	34.5	1660
			MeN	2.85	26.95(9.8)		
			COCH ₃	2.30(5.0)	23.24(23.4)		
			C=O		173.82(29.3)		
Et	47–51/0.9	73	CH ₃ CH ₂ P	0.70–1.88	8.83(15.6)	58.0	1665
			CH ₃ CH ₂ P		20.84(13.7)		
			MeN	2.78	26.62(9.8)		
			COCH ₃	2.31(4.6)	23.50(23.4)		
			C=O		173.94(33.4)		
<i>i</i> -Pr	40–43/0.15	81	CH ₃ CHP	0.87–1.32	18.91(23.4)	76.0	1665
					19.39(12.7)		
			CH ₃ CHP	2.04	23.78(21.5)		
			MeN	2.83	30.15(7.8)		
			COCH ₃	2.31(4.5)	25.86(15.6)		
			C=O		176.27(25.4)		
<i>t</i> -Bu	58–60/0.05	75	CH ₃ CP	1.25(12.6)			1665
			CH ₃ CP				
			MeN	3.08			
			COCH ₃	2.36(4.8)			
Ph	135–150/0.5	80	MeN	2.66	31.64(7.8)	54.8	1665
			COCH ₃	2.43(4.8)	23.39(21.5)		
			Ph(<i>p</i>)		128.52		
			(<i>m</i>)	7.36	129.23(9.8)		
			(<i>o</i>)		131.86(20.5)		
			(<i>i</i>)		135.81(14.7)		
			C=O		175.49(29.3)		

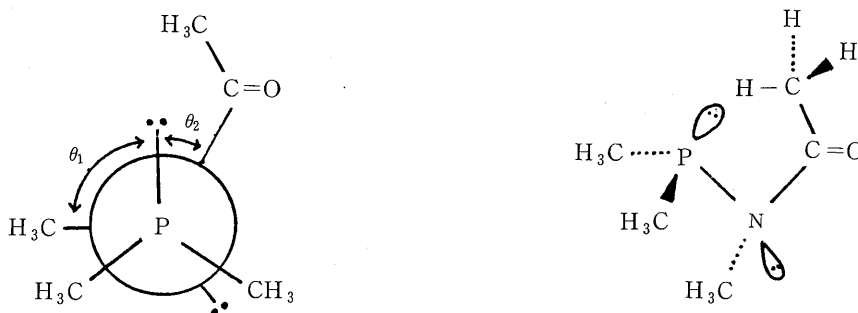
over temperature range –120–+80°C. The ¹³C{¹H} NMR spectrum of 2 a consists of the following resonances; Me₂P (δ =14.87, ¹*J*_{PC}=17.6 Hz), MeN (δ =26.95, ²*J*_{PC}=9.8 Hz), PNCMe (δ =23.24, ³*J*_{PC}=23.4 Hz) and CO (δ =173.82, ²*J*_{PC}=29.3 Hz), which are assigned on the basis of the selective decoupling and the comparison with the similar compound obtained by the reaction with other acid anhydrides such as propionic anhydride and isobutyric anhydride. Both ¹*J*_{PC} and ²*J*_{PH} coupling constants of alkyl groups on phosphorus of 2 are suitable for trivalent phosphorus compounds. But the *J*_{PH} and *J*_{PC} values of two methyl groups of PNCH₃COCH₃ in 2 a-e are worthy of attention because the ³*J*_{PNCH} coupling constants are usually 9–10 Hz and the ⁴*J*_{PNCH} is very small.⁵⁾

It has been reported that the [1,3]-migration of trimethylsilyl or germyl groups on nitrogen to the oxygen in γ -position are observed for trimethylsilyl⁶⁾ or-germyl⁷⁾ substituted

amides. Thus in this stage, there is a possibility of phosphino migration from the nitrogen to the oxygen of 2. However the imide structure is excluded by the chemical behaviors of 2 and conformational analyses by NMR.

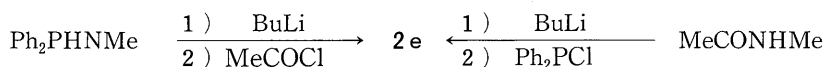


The conformational dependence of phosphorus coupling constants in trivalent phosphorus amides can be explained in terms of the dihedral angles between phosphorus lone pair and the N-C bonds.⁸⁾

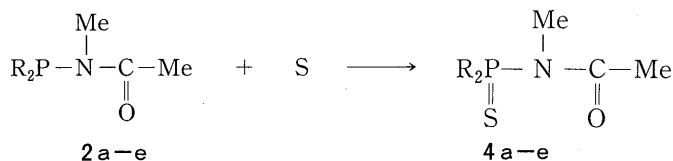


A large dihedral angle θ_1 between the lone pair of phosphorus and the N-CH₃ bond of 2a would lead to the small $^2J_{\text{PC}}$ value for PNCH₃, whereas a small angle θ_2 would lead to the large $^2J_{\text{PC}}$ value for the PNCO group. The small $^3J_{\text{PH}}=0$ value for NCH₃ would be also due to the dependence on a Karplus-like dihedral angle. The large coupling $^4J_{\text{PH}}$ (5 Hz) for the acetyl group is probably due to an interaction of the phosphorus lone pair with a methyl proton activated by the adjacent C=O group. A similar large coupling $^4J_{\text{PH}}$ is observed for the NH proton of Ph₂PN(R¹)CONHR².⁹⁾

The phosphinoacetamide 2e was synthesized by alternative ways. Lithiation of methyl(diphenylphosphino) amine and the following treatment with acetyl chloride gave 2e in a 40% yield. 2e was also prepared in a 56% yield by the reaction of chlorodiphenylphosphine with the lithium salt of *N*-methylacetamide which acted as a *N*-nucleophile, and the isomeric *O*-phosphinoamidate was not formed.



The phosphinoacetamides 2a-e reacted with sulfur to give the corresponding thio-phosphorylacetamides 4a-e.

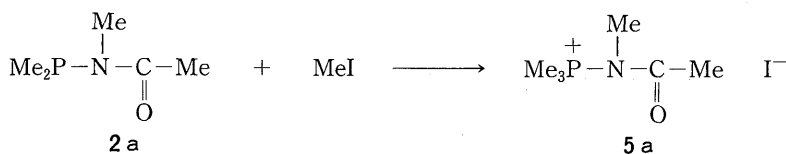


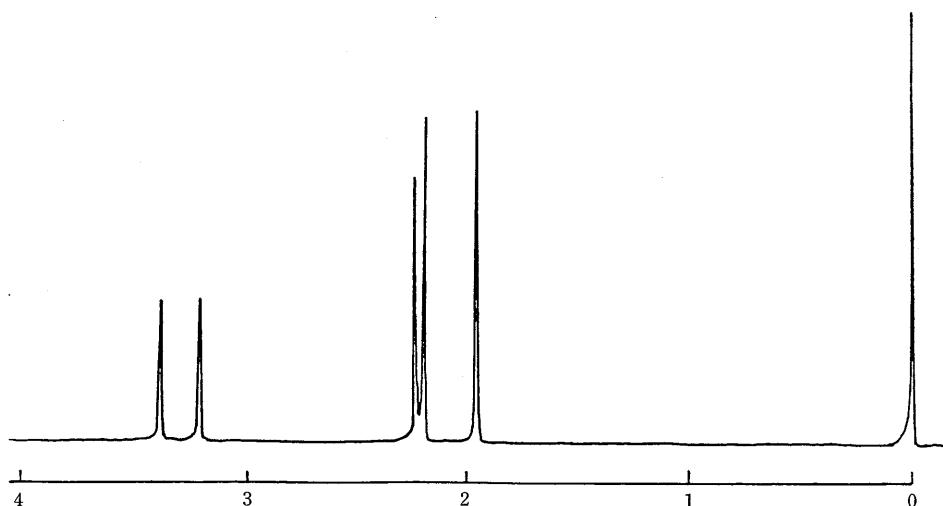
The doublet NCOCH_3 peak of **2 a** becomes a singlet peak in the phosphine sulfide **4 a** and the singlet NMe of **2 a** becomes a doublet in the ^1H NMR spectrum of **4 a** (Fig. 2). In the ^{13}C NMR spectra of **4**, $^3J_{\text{PC}}$ coupling constants of PNCCH_3 also are very small values. The large phosphorus–hydrogen coupling constant for the NMe signal of **4** ($^3J_{\text{PH}}=8.8\text{--}10.8\text{ Hz}$) in the ^1H NMR and the chemical shift in the ^{31}P NMR are reasonable for the pentavalent four coordinate thiophosphoryl amide structure.^{5,10)}

Table 2. NMR and IR Data for *N*-Methyl-*N*-(dialkylthiophosphoryl)acetamides (**4 a–e**)

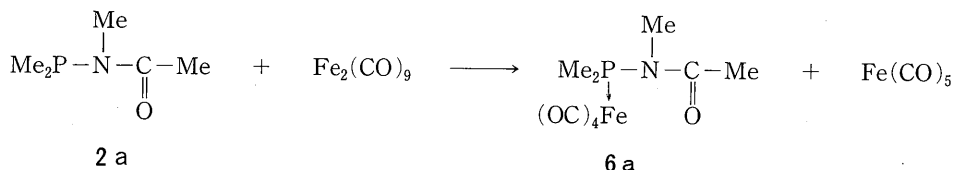
R	NMR spectra				IR, cm^{-1}	
	signal	$^1\text{H } \delta(J_{\text{PH}})$	$^{13}\text{C } \delta(J_{\text{PC}})$	$^{31}\text{P } \delta$	C=O	P=S
Me	Me_2P	2.08(14.2)	23.83(68.4)	72.8	1660	563
	MeN	3.30(10.8)	32.95(6.8)			735
	COCH_3	2.24	25.09			
	C=O		173.30			
Et	$\text{CH}_3\text{CH}_2\text{P}$	0.82–1.42			1650	726
	$\text{CH}_3\text{CH}_2\text{P}$					
	MeN	3.26(8.8)				
	COCH_3	2.25				
<i>i</i> -Pr	CH_3CHP	0.80–1.44	17.15(17.6)	110.3	1660	545
			17.28(13.7)			712
	CH_3CHP		29.69(56.6)			
	MeN	3.26(8.8)	34.24(3.9)			
	COCH_3	2.24	24.66(2.9)			
	C=O		174.84			
<i>t</i> -Bu	CH_3CP	1.41(16.8)			1665	690
	CH_3CP					
	MeN	3.37(9.0)				
	COCH_3	2.25				
Ph	MeN	2.06(9.0)	33.98(5.9)		1676	614
	COCH_3	2.10	25.40			728
	Ph(<i>m</i>)	7.15–8.12	128.52(13.7)			
	(<i>o</i>)		131.67(10.7)			
	(<i>p</i>)		131.90(3.9)			
	(<i>i</i>)		133.13(103.5)			
	C=O		174.13			

Reaction of **2 a** with iodomethane gave the phosphonium salt (**5 a**).



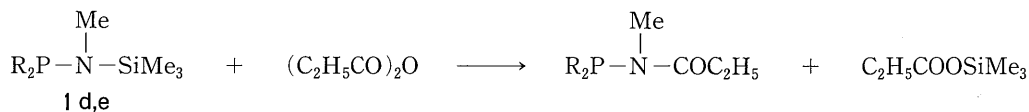
Figure 2. ^1H NMR Spectrum of $\text{Me}_2\text{P}(\text{S})\text{N}(\text{Me})\text{COMe}$ **4 a**.

Treatment of **2 a** with $\text{Fe}_2(\text{CO})_9$ afforded the phosphine iron carbonyl complex (**6 a**).

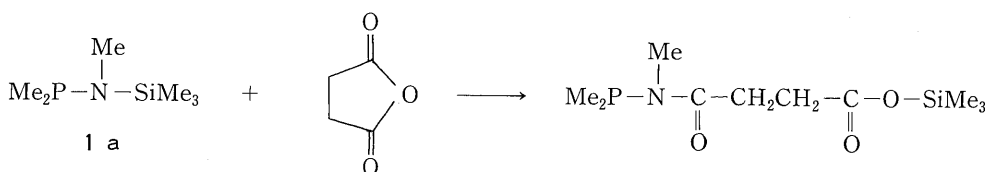


As the reaction products of **1** with acetic anhydride are trimethylsilyl acetate and phosphinoacetamides **2**, nucleophilic attack by the nitrogen to the carbonyl carbon and electrophilic attack by the silicon to the ether oxygen of acetic anhydride would occur in this reaction. The reaction of **1a** with acetic anhydride was carried out in ether, in dichloromethane or pentane, and also without solvent. The yields of **2 a** in each solvent were not so affected by the solvent polarity (ether 86%, dichloromethane 85%, pentane 92%, and no solvent 86%). These phenomena suggest that the reaction intermediate is not so ionic and that the reaction would proceed through a four-centered transition state.

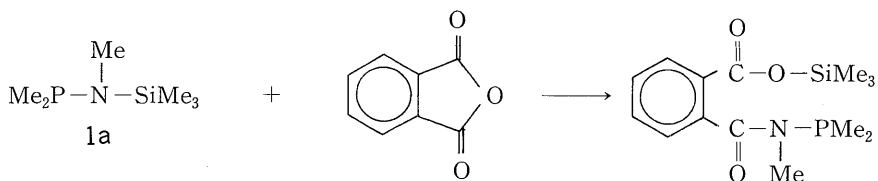
Propionic anhydride reacted with **1 d** and **1 e** in a similar manner to give trimethylsilyl propionate and the corresponding *N*-methyl-*N*-(dialkylphosphino)propionamides.



Reaction of succinic anhydride with **1a** gave trimethylsilyl 3-(*N*-methyl-*N*-dimethylphosphinocarbamoyl)propionate in a 77% yield.



Phthalic anhydride reacted with 1a to afford trimethylsilyl 2-(*N*-methyl-*N*-dimethylphosphinocarbamoyl)benzoate.



The reaction of acetic anhydride with [bis(trimethylsilyl) amino] dimethylphosphine or [t-butyl(trimethylsilyl) amino] dimethylphosphine gave trimethylsilyl acetate and several phosphorus compounds which could not be isolated by fractional distillation.

3. Experimental Section

All reactions were performed under an atmosphere of nitrogen or argon with reagents being transferred by a syringe. The ^1H NMR spectra were obtained with a JEOL C-60 HL or JNM FX-60 FT instrument using CDCl_3 as a solvent and tetramethylsilane as an internal standard. The ^{13}C and ^{31}P NMR spectra were recorded on a JEOL FX-60 FT spectrometer. The ^{31}P NMR chemical shifts were referenced to external 85% H_3PO_4 . The infrared spectra were measured on a Shimadzu IR-430 or JASCO A-1 spectrometer.

Materials. [Methyl(trimethylsilyl) amino] dimethylphosphine (1a) and diethylphosphine (1b) were prepared by the Wilburn-Neilson method.¹¹⁾ [Methyl(trimethylsilyl) amino]-diisopropylphosphine (1c), -di-*t*-butylphosphine (1d) and -diphenylphosphine (1e) were prepared according to the published procedures.¹²⁾ Acetic anhydride, propionic anhydride, succinic anhydride, phthalic anhydride, iodomethane, sulfur and dichloromethane were obtained from commercial sources and used without further purification. Diethyl ether, pentane, THF and benzene were dried by distillation over calcium hydride prior to use.

Reaction of [Methyl(trimethylsilyl) amino] dialkylphosphines with Acetic Anhydride. Acetic anhydride (1.05 g, 10.3 mmol) was added to a magnetically stirred solution of [methyl(trimethylsilyl) amino] dimethylphosphine (1.67 g, 10.2 mmol) in 10 mL of ether at 0°C . The mixture was allowed to warm to room temperature and stirred overnight. Solvent and volatile compounds were evaporated through a trap cooled at -50°C . This trap fraction was distilled to give trimethylsilyl acetate (1.04 g, 77%), bp $40-43^\circ\text{C}/80\text{ mmHg}$: ^1H NMR $\delta=0.20(\text{s}, 3\text{ H})$ and $1.96(\text{s}, 1\text{H})$, ^{13}C NMR $\delta=2.21, 22.94$, and 171.85 . IR(neat) 1724 cm^{-1} . From the residue *N*-methyl-*N*-(dimethylphosphino)acetamide (1.17 g, 86%) was obtained by distillation under reduced pressure, bp $77-79^\circ\text{C}/12\text{ mmHg}$, mp 39°C . Similar treatment of [methyl(trimethylsilyl) amino] diethylphosphine (1.43 g, 7.47 mmol) and acetic anhydride (0.78 g, 7.64 mmol) gave *N*-methyl-*N*-(diethylphosphino)acetamide (0.88 g, 73%) and trimethylsilyl acetate (0.90 g, 91%). Reaction of [methyl(trimethylsilyl) amino] diisopropylphosphine (1.95 g, 8.89 mmol) with an equimolar amount of acetic anhydride gave *N*-methyl-*N*-(diisopropylphosphino)acetamide (1.35 g, 81%) and trimethylsilyl acetate (1.01 g, 86%). Equimolar reaction of [methyl(trimethylsilyl) amino] di-*t*-butylphosphine (1.14 g, 4.61 mmol) with acetic anhydride afforded *N*-methyl-*N*-(di-*t*-butylphosphino)acetamide

(0.75 g, 75%) and trimethylsilyl acetate (0.49 g, 80%). *N*-Methyl-*N*-(diphenylphosphino)-acetamide (2.49 g, 80%) and trimethylsilyl acetate (1.55 g, 97%) were obtained by the equimolar reaction of [methyl(trimethylsilyl)amino] diphenylphosphine (3.57 g, 12.4 mmol) with acetic anhydride. Preparative and spectroscopic data for the *N*-methyl-*N*-(dialkylphosphino)acetamides were shown in Table 1.

*Reaction of [Methyl(trimethylsilyl)amino]di-*t*-butylphosphine with Propionic Anhydride.* Propionic anhydride (0.64 g, 4.92 mmol) was added to [methyl(trimethylsilyl)amino] di-*t*-butylphosphine (1.19 g, 4.81 mmol) at 0°C. The reaction mixture was allowed to stand overnight at room temperature. After removal of trimethylsilyl propionate, distillation under vacuum gave *N*-methyl-*N*-(di-*t*-butylphosphino)propionamide (0.42 g, 38%), bp 43–50°C/0.02 mmHg. ^1H NMR (CDCl_3) δ =1.25 (18 H, d, *t*-BuP, $^3J_{\text{PH}}=12.8$ Hz), 2.88 (2 H, dq, CH_3CH_2 , $^4J_{\text{PH}}=2.0$ Hz), and 3.08 (3 H, s, NMe). IR 1658 cm^{-1} (C=O).

Reaction of [Methyl(trimethylsilyl)amino]diphenylphosphine with Propionic Anhydride. Propionic anhydride (1.19 g, 9.14 mmol) was added slowly to [methyl(trimethylsilyl)amino] diphenylphosphine (2.76 g, 9.60 mmol) at 0°C. After removal of trimethylsilyl propionate, *N*-methyl-*N*-(diphenylphosphino)propionamide (2.30 g, 93%) was obtained by vacuum distillation (bp 135–140°C/0.03 mmHg). ^1H NMR δ =1.24 (3 H, t, CH_3CH_2 , $^3J_{\text{HH}}=7.8$ Hz), 2.95 (2 H, q, CH_3CH_2 , $^2J_{\text{HH}}=7.8$ Hz), 2.74 (3 H, s, NMe), and 7.36–7.43 (10 H, m, C_6H_5). ^{13}C NMR δ =10.36 (d, CH_3CH_2 , $J_{\text{PC}}=6.8$ Hz), 28.78 (d, CH_3CH_2 , $J_{\text{PC}}=21.5$ Hz), 31.84 (d, NMe, $J_{\text{PC}}=7.8$ Hz), 128.78 (d, *m*-, $J_{\text{PC}}=5.9$ Hz), 129.62 (s, *p*-), 131.99 (d, *o*-, $J_{\text{PC}}=20.5$ Hz), 135.31 (d, *i*-, $J_{\text{PC}}=14.7$ Hz), and 179.46 (d, C=O, $J_{\text{PC}}=27.3$ Hz). ^{31}P NMR δ =52.06. IR 1658 cm^{-1} (C=O).

Reaction of [Methyl(trimethylsilyl)amino]dimethylphosphine with Succinic Anhydride. A CH_2Cl_2 (20 mL) solution of succinic anhydride (0.9 g, 8.5 mmol) was added dropwise to [methyl(trimethylsilyl)amino]dimethylphosphine (1.4 g, 8.5 mmol) at -50°C . The mixture was stirred at room temperature overnight. Solvent was removed, and the residue was distilled (bp 88–90°C/0.08 mmHg) to give trimethylsilyl 3-(*N*-methyl-*N*-dimethylphosphinocarbamoyl)propionate (1.7 g, 77%). ^{13}C NMR δ =1.49 (Me_3Si), 14.90 (d, Me_2P , $J_{\text{PC}}=16.6$ Hz), 31.36 (d, NMe, $J_{\text{PC}}=5.9$ Hz), 30.10 (d, PNCC, $J_{\text{PC}}=10.7$ Hz), 26.23 (PNCCC), 172.84 (d, PNC=O, $J_{\text{PC}}=15.6$ Hz), and 177.32 (COOSi). ^{31}P NMR δ =31.9. IR 1660 cm^{-1} (PNC=O), 1716 cm^{-1} (COOSi).

Reaction of [Methyl(trimethylsilyl)amino]dimethylphosphine with Phthalic Anhydride. [Methyl(trimethylsilyl)amino]dimethylphosphine (1.9 g, 1.2 mmol) was added dropwise to a solution (THF 15 mL) of phthalic anhydride (1.8 g, 1.2 mmol) at -50°C . The reaction mixture was allowed to stand overnight at room temperature. The solvent was removed, and the residue was distilled (bp 98–102°C/0.07 mmHg) to give trimethylsilyl 2-(*N*-methyl-*N*-dimethylphosphinocarbamoyl)benzoate (0.3 g, 24%). ^{13}C NMR (CDCl_3) δ =0.06 (Me_3Si), 14.35 (d, Me_2P , $J_{\text{PC}}=17.6$ Hz), 26.91 (d, MeN, $J_{\text{PC}}=8.8$ Hz), 165.44 (OC=O), 175.15 (d, NC=O, $J_{\text{PC}}=38.1$ Hz), and 126.81–132.46 (Ph).

Preparation of N-Methyl-N-(diphenylphosphino)acetamide. 10.5 mL of *n*-BuLi (0.4 M, hexane) was added dropwise to 0.9 g (4.2 mmol) of Ph_2PNHMe in 10 mL of ether at -40 – -35°C . The mixture was warmed up to room temperature and was refluxed for 30 min. 0.3

g (4.2 mmol) of acetyl chloride was added slowly to this lithium amide solution at -40 – -35 °C. Immediately a white precipitate was formed, and the mixture was refluxed for 20 min. After removal of the precipitate and the solvents, a viscous yellow liquid was obtained. Distillation under vacuum gave *N*-methyl-*N*-(diphenylphosphino)acetamide (0.4 g, 40%), bp 37 – 45 °C/1.1 mmHg.

34.9 mL of *n*-BuLi (0.86 M in petroleum ether) was added to 2.5 g (34 mmol) of $\text{CH}_3\text{-CONHCH}_3$ in 100 mL of ether at 0°C. The mixture was stirred for 20 min at 0°C. 6.6 g (30 mmol) of Ph_2PCl in 30 mL of ether was added dropwise to the above lithium salt solution at 0°C and was stirred for 1 h at 0°C and then refluxed for 20 min. The precipitate of LiCl was filtered off and the organic layer was collected. Distillation gave *N*-methyl-*N*-(diphenylphosphino)acetamide (4.4 g, 56%).

Reaction of N-Methyl-N-(dialkylphosphino)acetamides with Sulfur. *N*-Methyl-*N*-(dimethylphosphino)acetamide (1.00 g, 7.51 mmol) was added to a stirred suspension of elemental sulfur (0.30 g, 9.38 mmol) in 10 mL of benzene. After 6 h of stirring, the solvent and excess sulfur were removed leaving *N*-methyl-*N*-(dimethylthiophosphoryl)acetamide in a 93% yield. Similar treatment of *N*-methyl-*N*-(dialkylphosphino)acetamides **2 b-e** with sulfur resulted in the formation of the corresponding thiophosphorylacetamides **4 b-e** in quantitative yields. Their ^1H , ^{13}C and ^{31}P NMR and IR spectral data were assembled in Table 2.

Reaction of N-Methyl-N-(dimethylphosphino)acetamide with Iodomethane. To an ethereal solution (20 mL) of *N*-methyl-*N*-(dimethylphosphino)acetamide (0.89 g, 6.69 mmol), iodomethane (1.62 g, 11.3 mmol) was added dropwise at 0°C. Removal of solvent gave the phosphonium iodide **5 a** (1.64 g, 89%) as white crystals, mp 102 – 3 °C. ^1H NMR δ = 1.69 (9 H, d, Me_2P , J_{PH} = 13.9 Hz), 3.28 (3 H, d, NMe, J_{PH} = 4.6 Hz), and 2.17 (3 H, s, COCH_3); ^{13}C NMR δ = 17.05 (d, Me_2P , J_{PC} = 69.3 Hz), 36.18 (d, NMe, J_{PC} = 2.0 Hz), 27.14 (COCH_3), and 174.27 (C=O); ^{31}P NMR δ = 61.2.

Reaction of N-Methyl-N-(dimethylphosphino)acetamide with $\text{Fe}_2(\text{CO})_9$. *N*-Methyl-*N*-(dimethylphosphino)acetamide (0.39 g, 2.93 mmol) and $\text{Fe}_2(\text{CO})_9$ (1.16 g, 3.18 mmol) in 30 mL of pentane were heated to 40 – 50 °C for 10 h with stirring. The reaction mixture was filtered through a glass-filter. By removal of the solvent and pentacarbonyliron, (*N*-acetyl-*N*-methylamino)dimethylphosphinetetracarbonyliron (0.54 g, 61%) was obtained as red crystals. ^1H NMR δ = 1.72 (6 H, d, Me_2P , J_{PH} = 9.0 Hz), 2.69 (3 H, d, NMe, J_{PH} = 9.3 Hz), and 2.54 (3 H, COCH_3); ^{13}C NMR δ = 22.95 (d, Me_2P , J_{PC} = 36.1 Hz), 36.00 (d, NMe, J_{PC} = 7.8 Hz), 23.50 (COCH_3), 173.10 (C=O), and 213.75 (d, FeCO, J_{PC} = 19.5 Hz); ^{31}P NMR δ = 125.1.

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