Synthesis and Properties of Some Silylphosphinoalkylamines

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Silylphosphinoalkylamines, $R^1_3Si\cdot NR^2\cdot PPh_2$ (R^1 = Me, R^2 = Me, Et, or Pr^i and R^1 = Ph, R^2 = Me), have been prepared by reactions of *N*-lithiated methylaminodiphenylphosphine with chlorosilanes, or of *N*-lithiated aminotrimethylsilanes with chlorodiphenylphosphine. The reaction of diphenylphosphino(trimethylsilyl)methylamine (R^1 = Me, R^2 = Me) to oxidation by sulphur or methyl iodide, cleavage by water, and cleavage by various halides of phosphorus [$Ph_2P(X)Cl$ (X = nothing or S), PCl_3, and $POCl_3$] have been investigated. All cleavage reactions take place preferentially at the silicon–nitrogen bond. The exchange reactions are compared with those between heptamethyldisilazane, $(Me_3Si)_2NMe$, and the phosphorus chlorides, $Ph_2P(X)Cl$ (X = nothing, O, or S). Aspects of the i.r. and ^1H n.m.r. spectra of these derivatives are reported and discussed.

THE chemistry of nitrogen-bridged tervalent phosphorus compounds,[1-3] $(R^1_2P)_2NR^2$ (diphosphinoamines), and of nitrogen-bridged silicon compounds,[4] $(R_3^1Si)_2NR^2$ (disilazanes) (R^1 = alkyl, aryl, or halogen; R^2 = H or alkyl), is reasonably well established. Their properties can often be rationalised in terms of electronegativity effects and conjugation of lone-pairs on the respective nitrogen atoms with the 3*d* orbitals of phosphorus or silicon.[5] Relatively little is known of the properties of silylphosphinoamines, $R^1_3Si\cdot N(R^1_2P)R^2$, which can provide information on the interdependence and relative strength of P–N and Si–N bonds.

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[1] G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, *J. Chem. Soc.*, 1964, 1543.

[2] A. B. Burg and J. Heiners, *J. Amer. Chem. Soc.*, 1965, **87**, 3072.

[3] J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2689.

[4] U. Wannagat, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 225.

[5] For a recent review, see K. A. R. Mitchell, *Chem. Rev.*, 1969, **69**, 157 and references therein.

Few examples of silylphosphinoamines have been reported. An unstable solid, formulated as dichlorophosphinotrimethylsilylamine, $Me_3Si{\cdot}NH{\cdot}PCl_2$, was obtained by reaction of phosphorus trichloride with hexamethyldisilazane, $(Me_3Si)_2NH$.[6] Recently, the syntheses of trimethylsilyl(di-t-butylphosphino)amine,[7] $Me_3Si{\cdot}NH{\cdot}PBu^t_2$, and of diphenylphosphino(trimethylsilyl)amine,[8] $Me_3Si{\cdot}NH{\cdot}PPh_2$, from chlorosilanes and metallated aminophosphines were described, and the reactivity of the NH group was discussed. The synthesis of compounds containing other types of Si–N–P skeleton has been reviewed recently.[9]

We have investigated the preparation of silyl(diphenylphosphino)alkylamines by the two general routes in the Scheme. The lithiated aminophosphines and aminosilanes were not isolated, but used *in situ*. In general, the yields were similar by both routes, but the former was preferred, because of difficulties in preparing *N*-methylaminotrimethylsilane.[10] Both series of reactions were carried out in solution in toluene at room temperature, except that a short period under reflux was necessary to complete the separation of lithium chloride by the first route. Diphenylphosphinomethyl(trimethylsilyl)amine (I), $Me_3Si{\cdot}NMe{\cdot}PPh_2$, and the analogous derivatives of ethylamine (II) and isopropylamine (III) were colourless, thermally stable liquids distillable under reduced pressure but diphenylphosphinomethyl(triphenylsilyl)amine (IV), $Ph_3Si{\cdot}NMe{\cdot}PPh_2$, readily crystallised.

$$\begin{tikzcd}
Ph_2P{\cdot}NHR + Bu^nLi \arrow[r, "i"] & Ph_2P{\cdot}N{\cdot}LiR + Bu^nH \arrow[d, "ii"] \\
 & Me_3Si{\cdot}NR{\cdot}PPh_2 \\
Me_3Si{\cdot}NHR + Bu^nLi \arrow[r, "i"] & Me_3Si{\cdot}N{\cdot}LiR \arrow[u, "iii"']
\end{tikzcd}$$

Reagents: i, toluene, 20°; ii, Me_3SiCl, toluene, 110°; iii, PhPCl, toluene, 20°.

SCHEME

The silylphosphinoalkylamines could also be formed from the reaction of heptamethyldisilazane, $(Me_3Si)_2NMe$, with chlorodiphenylphosphine at *ca.* 100°. However, compound (I) was not detected in the products, even with a 1 : 1 molar ratio of reactants, although reaction (1) might be expected to occur. Instead, the

$$Ph_2PCl + (Me_3Si)_2NMe \longrightarrow Me_3Si{\cdot}NMe{\cdot}PPh_2 + Me_3SiCl \quad (1)$$

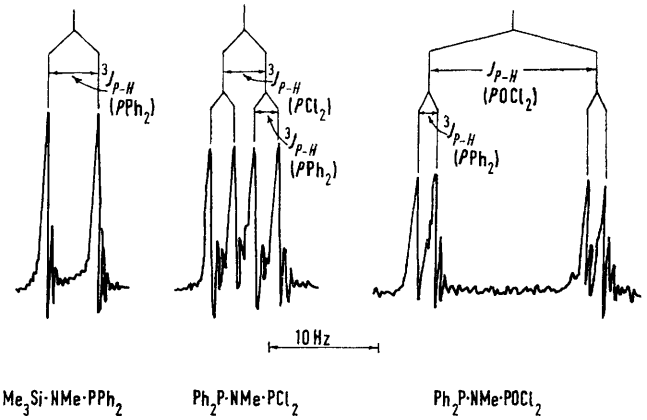
formation of bis(diphenylphosphino)methylamine, $(Ph_2P)_2NMe$,[1] was favoured, and unchanged heptamethyldisilazane was left. A similar reaction occurs with hexamethyldisilazane, $(Me_3Si)_2NH$.[11] Compound (I) appears to be more reactive than heptamethyldisilazane towards chlorodiphenylphosphine, and reaction (2) took place under similar conditions, but the relative reactivity

$$Me_3Si{\cdot}NMe{\cdot}PPh_2 + Ph_2PCl \longrightarrow (Ph_2P)_2NMe + Me_3SiCl \quad (2)$$

of (I) and heptamethyldisilazane towards chlorodiphenylphosphine could not be assessed in a simple way. In contrast, heptamethyldisilazane reacted with the analogous phosphorus(V) chlorides, $Ph_2P(X)Cl$ (X = O or S), with cleavage of only one Si–N bond.*

$$(Me_3Si)_2NMe + Ph_2P(X)Cl \longrightarrow Me_2Si{\cdot}NMe{\cdot}P(X)Ph_2 + Me_3SiCl$$

The sulphides of (I), (II), and (III) were obtained by reaction with elemental sulphur, and a quaternary salt of (I) was obtained by reaction with methyl iodide. The latter salt was not isolated in a pure state, but its hydrolysis product, methylaminodiphenylphosphine methiodide, suggested that phosphorus, rather than nitrogen in (I) was the site of quaternisation as expected.[12]



^1H N.m.r. spectrum of the *N*-methyl-signal of (I), and of the products obtained by reaction with phosphorus trichloride and oxychloride. In all cases, the integrated intensity of the signal, relative to the intensity of the aromatic proton signals, was consistent with the formulation suggested

Hydrolysis of (I), (II), and (III) was slow (several hours) in neutral or alkaline aqueous solutions, but very rapid in aqueous acid solution. The phosphine (I) was considerably more stable to hydrolysis than its oxide, sulphide, or methyl iodide quaternary salt. In all cases, the Si–N bond was cleaved before the P–N bond [reaction (3)].

$$Me_3Si{\cdot}NMe{\cdot}P(X)Ph_2 \xrightarrow{H_2O} (Me_3Si)_2O + NHMe{\cdot}P(X)Ph_2 \quad (3)$$

(X = nothing, O, S, or MeI)

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* When X = S, the reaction was not driven completely to the right under the conditions employed.

[6] M. Becke-Goehring and H. Krill, *Chem. Ber.*, 1961, **94**, 1059.

[7] O. J. Scherer and G. Schieder, *Chem. Ber.*, 1968, **101**, 4184.

[8] O. Schmitz-Dumont and W. Jansen, *Angew. Chem. Internat. Edn.*, 1968, **7**, 382.

[9] O. J. Scherer, *Organometallic Chem. Rev.*, 1968, *A*, **3**, 281.

[10] K. O. Sauer and R. H. Hasek, *J. Amer. Chem. Soc.*, 1964, **68**, 241.

[11] H. Nöth and L. Meinel, *Z. anorg. Chem.*, 1967, **349**, 225.

[12] G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.*, 1962, 3984.

The products were identified by ^{1}H n.m.r. spectroscopy and by isolation of the four (methylamino)phosphorus derivatives, NHMe·P(X)Ph$_2$. These results suggest that the silicon atom is the site of hydrolytic attack. A formal increase in the positive charge at phosphorus is likely to result from oxidation at that centre. The transmission of this effect to silicon should render the latter atom more susceptible to nucleophilic attack than in the case of (I). The sulphides of (II) and (III) were less susceptible to hydrolysis than that of (I), suggesting that nucleophilic attack at silicon can be sterically hindered by large *N*-alkyl substituents (assuming that differences in inductive effects of the alkyl substituents are small).

I.r. and ^{1}H n.m.r. data [a]

Compound	ν_{as} (Si–N–P) or ν_{as} (P–N–P) (cm^{-1})	τ (NMe)	^3J (P^{III}–N–C–H) (Hz)	^3J (P^{V}–N–C–H) (Hz)	τ (SiMe)	^4J (P^{III}–N–Si–C–H) (Hz)
Me$_3$Si·NMe·PPh$_2$ (I)	872 [b]	7·67	5·1		9·76	1·3
Me$_3$Si·NMe·P(:S)Ph$_2$	880 [b]	7·46		15·2	9·82	0
Me$_3$Si·NMe·P(:O)Ph$_2$	882 [b]	7·99		13·6	9·79	0
Me$_3$Si·NMe·P$^+$MePh$_2$I$^-$ [c]		*ca.* 7·1		12·6 or 14·6 [d]	9·80	0
Ph$_2$P·NMe·PPh$_2$	849 [e]	7·60	2·9 (triplet)			
Ph$_2$P·NMe·P(:S)Ph$_2$	853 [e]	7·38	1·7	11·8		
Ph$_2$P·NMe·P(O)Cl$_2$ [c]		6·85	1·6	16·0		
Ph$_2$P·NMe·PCl$_2$ [c]		7·23	2·3, 4·1 (PCl$_2$)			
Me$_3$Si·NEt·PPh$_2$ (II)	890 [b]	6·93 [f]	6·8		9·71	1·2
Me$_3$Si·NEt·P(:S)Ph$_2$		6·90 [f]		19·2	9·74	0
Me$_3$Si·NPr^i·PPh$_2$ (III)	860 or 883 [b]	6·3 [f]			9·84	0·9
Me$_3$Si·NPr^i·P(:S)Ph$_2$		6·2 [f]			9·77	0
Ph$_3$Si·NMe·PPh$_2$ (IV)	873 [e]	7·48	4·1			

[a] For solution in deuteriochloroform at 33°. [b] As liquid film. [c] Not purified, tentative assignments only. [d] PMe and NMe signals not distinguished. [e] For KBr disc. NCH$_2$ or NCH protons.

The reactions of silylamines with compounds containing P–Cl bonds provide a convenient route to P–N derivatives.[13] It is therefore not surprising that the reactions of (I) with halides of phosphorus provide a method of introducing the Ph$_2$P–NMe substituent [equation (4)]. The reactions with phosphorus trichloride and oxychloride were strongly exothermic and

$$\mathrm{Me_3Si{\cdot}NMe{\cdot}PPh_2 + XCl \longrightarrow XNMe{\cdot}PPh_2 + Me_3SiCl} \quad (4)$$

$$[\mathrm{X = PCl_2,\ PPh_2\ P(O)Cl_2,\ or\ P(S)Ph_2}]$$

^{1}H n.m.r. spectroscopy indicated that Ph$_2$P·NMe·PCl$_2$ and Ph$_2$P·NMe·P(O)Cl$_2$ were formed. However, in both cases, attempted distillation gave chlorodiphenylphosphine and nonvolatile materials which have not yet been characterised. Presumably, polymers or oligomers are formed by condensation [*e.g.*, equation (5)]:

$$e.g.\quad n\mathrm{Ph_2P{-}N(Me){-}PCl_2} \longrightarrow [\mathrm{N(Me){-}PCl}]_n + n\mathrm{Ph_2PCl} \quad (5)$$

The formation from (I) of compounds containing P–N bonds could be favoured by loss of volatile chlorotrimethylsilane (b.p. 59°). Reaction of (IV) with chlorodiphenylphosphine in a 1 : 1 molar ratio shows that here also P–N bond formation is favoured in the presence of nonvolatile chlorotriphenylsilane [equation (5)]. The

$$\mathrm{Ph_3Si{\cdot}NMe{\cdot}PPh_2 + Ph_2PCl \longrightarrow (Ph_2P)_2NMe + Ph_3SiCl} \quad (6)$$

same reaction of (I) with chlorodiphenylphosphine in a sealed tube was followed by ^{1}H n.m.r. spectroscopy. Bis(diphenylphosphino)methylamine (>95%) was formed in the presence of chlorotrimethylsilane.

The i.r. spectra of the silyl(phosphino)amines and their derivatives all feature strong bands in the region 1000—800 cm^{-1}. A band generally near 840 cm^{-1} is associated with a deformation mode of the trimethylsilyl group.[14] The remaining band in this region is related to the P–N and Si–N stretching modes. By analogy with studies on disilazanes [15] and diphosphinoamines [2,3] it appears likely that this band arises from the asymmetric stretching mode ν_{as} (Si–N–P). Suggested assignments are listed in the Table.

The ^{1}H n.m.r. data for the compounds isolated in this study are also listed in the Table. For a wide range of alkylamino-derivatives of tervalent phosphorus, the *P*–N–C–*H* coupling constant $^3J_{\mathrm{P-H}}$ is in the range 9—16 Hz.[16] However, the values reported here are generally much smaller. These coupling constants are thus reduced by replacement of the bond to an alkyl-group (R) at the nitrogen atom in an aminophosphine, Ph$_2$P·N(R)Me, by a bond to a silicon or phosphorus atom in the group Y to produce a derivative, Ph$_2$P·NMeY. This effect is also apparent in the related derivatives, (X$_2$P)$_2$NMe (X = Cl or F) [3] ($^3J_{\mathrm{P-H}}$ 3·0 and 3·2 Hz respectively), and in hydrazino-derivatives of phosphorus PhP(NMe·NMe$_2$)$_2$ [17] or (CF$_3$)$_2$PN·MeNMe$_2$ [18] ($^3J_{\mathrm{P-H}}$ 5·0 and 3 Hz respectively).

$^3J_{\mathrm{P-H}}$ is reduced relative to the value in bis(diphenylphosphino)methylamine (Y = PPh$_2$) by oxidation of the

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[13] E. W. Abel, D. A. Armitage, and G. R. Willey, *J. Chem. Soc.*, 1965, 57.

[14] H. Bürger, *Organometallic Chem. Rev.*, 1968, *A*, **3**, 425.

[15] J. Goubeau and J. Jiménez-Barbará, *Z. anorg. Chem.*, 1960, **303**, 217.

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[17] J. M. Kanamueller and H. H. Sisler, *Inorg. Chem.*, 1967, **6**, 1767.

[18] L. K. Peterson, G. L. Wilson, and K. I. Thé, *Canad. J. Chem.*, 1969, **47**, 1025.

phosphorus atom in the group Y [*e.g.* to give Y = P(S)Ph_2], or by an increase in the electronegativity of the groups bonded to phosphorus in Y (*e.g.* when Y = PCl_2). Both substituent effects may be expected to strengthen the N–Y bond and weaken the Ph_2P–N bond. Evidence also in favour of this effect of oxidation on P–N bond strengths comes from the recent observation[19] that the P^V–N bond in $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$ is significantly shorter than the P^{III}–N bond. A correlation may exist, therefore, between $^3J_{P-H}$ and P–N (or N–Y) bond strengths; this is under investigation.

Coupling between phosphorus(V) and the *N*-methyl protons is within the range 11—16 Hz, as expected from literature values.[16]

EXPERIMENTAL

All operations were carried out under dry nitrogen. Chlorotrimethylsilane, chlorodiphenylphosphine, phosphorus trichloride, phosphorus oxychloride, and chlorotriphenylsilane were obtained commercially and all, except the latter, were distilled before use. Chlorodiphenylphosphine oxide and sulphide were prepared by oxidation of chlorodiphenylphosphine by dimethyl sulphoxide and sulphur, respectively. Alkylaminosilanes, heptamethyldisilazane,[20] and methylaminodiphenylphosphine[21] were prepared by literature methods. n-Butyl-lithium was obtained commercially, or prepared from n-butyl chloride and lithium in pentane.[22]

I.r. spectra were recorded with Perkin-Elmer 225 and 457 spectrometers, for liquid films, or potassium bromide discs. ^1H N.m.r. spectra were recorded on Perkin-Elmer R10 and/or Varian HA100 spectrometers, operating at 60 and 100 MHz, respectively. Mass spectra were obtained on an A.E.I. MS12 spectrometer.

Diphenylphosphinomethyl(trimethylsilyl)amine (I).—(a) *From (methylamino)diphenylphosphine.* In a typical experiment, to methylaminodiphenylphosphine (12·4 g, 0·057 mol) in toluene (250 ml) was added with stirring to a 2·20 M-solution of n-butyl-lithium in hexane (26·1 ml, 0·057 mol). The mixture soon boiled and was allowed to cool (30 min) before trimethylchlorosilane (7·3 ml, 0·057 mol) was added. The mixture was then boiled under reflux and a white precipitate formed after *ca.* 15 min. The mixture was heated under reflux for a further 45 min, and then cooled, and the precipitate was filtered off. Toluene and hexane were distilled from the filtrate at atmospheric pressure and the oily residue was fractionally distilled under reduced pressure to give *diphenylphosphinomethyl(trimethylsilyl)amine* (I) (12·5 g, 75%), b.p. 106—109°/0·03 mm [Found: C, 66·9; H, 7·7; N, 4·3%; *M* (mass spectrum), 287. $C_{16}H_{22}NPSi$ requires C, 66·9; H, 7·65; N, 4·9%; *M*, 287 (for $C_{16}H_{22}NP^{28}Si$)].

(b) *From (methylamino)trimethylsilane.* (Methylamino)trimethylsilane (5·85 g, 0·056 mol) dissolved in toluene (80 ml) was mixed with a 2·20 M-solution of n-butyl-lithium (25·6 ml, 0·056 mol). The mixture was stirred (15 min) and chlorodiphenylphosphine (12·42 g, 0·056 mol) was added. A white precipitate was formed immediately, which was filtered off after the solution had been stirred for 1 hr. Solvent was removed from the filtrate and the residue was distilled under reduced pressure to give *diphenylphosphinomethyl(trimethylsilyl)amine* (12·8 g, 79%), b.p. 94—98°/0·005 mm [^1H n.m.r. and i.r. spectra identical with the product from route (a)].

Diphenylphosphinoethyl(trimethylsilyl)amine (II), and *diphenylphosphinoisopropyl(trimethylsilyl)amine* (III) were prepared by a method similar to (b) from ethyl(trimethylsilylphosphine)amine and isopropyl(trimethylsilyl)amine, respectively to give (II) (69%), b.p. 110—115°/0·01 mm. (Found: C, 68·0; H, 7·9; N, 4·6. $C_{17}H_{24}NPSi$ requires C, 67·8; H, 8·0; N, 4·6%), and (III) (61%), b.p. 118—120°/0·4 mm (Found: C, 68·2; H, 8·0; N, 4·0. $C_{18}H_{26}NPSi$ requires C, 68·6; H, 8·3; N, 4·4%).

Diphenylphosphinomethyl(triphenylsilyl)amine (IV).—Methylaminodiphenylphosphine (2·68 g, 0·0125 mol) in toluene (30 ml) and a 1·60 M-solution of n-butyl-lithium (7·8 ml, 0·0125 mol) in hexane were stirred (20 min). Triphenylsilyl chloride (3·68 g, 0·0124 mol) in toluene (40 ml) was added and the mixture was boiled under reflux (3 hr). Lithium chloride was filtered off and the solvent was distilled off at atmospheric pressure. A solution of the oily residue in the minimum volume of light petroleum (b.p. 60—80°) was filtered and crystals were formed when the filtrate was set aside. Recrystallisation from light petroleum (b.p. 40—60°)–chloroform (10 : 1) gave *diphenylphosphinomethyl(triphenylsilyl)amine* (IV) (2·6 g, 44%), m.p. 115—116° [Found: C, 76·8; H, 6·0; N, 3·5; *M* (mass spectrum), 473. $C_{31}H_{28}NPSi$ requires C, 78·6; H, 5·9; N, 3·0; *M*, 473 (for $C_{31}H_{28}NP^{28}Si$)].

Diphenylphosphinothioylmethyl(trimethylsilyl)amine.—*Diphenylphosphinomethyl(trimethylsilyl)amine* (I) (1·4 g, 0·0048 mol), was heated (*ca.* 100°) with sulphur (0·015 g, 0·0048 mol) (10 min). The product was distilled to give (diphenylphosphinothioyl)methyltrimethylsilylamine (0·7 g, 45%), b.p. 150—155°/0·001 mm (Found: C, 59·6; H, 6·6; P, 10·2. $C_{16}H_{22}NPSSi$ requires C, 60·2; H, 6·9; P, 9·7%). This derivative hydrolysed rapidly in air to give diphenylphosphinothioylmethylamine, m.p. 135° (Found: C, 64·5; H, 5·1. $C_{13}H_{13}NPS$ requires C, 64·6; H, 5·4%).

Similar reaction of compounds (II) and (III) with sulphur and subsequent crystallisation from light petroleum (b.p. 40—60°)–ether (1 : 1) gave *diphenylphosphinothioylethyl(trimethylsilyl)amine* (84%), m.p. 109—110° (Found: C, 60·4; H, 6·8; N, 4·3. $C_{17}H_{24}NPSSi$ requires C, 61·3; H, 7·2; N, 4·2%) and *diphenylphosphinothioylisopropyl(trimethylsilyl)amine* (72%), m.p. 101—102° (Found: C, 62·3; H, 7·3; N, 4·0. $C_{18}H_{26}NPSSi$ requires C, 62·2; H, 7·5; N, 4·0%).

Reactions of diphenylphosphinomethyl(trimethylsilyl)amine (I).—(a) *With water.* Equal volumes of compound (I) and water were heated in air (1 hr) at 100°. The ^1H n.m.r. spectrum of the resultant chloroform-miscible portion showed that <10% of (I) had been hydrolysed to methylaminophenylphosphine and hexamethyldisiloxane. Similar results were obtained with dilute sodium hydroxide solution, but in dilute hydrochloric acid the silicon–nitrogen bond was cleaved completely within *ca.* 10 min.

(b) *With chlorodiphenylphosphine.* Compound (I) (1·3 g,

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[19] K. M. Ghouse, R. Keat, H. H. Mills, and J. M. Robertson, *Chem. Comm.*, 1969, 1195.

[20] R. C. Osthoff and S. W. Viantor, *Inorg. Synth.*, 1957, **5**, 58.

[21] W. Sim, Ph.D. Thesis, Glasgow, 1968.

[22] E. H. Amonoo-Neizer, R. A. Shaw, B. O. Skevlin, and B. C. Smith, *Inorg. Synth.*, 1966, **8**, 20.

0·0045 mol) and chlorodiphenylphosphine (1·0 g, 0·0045 mol) were heated (120°) at atmospheric pressure (2 hr). Trimethylchlorosilane distilled off and the residue was recrystallised from ethanol to give bis(diphenylphosphino)-methylamine[12] (1·4 g, 78%), m.p. 114—116°. This reaction was repeated in a sealed n.m.r. tube with equimolar quantities of reactants. The ^{1}H n.m.r. spectrum showed that bis(diphenylphosphino)methylamine (>95%) had been formed.

(c) *With chlorodiphenylphosphine sulphide.* Compound (I) (0·96 g, 0·0033 mol) and chlorodiphenylphosphine sulphide (0·84 g, 0·0033 mol) were heated at atmospheric pressure until trimethylchlorosilane distilled out (oil-bath; 150°). The oily residue was recrystallised from benzene–light petroleum (b.p. 60—80°) (1 : 1) to give diphenylphosphinomethyl(diphenylphosphinothioyl)amine (0·65 g, 52%). m.p. 150—151° (Found: C, 70·05; H, 5·6; N, 3·5. $C_{25}H_{23}NP_2S$ requires C, 69·7; H, 5·3; N, 3·1%).

(d) *With phosphorus trichloride.* Phosphorus trichloride (0·43 g, 0·0031 mol) was condensed onto compound (I) (0·89 g, 0·0031 mol) *in vacuo*. Nitrogen was then introduced over the mixture and the mixture turned yellow. Trimethylchlorosilane was distilled out and the residue was heated *in vacuo*. Chlorodiphenylphosphine, b.p. 116°/0·3 mm, distilled off and was identified by its i.r. and ^{1}H n.m.r. spectra. The residue decomposed before distillation occurred. The experiment was repeated in deuteriochloroform solution in an n.m.r. tube. The ^{1}H n.m.r. spectrum (Figure) initially showed a doublet centred at τ 7·67 (I) which quickly disappeared on addition of phosphorus trichloride to give a four-line signal centred at τ 7·23 and a singlet at τ 9·66 (trimethylchlorosilane). The signal at τ 7·23, and its integrated intensity indicated the formation of diphenylphosphino(dichlorophosphino)methylamine. However, satisfactory analytical data were not obtained from the yellow residue left after removal of deuteriochloroform and trimethylchlorosilane.

(e) *With phosphorus oxychloride.* Equimolar quantities of compound (I) and phosphorus oxychloride were heated as in (d) to give chlorodiphenylphosphine. The reaction was repeated in an n.m.r. tube and the ^{1}H n.m.r. spectrum (Figure) suggested that diphenylphosphino(dichlorophosphinyl)methylamine had been formed.

(f) *With methyl iodide.* Addition of methyl iodide (0·28 g, 0·020 mol) to a solution of (I) (0·5 g, 0·017 mol) in ether (10 ml) rapidly gave a colourless oil. The ether was removed leaving a hygroscopic white solid, m.p. 90—95°. Satisfactory analytical data were not obtained, but the ^{1}H n.m.r. spectrum indicated the presence of two types of methyl group and the integrated intensities of the four groups of protons were consistent with those expected for diphenylphosphinomethyl(trimethylsilyl)amine methiodide. Hydrolysis occurred rapidly in air to give methylaminophenylphosphine methiodide,[1] m.p. 108—110°.

Reaction of Diphenylphosphinomethyl(triphenylsilyl)amine (IV) *with Chlorodiphenylphosphine.*—Equimolar quantities of (IV) and chlorodiphenyl phosphine were heated (140°) for 12 hr. The ^{1}H n.m.r. spectrum of the products showed that *ca.* 95% conversion into bis(diphenylphosphino)-methylamine had taken place.

Reactions of Heptamethyldisilazane.—(a) *With chlorodiphenylphosphine.* Chlorodiphenylphosphine (5·6 g, 0·025 mol) and heptamethyldisilazane (4·4 g, 0·025 mol) were mixed at 0°. The mixture was heated (oil-bath, *ca.* 100°) and trimethylchlorosilane (2·4 g) distilled out. The ^{1}H n.m.r. spectrum of the residue indicated the presence of unchanged heptamethyldisilazane. Crystals of bis(diphenylphosphino)methylamine[1] (2·4 g, 47%, based on Ph_2PCl) m.p. 114—116°, were formed when a solution of the residue in ether was set aside. The reaction was repeated with a 2 : 1 molar ratio of chlorodiphenylphosphine to heptamethyldisilazane. Bis(diphenylphosphino)methylamine was obtained (78%).

(b) *With chlorodiphenylphosphine oxide.* Chlorodiphenylphosphine oxide (2·6 g, 0·011 mol) and heptamethyldisilazane (1·95 g, 0·011 mol) were heated (*ca.* 100°) and chlorotrimethylsilane distilled out. The residue was then fractionally distilled to give (*diphenylphosphinyl*)*methyltrimethylsilylamine* (1·9 g, 55%), b.p. 140—145°/0·005 mm (Found: C, 62·9; H, 7·0; P, 10·6. $C_{16}H_{22}NOPSi$ requires C, 63·3; H, 7·3; P, 10·2%).

(c) *With chlorodiphenylphosphine sulphide.* Chlorodiphenylphosphine sulphide and heptamethyldisilazane (1 : 1 mol ratio) were heated together, but distillation occurred at 148—150° and the distillate was identified as unchanged heptamethyldisilazane. ^{1}H N.m.r. examination of the residue showed, however, that some reaction had occurred, for small quantities of material with identical ^{1}H n.m.r. parameters to (diphenylphosphinotrimethylsilylthioyl)-methylamine (reported before) were present.

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