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Synthesis of Dichlorophosphinyl and Dichlorophosphinothioyl Derivatives of Methylamine

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Bis(dichlorophosphinyl)methylamine, $[Cl_2P(:O)]_2NMe$, has been prepared by the reaction of phosphoryl(V) chloride with dichlorophosphinylmethylamine, Cl₂P(:O) NHMe, and with heptamethyldisilazane, (Me₃Si)₂NMe. The former reaction has been extended to prepare the analogous monophenyl derivative, Cl₂P(:O)·NMe·P(:O)ClPh, and reactions involving heptamethyldisilazane were adapted to give the dichlorophosphinyl derivatives, Cl₂P-characterised by elemental analyses, and by i.r., mass, ¹H and -¹P n.m.r. spectroscopy. The n.m.r. results are discussed in detail.

MANY phosphorus-nitrogen compounds containing the $X_2P(Y)-N-P(Y)X_2$ skeleton are known in which a range of substituents $(X = F^{1}, C^{1,2}, alkyl^{3,4}, or Ph^{5})$ are bonded to phosphorus(III) atoms (Y = lone pair), or $(X = Ph^{5} \text{ or NHMe }^{6})$ bonded to phosphorus(v) (Y = O)or S). In the latter series, no examples * where X is a halogen atom have been reported [except for $Cl_2P(:O)\cdot NH\cdot P(:O)F_2$ ⁷] because of an absence of suitable synthetic routes.

We now describe the syntheses of bis(dichlorophosphinyl)methylamine, [Cl₂P(:O)]₂NMe, from reactions of phosphoryl(v) chloride with dichlorophosphinylmethylamine, Cl₂P(:O)·NHMe, or heptamethyldisilazane, (Me₃Si)₂NMe. The latter route proved particularly versatile because we were able to isolate the intermediate, dichlorophosphinylmethyl(trimethylsilyl)amine, $Cl_2P(:O)$ ·NMe·SiMe₃, and cleave the second siliconnitrogen bond by reaction with phosphorus trichloride to give dichlorophosphino(dichlorophosphinyl)methylamine, Cl₂P(:O)·NMe·PCl₂. Related procedures were utilised to synthesise Cl₂P(:S)·NMe·PCl₂ and Cl₂P-(:O)·NMe·P(:S)Cl₂.

The reaction between methylamine hydrochloride and phosphoryl(v) chloride was first investigated by Michaelis,⁸ who isolated a methylamino-derivative, $Cl_2P(:O)$ ·NHMe [reaction (1)]. This reaction has been

$$\frac{\text{MeNH}_{3}\text{Cl}^{-} + P(:O)\text{Cl}_{3} \longrightarrow}{\text{Cl}_{2}P(:O)\cdot\text{NHMe} + 2\text{HCl}} (1)$$

repeated,^{9,10} but attempts to eliminate a second mole of hydrogen chloride were unsuccessful. We have found that most of the methylamino-derivative, $Cl_2P(:O)$ ·NHMe, may be converted to $[Cl_2P(:O)]_2$ NMe after a prolonged reflux (ca. 3 weeks) [reaction (2)].

$$Cl_{2}P(:O)\cdot NHMe + P(:O)Cl_{3} \longrightarrow \\ [Cl_{2}P(:O)]_{2}NMe + HCl \quad (2)$$

Complete removal of the hydrogen chloride was never

achieved. A disadvantage of this procedure is that it is difficult to separate $[Cl_2P(:O)]_2$ NMe from $Cl_2P(:O)$ ·NHMe by distillation, because their boiling points are similar. The reactions may be contrasted with those of phosphorus trichloride and methylamine hydrochloride,¹ where no evidence for the presence of the methylaminoderivative, Cl₂P·NHMe, has yet been reported.

Bis(dichlorophosphinyl)methylamine, [Cl₂P(:O)]₂NMe, was more conveniently obtained from a mixture of dichlorophosphinylmethylamine, phosphoryl(v) chloride, and triethylamine in ether, where hydrogen chloride was removed by precipitation of triethylamine hydrochloride. The analogous monophenyl derivative was obtained in a similar manner [reaction (3)]. These con-

$$Cl_{2}P(:O)\cdot NHMe + P(:O)Cl_{2}X \xrightarrow{Et_{3}N} Cl_{2}P(:O)\cdot NMe \cdot P(:O)ClX + HCl \quad (3)$$
$$(X = Cl \text{ or } Ph)$$

densations probably proceed by nucleophilic attack of Cl₂P(:O)·NHMe, or, more likely, its deprotonated (by Et₃N) analogue, $Cl_2P(:O)\cdot \overline{N}Me$ on $P(:O)Cl_2X$. When X = Cl or Ph, the phosphoryl centre in P(:O)Cl₂X is likely to be more receptive to nucleophiles than when X = NHMe, which is consistent with the fact that self condensation of type (4) is not observed in these reactions.

$$2\text{Cl}_{2}P(:O)\cdot\text{NHMe} \xrightarrow{\text{Et}_{2}N} \\ \text{Cl}_{2}P(:O)\cdot\text{NMe}\cdotP(:O)\text{Cl}\cdot\text{NHMe} + \text{HCl} \quad (4)$$

A second route to $[Cl_2P(:O)]_2$ NMe was found in the reaction of heptamethyldisilazane with excess of refluxing phosphoryl(v) chloride. It has been demonstrated ¹¹ that phosphoryl(v) chloride and hexamethyldisilazane, (Me₃Si)₂NH, give a solid, Cl₂P(:O)·NH·SiMe₃, and that

⁵ G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, J. Chem. Soc., 1964, 1543. ⁶ R. R. Holmes and J. A. Forstner, Inorg. Chem., 1962, 1,

89. ⁷ O. Glemser, H. W. Roesky, and P. R. Heinze, *Inorg.* Nuclear Chem. Letters, 1968, 4, 179.

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 T. Mizuma, Y. Minaki, and S. Toyoshima, J. Pharm. Soc. Japan, 1961, 81, 48; Chem. Abs., 1961, 55, 13,403.
- ¹⁰ A. Schmidpeter and R. Böhm, Z. anorg. Chem., 1968, 362,

65. ¹¹ M. Becke-Goehring and G. Wunsch, Chem. Ber., 1960, 93, 326.

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^{*} Since this paper was completed, the compounds $[F_2P(:X)]_2NMe$ (X = O or S) have been reported; T. L. Charlton and P. Coursell large Cham 1070, 0, 270 and R. G. Cavell, Inorg. Chem., 1970, 9, 379.

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 S. Goldschmidt and H. L. Krauss, Annalen, 1955, 595, 193. ³ A. B. Burg and J. Heners, J. Amer. Chem. Soc., 1965, 87, 3092.

⁴ O. J. Scherer and J. Wokulat, Z. anorg. Chem., 1968, 361, 296; O. J. Scherer and W. Gick, Chem. Ber., 1970, 103, 71.

the fluorinated derivatives, F₂P(:O)·NH·SiMe₃¹² and $XX'P(:S)\cdot NH\cdot SiMe_3$ (X = X' = F; X = Cl, X' = F),¹³ may be obtained from phosphorus(v) chloride-fluorides and purified by distillation in vacuo. Not surprisingly, we have found that heptamethyldisilazane and P(X)Cl₂ (X = O or S) undergo analogous reactions (5) at 0° .

$$(Me_{3}Si)_{2}NMe + P(:X)Cl_{3} \longrightarrow Cl_{2}P(:X)\cdot NMe \cdot SiMe_{3} + Me_{3}SiCl$$
(5)

However these compounds may be purified by distillation in vacuo, and are more thermally stable than the phosphorus(III) analogue, Cl₂P·NMe·SiMe₃,¹⁴ the reasons for which are not clear. Loss of trimethylsilyl chloride occurs on heating $Cl_2P(X)$ ·NMe·SiMe₃ (X = 0 or S) to ca. 140° , with the formation of as yet, unidentified material. At lower temperatures, Cl₂P(:O)·NMe·SiMe₃ undergoes further reaction [(6) and (7)] with refluxing phosphoryl(v) chloride or phosphorus trichloride. An

$$\begin{array}{c} \text{Cl}_2\text{P}(\text{:O})\cdot\text{NMe}\cdot\text{SiMe}_3 + \text{P}(\text{:O})\text{Cl}_3 \longrightarrow \\ & [\text{Cl}_2\text{P}(\text{:O})]_2\text{NMe} + \text{Me}_3\text{SiCl} \quad (6) \\ \text{Cl}_2\text{P}(\text{:O})\cdot\text{NMe}\cdot\text{SiMe}_3 + \text{PCl}_3 \longrightarrow \\ & \text{Cl}_2\text{P}(\text{:O})\cdot\text{NMe}\cdot\text{PCl}_2 + \text{Me}_3\text{SiCl} \quad (7) \end{array}$$

attempt to obtain the unsymmetrical compound, $Cl_2P(:O)$ ·NMe·P(:S)Cl₂, by a similar reaction failed, however, because the product contained a number of unidentified materials which were not separated by distillation.

[CIP(:S)·NMe]₂,¹⁵ were not obtained from any of the above reactions, although the products of thermal decomposition of Cl₂P(:X)·NMe·SiMe₃ might be expected to include such oligomers.

Bis(dichlorophosphinyl)methylamino, [Cl₂P(:O)]₂NMe, hydrolyses only slowly in air to give (initially) Cl₂P(:O)·NHMe and other unidentified products, but $Cl_2P(:O) \cdot NMe \cdot P(:S)Cl_2$ is unaffected under the same conditions. This hydrolytic stability is probably related to the fact that both are crystalline solids, for most liquid alkylamino-derivatives of phosphoryl and thiophosphoryl chloride are very readily hydrolysed. The unsymmetrical derivative, Cl₂P(:O)·NMe·P(:S)Cl₂, was heated at 120° for 24 h under dry nitrogen, but no evidence for exchange of groups at nitrogen of type (9) was obtained.

$$2\text{Cl}_{2}P(:O)\cdot\text{NMe}\cdotP(:S)\text{Cl}_{2} \not\xrightarrow{} \\ [\text{Cl}_{2}P(:O)]_{2}\text{NMe} + [\text{Cl}_{2}P(:S)]_{2}\text{NMe}$$
(9)

The derivatives, $Cl_2P(X) \cdot NMe \cdot PCl_2$ (X = O or S), are the first examples of halogeno-derivatives of phosphorus in two oxidation states bridged by a nitrogen atom. They showed no tendency to rearrange on distillation or on standing. The fact that no evidence for the formation of (Cl₂P)₂NMe¹ from either Cl₂P(:X)·NMe·SiMe₃ (X = 0 or S) and excess of phosphorus trichloride is consistent with the possibility that the PV-N bonds are thermodynamically stronger than the PIII-N bonds in

TABLE 1

¹H and ³¹P n.m.r. data

Compound	³¹ P Shift/p.p.m.*	$^{2}J_{P-N-P}/Hz$	$\tau(\text{NCH}_3)$ †	${}^{3} \int_{P(V)-N-C-H}/Hz$	$^{3}J_{P}(\mathrm{III})_{\mathrm{N-C-H}}/\mathrm{Hz}$
$Cl_{2}P(.O)$ ·NHMe $Cl_{3}P(.O)$ ·NMe·SiMe	-18.4 -17.8		7.23	19.5 ‡ 21.3	
$[Cl_2P(:O)]_2NMe$	-10.3		6.64	13.8	
$Cl_2P(:O) \cdot NMe \cdot P(:O) ClPh$	-33.2, -12.0 §	< 15	6·69	$15.3, \S 11.0$	
$Cl_2P(.O)$ ·NMe·P(.S) Cl_2 $Cl_3P(.O)$ ·NMe·PCl.	-49.4, -10.4 § -170.1, -12.9 §	$\frac{<10}{80+2}$	6·54 6·75	13.7,8 10.2	1.5
$Cl_2^{\circ}P(:S) \cdot NMe \cdot SiMe_3$	$-62 \cdot 2$	••	7.08	21.7	
$Cl_2P(:S)\cdot NMe \cdot PCl_2$	-167.7, -51.4 ¶	122 ± 2	7.08	15.7	$1 \cdot 2$

* Relative to 85% H_3PO_4 external standard as neat sample (liquids) or in CH_2Cl_2 solution (solids). † In $CDCl_3$ solution. ‡ $2J_{P-N-H} = 5.0$ Hz. § Involving the $-P(:O)Cl_2$ group. ¶ Involving the $-P(:S)Cl_2$ group.

The analogous sulphur compound, Cl₂P(:S)·NMe·SiMe_a, was less reactive to phosphorus trichloride and the reaction times for complete conversion to Cl₂P(:O)·NMe·PCl₂ and Cl₂P(:S)·NMe·PCl₂ were 12 h and 7 days respectively. The tervalent phosphorus atoms were unreactive to elemental sulphur at 110°, but the unsymmetrical derivative, Cl₂P(:O)·NMe·P(:S)Cl₂ was conveniently obtained by reaction (8). The known four-

$$\begin{array}{l} \textbf{(:S)} \cdot \text{NMe} \cdot \text{SiMe}_3 + \text{P(:O)Cl}_3 \longrightarrow \\ \text{Cl}_2 \text{P(:O)} \cdot \text{NMe} \cdot \text{P(:S)Cl}_2 + \text{Me}_3 \text{SiCl} \quad (8) \end{array}$$

membered ring compounds, [CIP(:O)·NMe], ^{15,16} and

 Cl_2P

compounds such as Cl₂P(:O)·NMe·PCl₂. A related situation is also implied by a consideration of the P-N bond lengths in Ph₂P(:S)·NMe·PPh₂.¹⁷

Good evidence for the structures assigned above comes from a consideration of the ¹H n.m.r. and especially the ³¹P n.m.r. data (Table 1). For example, the single ³¹P signal with a quartet structure and the triplet observed in the ¹H spectrum confirms the symmetrical nature of [Cl₂P(:O)]₂NMe. The ¹H chemical shifts for this derivative, and for the following unsymmetrical derivative, are at the lowest τ values so far observed for a methylamino-derivative of phosphorus and suggest very

¹⁵ M. Becke-Goehring, L. Leichner, and B. Scharf, Z. anorg. Chem., 1966, 343, 154.

¹⁶ M. Green, R. N. Haszeldine, and G. S. A. Hopkins, J. Chem. Soc. (A), 1966, 1766.
 ¹⁷ K. M. Ghouse, H. H. Mills, R. Keat, and J. M. Robertson,

unpublished results.

¹² O. Glemser, U. Biermann, and S. P. von Halasz, Inorg. Nuclear Chem. Letters, 1969, 5, 501.

¹³ O. Glemser, U. Biermann, and S. P. von Halasz, Inorg. Nuclear Chem. Letters, 1969, 5, 643.

¹⁴ R. Keat and L. Stobbs, unpublished results.

considerable electron drainage from the respective bridging nitrogen atoms. The unsymmetrical derivative, Cl₂P(:O)·NMe·P(:S)Cl₂, gave two ³¹P signals, each with a broadened quartet structure. The low-field signal was assigned to the sulphurated phosphorus atom in accordance with established trends.¹⁸ Likewise, the phenyl derivative, Cl₂P(:O)·NMe·P(:O)ClPh, gave two broadened signals, the broadest of which occurred at lowest field strength and was assigned to the phenylated phosphorus atom. No P-N-P spin-spin coupling was observed in either of these cases.

The different oxidation states of the phosphorus atoms in the Cl₂P(:X)·NMe·PCl₂ derivatives were easily identified from ³¹P shifts, where the P^{III} signal lay well to low field of the P^{∇} signal. These observations also served to eliminate the possibility that the isomeric phosphazenes, Cl₂P(:X)·N=P(Me)Cl₂, were present, for ³¹P signals from the related Cl₃P=N group are expected near the signals from the H_3PO_4 reference.¹⁹ The only ${}^{3}J_{P-N-O-H}$ coupling detected in the ³¹P spectra was that involving the P^{∇} nuclei (ca. 16 Hz). The relatively small magnitude of the coupling for the PIII nuclei was expected from previous work 20 and confirmed by the 1H spectra ${}^{3}J_{P-N-C-H}$ ca. 1 Hz). These derivatives showed remarkably large values for ${}^{2}J_{P-N-P}$, the value for the sulphur derivative of 122 Hz being the largest known for a non-fluorine-containing derivative (including the formally unsaturated phosphazenes). Another example of relatively large PV-N-PIII coupling (93.4 Hz) was recently reported for PhaP=N-PPha.21

The most characteristic bands in the i.r. spectra of the derivatives reported here are associated with the P-N-Si or P-N-P asymmetric stretching modes (v_{as}) in the range 800-1000 cm⁻¹ as given in Table 2. The bands

Table	2
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I.r. assignments							
	P-N-Si						
ν_{as}	or						
	P-N-P/	$\nu(P-O)/$	$\nu(P-S)/$				
Compound *	cm-1	cm-1	cm ⁻¹				
$Cl_2P(:O)\cdot NMe \cdot SiMe_3$	910	1257 or 1285					
$[Cl_{2}P(O)]_{2}NMe$	912	1290, 1310					
$\tilde{Cl}_2 \tilde{P}(:O) \cdot \tilde{N} Me \cdot P(:O) ClPh$	907	1247 or 1287					
$Cl_2P(:O) \cdot NMe \cdot PCl_2$	875	1286					
Cl ₂ P(:S)·NMe·SiMe ₃	905		738 or 762				
$Cl_2P(:O) \cdot NMe \cdot P(:S)Cl_2$	885	1285	742				
Cl ₂ P(:S)·NMe·PCl ₂	855		749				

* Data recorded from Nujol mulls (solids) or as liquid films.

associated with this mode for the P-N-P- compounds increase in wave number in the order: Cl₂P(:S)·NMe-- $\begin{array}{l} PCl_2 < Cl_2P(\textbf{:}O) \cdot NMe \cdot PCl_2 < Cl_2P(\textbf{:}O) \cdot NMe \cdot P(\textbf{:}S)Cl_2 < \\ Cl_2P(\textbf{:}O) \cdot NMe \cdot P(\textbf{:}O)ClPh < [Cl_2P(\textbf{:}O)]_2NMe. \quad In \ view \ of \end{array}$ the fact that oxidation at a phosphorus(III) atom may be

¹⁸ V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, 'Topics in Phosphorus Chemistry,' Interscience, New York, 1967, vol. 5, p. 227.
¹⁹ E.g., E. Fluck, Chem. Ber., 1961, 94, 1388; Z. anorg. Chem., 1963, 320, 64.
²⁰ R. Keat, J. Chem. Soc. (A), 1970, 1795.

expected to shorten adjacent P-N<15,22 bonds, it is tempting to suggest that this trend reflects an increase in P-N bond orders. However, any more definite conclusion on this trend must await the calculation of force constants for the P-N bonds.

EXPERIMENTAL

Solvents were dried by conventional means. Triethylamine was distilled from sodium before use. Phosphorus trichloride, phosphoryl(v) chloride, and thiophosphoryl chloride were purified by distillation. Heptamethyldisilazane was prepared as described in the literature.²³ All operations were carried out under dry nitrogen or on connections to a conventional vacuum manifold. ¹H and ³¹P spectra were measured on a Perkin-Elmer R10 Spectrometer at 60 and 24.3 MHz, respectively. The ³¹P spectra were obtained from samples contained in 8.5 mm o.d. nonspinning tubes and 85% H₃PO₄ was used as an external standard. I.r. spectra were recorded on Perkin-Elmer 225 or 457 Spectrometers. Mass spectra were obtained from an A.E.I. MS12 spectrometer.

Bis(dichlorophosphinyl)methylamine.—(a) From methylamine hydrochloride and phosphoryl(v) chloride. Methylamine hydrochloride (dried by heating at 120° for 2 h in vacuo) and phosphoryl(v) chloride (1:5 molar ratio) were boiled under reflux (24 h) and the resultant solution was distilled under a water-pump vacuum to give dichlorophosphinylmethylamine, b.p. 120°/10 mmHg (ca. 40%) yield). A considerable quantity of unidentified involatile residue remained in the distillation flask. Dichlorophosphinylmethylamine (16.3 g, 0.11 mol) in ether (500 ml) was mixed with phosphoryl(v) chloride (16.9 g, 0.11 mol). The mixture was cooled to 0°, and triethylamine (11.1 g, 0.11 mole) was added with vigorous stirring. The mixture was boiled under reflux (2 h), cooled, and the triethylamine hydrochloride was filtered off. Ether was removed from the filtrate and the residue was distilled in vacuo to give bis(dichlorophosphinyl)methylamine (18.0 g, 62%), b.p. 65-70°/0.01 mmHg, m.p. 53-54° [Found: C, 4.9; H, 1.2; Cl, 52.4; P, 23.7%: M (mass spectrometric), 263. CH₃Cl₄NO₂P₂ requires C, 4.5; H, 1.1; Cl, 53.6; P, 23.4%; M (for $CH_3^{35}Cl_4NO_2P_2$), 263].

A similar procedure was adopted to give chlorophenylphosphinyl(dichlorophosphinyl)methylamine (66%), b.p. 150-155°/0·1 mmHg, m.p. 79-80° (Found: C, 26·9; H, 2.4; P, 19.5. C₇H₈Cl₃NO₂P₂ requires C, 27.4; H, 2.6; P, 20.2%).

Attempted preparation of bis(dichlorophosphinyl)methylamine with prolonged reaction time. Methylamine hydrochloride and an excess of phosphoryl(v) chloride were boiled under reflux (3 weeks) to give a mixture of bis(dichlorophosphinyl)methylamine and dichlorophosphinylmethylamine (ca. 4: 1 molar ratio, estimated by ³¹P n.m.r.). Attempts to separate this mixture by fractional distillation were unsuccessful.

(b) From heptamethyldisilazane. Heptamethyldisilazane (6.5 g, 0.036 mol) was boiled under reflux with a 5 molar

²¹ H. G. Maidersteig, L. Meinel, and H. Nöth, Z. anorg. Chem., 1969, 368, 254.

²² E. D. Morris and C. E. Nordman, Inorg. Chem., 1969, 8, 1673; M. D. La Prade and C. E. Nordman, Inorg. Chem., 1969,

 <sup>8, 1669.
 &</sup>lt;sup>23</sup> R. C. Osthoff and S. W. Kantor, Inorg. Synth., 1957, 5, 58.

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excess of phosphoryl(v) chloride (12 h). Excess of phosphoryl(v) chloride and trimethylsilyl chloride were removed under reduced pressure and the oily residue was distilled to give bis(dichlorophosphinyl)methylamine (8.0 g, 83%), m.p. 53—54°; i.r. and n.m.r. spectra were identical with those of the sample described above.

Dichlorophosphinylmethyl(trimethylsilyl)amine.— Heptamethyldisilazane (5·1 g, 0·029 mol) and excess of phosphoryl(v) chloride were mixed at 0° and stirred (1 h). Removal of phosphoryl(v) chloride and trimethylsilyl chloride gave an oil which was distilled to give dichlorophosphinylmethyl(trimethylsilyl)amine (4·3 g, 68%), b.p. $30-32^{\circ}/0.02$ mmHg (Found: C, 21·6; H, 5·3; Cl, 32·4; P, 14·5. C₄H₁₂Cl₂NOPSi requires C, 21·8; H, 5·5; Cl, 32·2; P, 14·1%).

On heating, this derivative evolved trimethylsilyl chloride at temperatures $>140^{\circ}$. A ¹H n.m.r. spectrum of the residue showed a broad N-methyl signal centred at τ 6.7.

Dichlorophosphinothioylmethyl(trimethylsilyl)amine.—This compound was prepared similarly in 72% yield, b.p. 36— 38°/0.03 mmHg (Found: C, 20.3; H, 5.1; Cl, 30.2; P, 13.3. C₄H₁₂Cl₂NPSSi requires C, 20.3; H, 5.1; Cl, 30.1; P, 13.1%). On heating, this derivative evolved trimethylsilyl chloride at temperatures >135°. A ¹H n.m.r. spectrum of the residue showed a broad N-methyl signal centred at τ 6.8.

Dichlorophosphino(dichlorophosphinyl)methylamine. Dichlorophosphinylmethyl(trimethylsilyl)amine (4·4 g, 0·020 mol) was boiled under reflux (12 h) with excess of phosphorus trichloride. Trimethylsilyl chloride and phosphorus trichloride were removed under reduced pressure and the residue was distilled to give dichlorophosphino(dichlorophosphinyl)methylamine (3.9 g, 78%), b.p. $50-52^{\circ}/0.05$ mmHg [Found: C, 4.7; H, 1.3; Cl, 56.5; P, 24.7%; M (mass spectrometric), 247. CH₃Cl₄NOP₂ requires C, 4.8; H, 1.2; Cl, 57.1; P, 24.9%; M (for CH₃³⁵Cl₄NOP₂), 247].

Dichlorophosphino(dichlorophosphinothioyl)methylamine. This compound was prepared in a similar manner, except that the reflux was continued for 7 days (yield 63%), b.p. 64—65°/0·4 mmHg [Found: C, 5·1; H, 1·3; Cl, 53·5; P, 22·7%; M (mass spectrometric), 263. CH₃Cl₄NP₂S requires C, 4·5; H, 1·1; Cl, 53·7; P, 23·4%; M (for CH₃³⁵Cl₄NP₂³²S), 263].

Dichlorophosphinothioyl(dichlorophosphinyl)methylamine. —Dichlorophosphinothioyl(dichlorophosphinyl)methylamine (3·2 g, 0·014 mol) was boiled under reflux (48 h) with excess of phosphoryl(v) chloride. Phosphoryl(v) chloride and trimethylsilyl chloride was removed under reduced pressure and the solid residue was recrystallised from light petroleum (b.p. 40—60°) to give dichlorophosphinothioyl(dichlorophosphinyl)methylamine (1·6 g, 42%), m.p. 84—85° (sublimes) [Found: C, 4·4; H, 1·2; Cl, 50·1; P, 21·9%; M (mass spectrometric), 279. CH₃Cl₄NOP₂S requires C, 4·3; H, 1·1; Cl, 50·6; P, 22·1%; M (for CH₃³⁵Cl₄NOP₂³²S), 279].

Unsuccessful attempts to exchange groups on the nitrogen atom in the above compound (12 h, 125°), and to sulphurise $Cl_2P(:O)\cdot NMe \cdot PCl_2$ or $Cl_2P(:S)\cdot NMe \cdot PCl_2$ (24 h, 125°) were carried out on the neat compounds in n.m.r. tubes. The identity of the products in each case was checked by ¹H n.m.r. spectroscopy.

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