Dimethylamino- and Methoxy-derivatives of Dichlorophosphino(dichlorophosphinyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$

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Dimethylaminolysis and methoxylation of dichlorophosphino(dichlorophosphinyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$, by dimethylaminotrimethylsilane and methoxytrimethylsilane respectively initially occurs at the tervalent phosphorus atom. The mono-dimethylamino-derivative $Cl(Me_2N)P{\cdot}NMe{\cdot}P(O)Cl_2$, rearranges to its isomer, $Cl_2P{\cdot}NMe{\cdot}P(O)ClNMe_2$ at ambient temperatures. Further dimethylaminolysis gives the bisdimethylamino-derivative, $Cl_2P{\cdot}NMe{\cdot}P(O)(NMe_2)_2$ which may also be formed by rearrangement of its isomer, $Cl(Me_2N)P{\cdot}NMe{\cdot}P(O)Cl(NMe_2)$. The mono-methoxy-derivative, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl(OMe)$, was obtained by cleavage of the silicon–nitrogen bond in the methoxy-derivative, $Cl(MeO)P(O){\cdot}NMe{\cdot}SiMe_3$ by phosphorus(III) trichloride, and the bis- and tris-methoxy-derivatives, $Cl_2P{\cdot}NMe{\cdot}P(O)(OMe)_2$, and, $Cl(MeO)P{\cdot}NMe{\cdot}P(O)(OMe)_2$, were prepared by the condensation of dimethoxy(methylamino)phosphine oxide, $(MeO)_2(MeNH)PO$, with phosphorus(III) trichloride and methoxyphosphorus(III) dichloride respectively in the presence of triethylamine. The results of the foregoing dimethylaminolysis and methoxylation experiments have been compared with the positions the equilibria observed when dimethylamino- and methoxy- groups are scrambled between phosphorus(III) trichloride and phosphoryl(V) chloride. The ^1H and ^{31}P n.m.r. spectra of these derivatives are reported.

THE dimethylaminolysis and methoxylation of many classes of phosphorus(III) and phosphorus(V) compounds have been extensively studied,[1] although comparisons of the relative reactivity of analogous phosphorus(III) and phosphorus(V) compounds are lacking. The availability [2] of compounds of type (I) can, in principle, enable such a comparison to be made and this we have undertaken using dimethylaminotrimethylsilane, Me_3SiNMe_2, and methoxytrimethylsilane, Me_3SiOMe, to effect dimethylaminolysis [3] and methoxylation respectively.

Compound (I) undergoes a ready reaction with Me_3SiNMe_2 at −78° in methylene chloride solution giving trimethylsilylchloride and, initially, the dimethylamino-derivative (II) as shown in the Scheme.

The ^1H n.m.r. spectrum of the reaction products showed, however, that the signals corresponding to (II)

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[1] K. Sasse, 'Methoden der Organischen Chemie,' 12/I, G. Thieme, Stuttgart, 1963.

[2] R. Keat, *J. Chem. Soc.* (*A*), 1970, 2732.

[3] For a preliminary account of the dimethylaminolysis reactions see R. Keat, *Phosphorus*, 1972, **1**, 253.

disappeared within *ca.* 20 min at ambient temperatures in the absence of solvent, leaving those signals assigned to an isomer of (II), compound (III). Evidence for the structure of (II) comes from a consideration of the ^1H n.m.r. data in Table 1. It has previously been observed [2-7] that the coupling constants, $^3J(P_A\text{–N–C–}H)$, involving the bridging *N*-methyl protons in compounds containing the $P_A\cdot NMe\cdot P_B$ grouping increase when electron supplying substituents are introduced at P_B, but decrease when electron supplying substituents are introduced at P_A. In this light, the data in Table 1 are consistent with (II) having the structure shown, assuming structure (III) to be correctly assigned. The latter assumption is justified, (*a*) by examination of the ^{31}P n.m.r. spectrum of (III) in which spin–spin coupling to the dimethylamino protons is only apparent in the P^V signal, and (*b*) by the method of synthesis of (III) from (IV) (Scheme).

$$\begin{tikzcd}
\begin{array}{c}Cl_2P\cdot NMe\cdot P(O)Cl_2\\(\mathrm{I})\end{array} \arrow[r, "Me_3SiNMe_2", "-Me_3SiCl"'] & \begin{array}{c}Cl(Me_2N)P\cdot NMe\cdot P(O)Cl_2\\(\mathrm{II})\end{array} \arrow[d] \\
\begin{array}{c}Me_3Si\cdot NMe\cdot P(O)ClNMe_2\\(\mathrm{IV})\end{array} \arrow[r, "PCl_3", "-Me_3SiCl"'] \arrow[d, "+Me_2N\cdot PCl_2 \atop -Me_3SiCl"] & \begin{array}{c}Cl_2P\cdot NMe\cdot P(O)ClNMe_2\\(\mathrm{III})\end{array} \arrow[d, "Me_3Si\cdot NMe_2 \atop -Me_3SiCl"] \\
\begin{array}{c}Cl(Me_2N)P\cdot NMe\cdot P(O)ClNMe_2\\(\mathrm{VI})\end{array} \arrow[r] & \begin{array}{c}Cl_2P\cdot NMe\cdot P(O)(NMe_2)_2\\(\mathrm{V})\end{array}
\end{tikzcd}$$

SCHEME

TABLE 1

^1H and ^{31}P N.m.r. data

Compound	τ(NMe) [a]	$^3J(P^V\text{–N–C–}H)$ /Hz	$^3J(P^{III}\text{–N–C–}H)$ /Hz	τ(NMe$_2$ or OMe)	$^3J(P^V$–N (or O)–C–$H)$/Hz	$^3J(P^{III}$–N (or O)–C–$H)$/Hz	$^{31}P^V$ Shift [b]	$^{31}P^{III}$ Shift [b]	$^2J(P\text{–N–P})$ /Hz
$Cl_2P\cdot NMe\cdot P(O)Cl_2$ (I) [c]	6·75	15·6	1·7				−12·9	−170·1	80
$Cl(Me_2N)P\cdot NMe\cdot P(O)Cl_2$ (II)	6·80	17·2	1·7	7·23		12·8			
$Cl_2P\cdot NMe\cdot P(O)(NMe_2)Cl$ (III)	6·83	11·9	2·4	7·16	13·5	[$^5J(P\text{–N–P–N–C–}H)$ 0·7 Hz]	−20·3	−169·9	87
$Me_3Si\cdot NMe\cdot P(O)(NMe_2)Cl$ (IV) [d]	7·28	14·2		7·30	16·3		−29·4		
$Cl_2P\cdot NMe\cdot P(O)(NMe_2)_2$ (V)	6·93	9·4	3·4	7·23	10·1		−21·0	−172·8	73
$Cl(Me_2N)P\cdot NMe\cdot P(O)(NMe_2)Cl$ (VI)	6·98	12·5	2·0	7·27 or 7·30	12·8 or 13·0	12·8 or 13·0	−24·0	−138·0	76
$[Cl(Me_2N)P]_2NMe$ (VIII)	6·92		5·5	7·32		12·6 [e]			
$Cl(MeO)P\cdot NMe\cdot P(O)Cl_2$ (IX)	6·92	17·2	1·9	6·26		14·7	−14·0	−167·3	66
$Me_3Si\cdot NMe\cdot P(O)(OMe)Cl$ (X)	7·31	16·3		6·20	14·3		−18·6		
$Cl_2P\cdot NMe\cdot P(O)(OMe)Cl$ (XI)	6·85	12·4	2·2	6·06	14·3		−11·0	−169·8	81
$Cl_2P\cdot NMe\cdot P(O)(OMe)_2$ (XII) [f]	7·00 (6·94)	9·4 (+9·60)	2·9 (+3·0)	6·25 (6·36)	12·2 (+11·8)	[$^5J(P\text{–N–P–O–C–}H)$ 0·8 Hz] (0·4)	−4·9 (−6·5)	−173·5 (−171)	74 (+74·5)
$Cl(MeO)P\cdot NMe\cdot P(O)(OMe)_2$ (XIII)	7·19	10·3	2·8	6·26, 6·35	11·3	14·8	−6·3	−176·6	66
$(MeO)_2P\cdot NMe\cdot P(O)(OMe)_2$ [f]	(7·43)	(+10·8)	(+2·4)	(6·25, 6·51)	(+11·0)	(+12·4)	(−9·7)	(−143·3)	(+54)
$(MeO)_2P(O)(NHMe)$	7·44	12·5		6·30	11·0		−14·0		

[a] In $CDCl_3$ or CH_2Cl_2 solution. [b] Relative to external 85% H_3PO_4, neat samples. [c] Data from ref. 3. [d] Incorrect ^1H data given for this in ref. 4. [e] Apparent $^3J(P\text{–N–C–}H)$. [f] Data in parentheses from ref. 7.

A ^{31}P n.m.r. spectrum of (II) was not obtained because concentration of a solution of (II) (necessary for ^{31}P n.m.r.) resulted in rapid rearrangement to (III).

Reaction of (I) with two molar equivalents of Me_3SiNMe_2 under similar conditions gave a bisdimethylamino-derivative (V), the structure of which is unambiguously established by ^{31}P n.m.r. It is possible that (V) was formed *via* (II), (III), and (VI), since the latter when prepared by the route shown in the Scheme slowly rearranged to (V) at ambient temperatures. The reaction of (I) with more than two molar equivalents of Me_3SiNMe_2 resulted in the formation of a complex mixture of products which appeared to arise from cleavage of the P–N–P bridge.

The dimethylaminolysis of (I) has been compared with that of bis(dichlorophosphino)methylamine, $(Cl_2P)_2NMe$ (VII).[8] Reaction of (VII) with two molar equivalents of $Me_3Si\cdot NMe_2$ resulted in the formation of an unstable bisdimethylamino-derivative (VIII):

$$2Me_3SiNMe_2 + (Cl_2P)_2NMe \longrightarrow \underset{(\mathrm{VIII})}{[(Me_2N)ClP]_2NMe} + 2Me_3SiCl$$

Attempted purification of (VIII) resulted in the formation of a complex mixture of products but its ^1H n.m.r. spectrum showed a 1 : 2 : 1 triplet for the bridging *N*-methyl protons, and a triplet, typical of an $(AX_6)_2$ spin system,[9] for the dimethylamino-protons. These observations provide good evidence for the structure shown rather than for the isomer $(Me_2N)_2P\cdot NMe\cdot PCl_2$. Two near identical sets of dimethylamino-proton signals were just resolved indicating that (VIII) was present as a 1 : 1 mixture of diastereoisomers.

The reaction of (I) with one molar equivalent of Me_3SiOMe led to a more complex mixture of products than the reaction with Me_3SiNMe_2, although a monomethoxy-derivative (IX) was identified from its ^1H and ^{31}P n.m.r. spectra:

$$Cl_2P\cdot NMe\cdot P(O)Cl_2 + Me_3SiOMe \longrightarrow \underset{(\mathrm{IX})}{Cl(MeO)P\cdot NMe\cdot P(O)Cl_2} + Me_3SiCl$$

Consistent with this assignment an isomer of (IX),

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[4] I. Irvine and R. Keat, *J.C.S. Dalton*, 1972, 17.

[5] I. A. Nuretdinov, E. I. Loginova, L. K. Nikoronova, and N. P. Grechkin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 914.

[6] I. A. Nuretdinov, V. V. Negrebetskii, A. Z. Yankelevich, A. V. Kessenikh, L. K. Nikoronova, and E. I. Loginova, *Izvest. Akad. Nauk S.S.S.R. Ser. khim.*, 1971, 2589.

[7] I. A. Nuretdinov, V. V. Negrebetskii, A. Z. Yankelevich, A. V. Kessenikh, E. I. Loginova, L. K. Nikoronova, and N. P. Grechkin, *Doklady Akad. Nauk S.S.S.R.*, 1971, **196**, 1369.

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

[9] R. K. Harris and E. G. Finer, *Bull. Soc. chim. France*, 1968, 2805.

compound (XI), was obtained by an independent route:

$$(Me_3Si)_2NMe + Cl_2P(O)OMe \longrightarrow Me_3Si{\cdot}NMe{\cdot}P(O)ClOMe + Me_3SiCl$$

$$\Big\downarrow {\scriptstyle +PCl_3 \atop -Me_3SiCl}$$

$$Cl_2P{\cdot}NMe{\cdot}P(O)Cl{\cdot}OMe$$

(XI)

It may be noted that (XI) was generated only in refluxing phosphorus(III) trichloride, whereas the analogous dimethylamino-derivative (III) was obtained by silicon–nitrogen bond cleavage of (II) at ambient temperatures. This is consistent with (IV) being a stronger nucleophile towards phosphorus(III) than (XI) (see below). No evidence for a rearrangement, (IX) ⟶ (XI), similar to that occurring in the dimethylamino-series was obtained, but this cannot be ruled out, because identification of (XI) in the mixture of products, proved difficult. Similar difficulties were experienced in attempts to identify the products of further methoxylation of (I), despite the fact that the properties of the bis (XII) and trismethoxy (XIII)-derivatives of (I) were known. These were characterised independently:

$$(MeO)_2P(O){\cdot}NHMe + (MeO)_nPCl_{3-n} \xrightarrow{Et_3N} Cl_{2-n}(MeO)_nP{\cdot}NMe{\cdot}P(O)(OMe)_2 + HCl$$

$(n = 0 \text{ or } 1)$

Compound (XII) and the tetramethoxy-derivative, $(MeO)_2P{\cdot}NMe{\cdot}P(O)(OMe)_2$, have previously been obtained[7] by a similar route (see Table 1).

Dimethylaminolysis of phosphorus halides by silylamines is often assumed to proceed by a nucleophilic attack of nitrogen at phosphorus,[10] followed by the formation of a four-centred intermediate containing five-co-ordinated phosphorus, although direct evidence for this is lacking. Qualitative observations on these reactions show that the rate of aminolysis is dependent on the base strength of the amine and the electrophilicity of the phosphorus compound (*e.g.* see ref. 4), so that in general these reactions may be expected to follow a second (or higher) order rate law. It seems unlikely that the reactivity at phosphorus(III) or phosphorus(V) is interpretable in terms of a rate determining ionisation process although the tendency to P–Cl bond heterolysis may be more advanced in the former oxidation state.

The fact that dimethylaminolysis of (I) initially occurs at the phosphorus(III) atom to give (II), and that this compound rearranges to its isomer, (III), suggests that (II) is formed as a result of kinetic control, and that (III) is the thermodynamically favoured product. The kinetic result might be expected from qualitative observations on the relative reactivity of amines towards tervalent and quinquivalent phosphorus halides, although quantitative comparisons are not available. It is worth noting, however, that the rate of reaction of *p*-toluenesulphenyl chloride, $CH_3{\cdot}C_6H_4{\cdot}S{\cdot}Cl$, with di-isopropylamine is some 500 times faster than the rate of reaction of *p*-toluenesulphinyl chloride, $CH_3{\cdot}C_6H_4{\cdot}S(O){\cdot}Cl$, with the same amine.[11] As in the reactions of phosphorus compounds, a decrease in the rate of aminolysis follows from an increase in the oxidation state of the atom where nucleophilic displacement occurs; this is not the result that might be anticipated from the principles of hard and soft acids and bases, assuming that the amines concerned are relatively ‘ hard ’ nucleophiles. These results suggest that steric effects play an important role in determining the relative reactivity of phosphorus(III) and phosphorus(V), as well as sulphur(II) and sulphur(IV), to nucleophiles.

The formation of the bisdimethylamino-derivative (V), containing the $(Me_2N)_2P(O)$-group, is somewhat surprising in view of the negative charge that must accumulate on the phosphorus(V) atom, as well as the observations that only two of the chlorine atoms in bis(dichlorophosphinyl)methylamine, $[Cl_2P(O)]_2NMe$, can be displaced by Me_3SiNMe_2 to give $[Cl(Me_2N)P(O)]_2NMe$ under similar conditions,[4] and that complete dimethylaminolysis of phosphoryl(V) chloride cannot be affected by the same reagent at room temperature.[12] These observations suggest that the rearrangement of the dimethylamino-group in (VI) proceeds by a lower energy pathway than is possible for direct aminolysis at the $Cl(Me_2N)P(O)$-group. It is not clear whether the rearrangement of (II) and of (VI) is inter- or intramolecular, but an oxygen transfer process is unlikely since the P=O bond in (V) would be expected to be weaker than that in (VI), other factors being roughly equal.

It seemed likely that parallel results to those above reflecting thermodynamic control might be observed in the exchange of dimethylamino-groups between tervalent and quinquivalent phosphorus chlorides. We found that this was the case for the reactions:

$$Me_2NPCl_2 + P(O)Cl_3 \longrightarrow PCl_3 + Me_2NP(O)Cl_2$$

$$(Me_2N)_2PCl + Me_2N{\cdot}P(O)Cl_2 \longrightarrow Me_2NPCl_2 + (Me_2N)_2P(O)Cl$$

which proceed completely to the right at *ca.* 100°. However, insofar as the reaction

$$Me_2NPCl_2 + Me_2NP(O)Cl_2 \not\longrightarrow (Me_2N)_2P(O)Cl + PCl_3$$

does not proceed to the right and that the reaction:

$$(Me_2N)_2PCl + (Me_2N)_2P(O)Cl \longrightarrow (Me_2N)_3PO + Me_2NPCl_2$$

gives only small quantities of $(Me_2N)_3PO$ (equilibrium constant $<0{\cdot}1$), there is no parallel with the rearrangement (VI) ⟶ (V). Further, there do not appear to be any significant contributions from structures such as (XIV) which might favour the formation of (V), since

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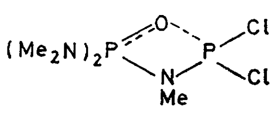
[10] O. J. Scherer, *Organometallic Chem. Rev.*, 1968, *A*3, 281.

[11] Unpublished results of A. Fava and G. Guaraldi, quoted by J. L. Kice in *Progr. Inorg. Chem.*, 1972, **17**, 159.

[12] R. Keat, unpublished results.

the ^{31}P n.m.r. shifts are well within the ranges expected for $(Me_2N)_2P(O)\cdot NMe$- and $Cl_2P\cdot NMe$-groups. Our inability to isolate a tris- or tetrakis-dimethylamino-derivative of (I) suggests that the bridging P–N bonds



(XIV)

are cleaved, and when the labile nature of the products of dimethylaminolysis of $(Cl_2P)_2NMe$ are considered, it is likely that the P^{III}–N bond will be cleaved before the P^{V}–N bond. In this case, the formation of $[Cl(Me_2N)P]_2NMe$ is again consistent with chlorine atom displacement by an associative, rather than a dissociative mechanism, similar to that inferred for the dimethylaminolysis of $[Cl_2P(O)]_2NMe$.[4] The ^1H n.m.r. data on $[(Me_2N)_2P]_2NMe$ have been published,[13] but no details of its preparation have appeared.

TABLE 2

Experimental details

Substrate (mmol)	Reactants (mmol)	Mixing conditions	Subsequent treatment	Product (% yield)	B.p./°C (mmHg)
$Cl_2P\cdot NMe\cdot P(O)Cl_2$ (I) (9·1)	Me_3SiNMe_2 (9·1)	CH_2Cl_2, −78 °C		$Cl(Me_2N)P\cdot NMe\cdot P(O)Cl_2$ rearranged to $Cl_2P\cdot NMe\cdot P(O)ClNMe_2$ (*ca.* 95) within 1 h at 30°	See below
$Cl_2P\cdot NMe\cdot P(O)Cl_2$ (I) (12·0)	Me_3SiNMe_2 (12·0)	CH_2Cl_2, − 78°		$Cl_2P\cdot NMe\cdot P(O)(NMe_2)_2$ (87)	78 (0·01)
$Cl_2P\cdot NMe\cdot P(O)Cl_2$ (I) (6·5)	Me_3SiNMe_2 (20·5)	CH_2Cl_2, − 78°		Complex mixture including $Cl_2P\cdot NMe\cdot P(O)(NMe_2)_2$	
$Me_3Si\cdot NMe\cdot P(O)ClNMe_2$ (IV) (22·0)	PCl_3 (excess)	Neat, *ca.* 20°	Stirred, 4 h	$Cl_2P\cdot NMe\cdot P(O)ClNMe_2$ (79)	78 (0·05)
$Me_3Si\cdot NMe\cdot P(O)ClNMe_2$ (IV) (5·7)	$Me_2N\cdot PCl_2$ (5·9)	Neat, *ca.* 20°	Stirred, 1 h	$Cl(Me_2N)P\cdot NMe\cdot P(O)(NMe_2)Cl$ rearranged to $Cl_2P\cdot NMe\cdot P(O)(NMe_2)_2$	
$Cl_2P\cdot NMe\cdot PCl_2$ (17·3)	Me_3SiNMe_2 (34·6)	CH_2Cl_2, −78°		$[Cl(Me_2N)P]_2NMe$—gave complex mixture on standing *ca.* 1 h at 30°	
$Cl_2P\cdot NMe\cdot P(O)Cl_2$ (I) (4·3)	Me_3SiOMe (4·3)	CH_2Cl_2, 0°		Mixture including $Cl(MeO)P\cdot NMeP(O)Cl_2$	
$Cl_2P\cdot NMe\cdot P(O)Cl_2$ (I) (3·2)	Me_3SiOMe (6·4)	CH_2Cl_2, 0°		Complex mixture	
$Cl_2P(O)\cdot NMe\cdot P(O)Cl_2$ (9·2)	Me_3SiOMe (18·4)	CH_2Cl_2, 20°	Refluxed, 24 h	No reaction	
$(Me_3Si)_2NMe$ (17·1)	$MeOP(O)Cl_2$ (17·1)	Neat, *ca.* 20°	Stirred, 1 h	$Me_3Si\cdot NMe\cdot P(O)(OMe)Cl$ (88)	55—60 (0·1)
$Me_3Si\cdot NMe\cdot P(O)(OMe)Cl$ (X) (14·1)	PCl_3 (an excess)	Neat, *ca.* 20°	Refluxed, 2 h	$Cl_2P\cdot NMe\cdot P(O)(OMe)Cl$ (82)	62—65 (0·05)
$(MeO)_2P(O)Cl$ (234)	NH_2Me (an excess)	Et_2O, 0°	Refluxed, 0·5 h	$(MeO)_2P(O)\cdot NHMe$ (71)	70—75 (0·1)
$(MeO)_2P(O)NHMe$ (14·4)	PCl_3 (14·4), Et_3N (14·9)	Et_2O, 0°	Refluxed, 1 h	$Cl_2P\cdot NMe\cdot P(O)(OMe)_2$ (78)	77—80 (0·1)
$(MeO)_2P(O)NHMe$ (30·2)	$MeOPCl_2$ (30·2), Et_3N (30·7)	Et_2O, 0°	Refluxed, 1 h	$Cl(MeO)P\cdot NMe\cdot P(O)(OMe)_2$	Decomposition to yellow solid
Me_2NPCl_2 (9·2)	$P(O)Cl_3$ (9·2)	Neat, *ca.* 20°	*ca.* 100°, 6 h	$Me_2NP(O)Cl_2 + PCl_3$ (*ca.* 100%)	
$(Me_2N)_2PCl$ (7·6)	$Me_2N\cdot P(O)Cl_2$ (7·6)	Neat, *ca.* 20°	*ca.* 100°, 6 h	$Me_2N\cdot PCl_2 + (Me_2N)_2P(O)Cl$ (*ca.* 100%)	
$(Me_2N)PCl_2$ (6·2)	$Me_2NP(O)Cl_2$ (6·2)	Neat, *ca.* 20°	*ca.* 100°, 6 h	No reaction	
$(Me_2N)_2PCl$ (4·8)	$(Me_2N)_2P(O)Cl$ (4·8)	Neat, *ca.* 20°	*ca.* 100°, 6 h	$Me_2NPCl_2 + (Me_2N)_3PO$ (*ca.* 20%)	
$MeOPCl_2$ (2·9)	$P(O)Cl_3$ (2·9)	Neat, *ca.* 20°	*ca.* 100°, 6 h	$PCl_3 + MeOP(O)Cl_2$ (*ca.* 10%)	

Methoxylation of (I) initially occurs at the P^{III} atom as expected from the aminolysis results, although a complex mixture of products was also obtained on standing at ambient temperatures. This is not unexpected in view of the fact that P–O bonds can readily be substituted for P–N as well as P–Cl bonds.[1] The bis-methoxy-derivative, $Cl_2P\cdot NMe\cdot P(O)(OMe)_2$ (XII) did not appear to be present in the products of methoxylation of (I), although like compound (V) this isomer seemed to be thermodynamically favoured. The fact that the reaction

$$Cl_2P\cdot OMe + P(O)Cl_3 \longrightarrow Cl_2P(O)\cdot OMe + PCl_3$$

goes slowly to the right again suggests that $Cl(MeO)P\cdot NMe\cdot P(O)Cl_2$ (IX), is the product of kinetic, rather than thermodynamic control.

The n.m.r. data in Table 1, which includes some recent results of Nuretdinov *et al.*,[7] are consistent with the structures formulated above. It has recently been shown[14] that certain phosphinyl(silyl)amines may exist in the alternative phosphazene form, so that compounds

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[13] H. G. Metzinger, *Org. Magnetic Resonance*, 1971, **3**, 485.

[14] G. Czieslik, G. Flaskerud, R. Höfer, and O. Glemser, *Chem. Ber.*, 1973, **106**, 399.

(IV) and (X) could be formulated as $Cl(Me_2N)(Me_3SiO)P{=}NMe$ and $Cl(MeO)(Me_3SiO)P{=}NMe$ respectively. It would appear that this is not the case for (IV) and (X) with ^{31}P shifts of −**29·4** and −**18·6** p.p.m. respectively, since the phosphazenes might be expected [14,15] to show ^{31}P signals to high field of phosphoric acid. The correlation noted above between the magnitude of $^3J(P{-}N{-}C{-}H)$ and the nature of the substituents on phosphorus holds well assuming that the overall electron supply of these substituents follows the order, $NMe_2 > OMe > Cl$. Interest has recently been focussed [5-7,16] on the magnitude of $J(P{-}N{-}P)$ and the electronegativity of substituents on phosphorus. Assuming that these couplings have the same relative sign, correlations with the electron supplying properties are somewhat erratic, although an overall decrease in the magnitude of $J(P{-}N{-}P)$ with decreasing number of chlorine atoms is discernable. Double resonance experiments show [17] that all the coupling constants in the Table for compounds (I) and (III) are positive, like those established for $(MeO)_2P{\cdot}NMe{\cdot}P(O)(OMe)_2$.[7]

EXPERIMENTAL

Solvents were dried by conventional means. Phosphoryl(V) chloride and phosphorus(III) trichloride were purified by distillation. Me_3SiNMe_2,[18] $(Me_3Si)_2NMe$,[19] Me_3SiOMe,[20] $(Me_2N)_nPCl_{3-n}$ $(n = 1,2)$,[1] $(Me_2N)_nP(O)Cl_{3-n}$ $(n = 1,2)$,[21] $MeOPCl_2$,[22] $MeOP(O)Cl_2$,[23] $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$,[2] $[Cl_2P(O)]_2NMe$,[2] $Me_3Si{\cdot}NMe{\cdot}P(O)ClNMe_2$,[4] and $(Cl_2P)_2NMe$ [8] were prepared by literature methods. All operations were carried out under an atmosphere of dry nitrogen. ^1H and ^{31}P N.m.r. spectra were measured on a Perkin-Elmer R 10 or JEOL C 60HL spectrometers at 60 and 24·3 MHz respectively. Mass spectra were obtained from an A.E.I. MS 12 spectrometer. Experimental methods were similar to those previously employed [2,4] and the details are summarised in Table 2. The exchange of dimethylamino- and methoxy-groups between phosphorus chlorides was followed by ^{31}P n.m.r. Analytical data for new compounds are given in Table 3.

TABLE 3

Analytical data

Compound	Found C	Found H	Found Cl	Found *m/e*	Calc. C	Calc. H	Calc. Cl	Calc. *m/e* [a]
$Cl_2P{\cdot}NMe{\cdot}P(O)(NMe_2)Cl$	14·1	3·8	41·1	256	14·0	3·5	41·4	256
$Cl_2P{\cdot}NMeP(O)(NMe_2)_2$	22·9	5·9	26·3	265	22·6	5·6	26·7	265
$Me_3Si{\cdot}NMe{\cdot}P(O)(OMe)Cl$	28·0	7·6	16·4	215	27·8	7·0	16·5	215
$Cl_2P{\cdot}NMe{\cdot}P(O)(OMe)Cl$	8·6	2·4	43·6	243	9·8	2·45	43·6	243
$Cl_2P{\cdot}NMe{\cdot}P(O)(OMe)_2$	14·7	3·2		239	15·0	3·8		239

[a] For ions containing ^{35}Cl.

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