Cyclisation of Bis(dichlorophosphino)-, Bis(dichlorophosphinoyl)-, and Bis(dichlorophosphinothioyl)-amines by Primary Amines †

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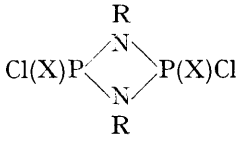
The compounds $[Cl_2P(X)]_2NR$ (IIIa, X = lone pair, R = Me, Et, or Bu^t; IIIb, X = O, R = Me or Et; IIIc, X = S, R = Me) react with 3 mol equiv. of t-butylamine to give cyclodiphosphazanes Cl(X)P·NR·P(X)Cl·NBu^t, (V). Preparation of the long-sought cyclophosph(III)azanes $(ClPNR)_n$ (R = Me or Et) from (IIIa) has also been attempted by the same route, and new n.m.r. and mass-spectroscopic evidence has been obtained for formation of these derivatives (n = 3 and 4, R = Me; n = 2 and 3, R = Et), but no pure products have been isolated. Only when X = O and R = Me or Et could evidence for the formation of derivatives $Cl_2P(X)$·NR·P(X)Cl·N(H)Bu^t, (II), be obtained, and possible reasons for the rapid cyclisation step involved are discussed. The known derivative $Cl_2P(O)$·NMe·P(O)Cl·N(H)Me, (IIb), was readily cyclised by t-butylamine to give $[ClP(O)·NMe]_2$, (Ib). Phosphoryl chloride reacts with 3 mol equiv. of primary amines to give mixtures of the derivatives $Cl_2P(O)$·N(H)R (R = Me, Et, Pr^i, or Bu^t) and $ClP(O)[N(H)R]_2$ (R = Me, Et, or Pr^i), rather than cyclodiphosphazanes as obtained in analogous reactions with phosphorus trichloride.

CYCLODIPHOSPHAZANES containing the ring system (I) (X = lone pair,[1-4] O,[5] or S[5]) are well known and have been prepared by several different methods. We recently showed[2] that cyclodiphosph(III)azanes (Ia)



R = Alkyl

(Ia) X = lone pair
(Ib) X = O
(Ic) X = S

result from reaction of phosphorus trichloride with primary aliphatic amines and closely related results have been reported[3] for primary aromatic amines using more forcing conditions. In the reactions with primary aliphatic amines it is probable that the intermediate $Cl_2P(X)$·NR·P(X)Cl·N(H)R (IIa; X = lone pair) is involved, which undergoes extremely rapid cyclisation. The mechanism of this cyclisation step may also be common to analogous phosphorus(V) compounds, since Kukhar'[6] has shown that (IIb; X = O, R = alkyl) may also be readily cyclised by triethylamine. We now show that compounds of the type $[Cl_2P(X)]_2NR$ (IIIa, X = lone pair, R = Me, Et, or Bu^t; IIIb, X = O, R = Me or Et; IIIc, X = S, R = Me) are readily cyclised by primary aliphatic amines and report the results of some studies into the factors underlying these cyclisations.

RESULTS AND DISCUSSION

Phosphorus trichloride readily reacts with i-propylamine[2] and with t-butylamine[1,2] to give the cyclodiphosph(III)azanes (Ia; R = Pr^i or Bu^t). No evidence was obtained for the formation of intermediates (IIa; R = Pr^i or Bu^t), despite the fact that the cyclic product (Ia; R = Bu^t) can also be obtained[1] from Cl_2P·N(H)Bu^t and triethylamine. A second possible route to intermediates (II) lies in reactions of primary amines with bis(dichlorophosphino)amines, (IIIa), which are best obtained from reactions of primary amine hydrochloride salts with phosphorus trichloride heated under reflux in *sym*-tetrachloroethane. Compounds (IIIa; R = Me and Et) were readily obtained,[7] but with t-butylammonium chloride the reaction was very slow. In this case a cyclic rather than an acyclic product was obtained [equation (1)]. We eventually obtained the derivative

$$2PCl_3 + 2Bu^tNH_3Cl \longrightarrow (ClPNBu^t)_2 + 6HCl \quad (1)$$

(IIIa; R = Bu^t) by the condensation (2). Subsequent

$$PCl_3 + Cl_2P·N(H)Bu^t \xrightarrow{Et_3N} (IIIa) + HCl \quad (2)$$

reactions of compounds (IIIa) with 2 mol equiv. of t-butylamine gave a mixture of starting materials and cyclodiphosph(III)azanes, (Va). The latter compounds were obtained in good yield on reaction with 3 mol equiv. of t-butylamine (see below).

In view of this finding, it seemed that cyclodiphosph(III)azanes with small alkyl groups, which have proved difficult to identify,[2] might best be prepared by cyclisation of compounds (IIIa) [equation (3)]. When

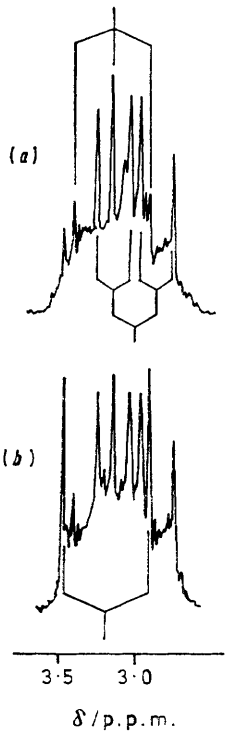
$$(IIIa;\ R = Me) + 3NH_2R \longrightarrow (Ia) + 2RNH_3Cl \quad (3)$$

reaction (3) was carried out with methylamine (R = Me), the products gave the ^1H n.m.r. spectrum shown in the Figure. $^1H\{^{31}P\}$ Double-irradiation n.m.r. experiments showed that this multiplet was connected with signals at δ 127 and 52 p.p.m. in the ^{31}P spectrum, well out of the range anticipated for compound (Ia; R = Me) (see below), but not far from that anticipated for $(ClPNMe)_3$.

† No reprints available.

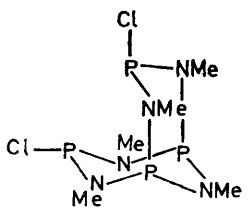
[1] O. J. Scherer and P. Klusmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 752.
[2] R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat, and L. Stobbs, *J.C.S. Dalton*, 1973, 1414.
[3] A. R. Davies, A. T. Dronsfield, R. N. Haszeldine, and D. R. Taylor, *J.C.S. Perkin I*, 1973, 379.
[4] F. L. Bowden, A. T. Dronsfield, R. N. Haszeldine, and D. R. Taylor, *J.C.S. Perkin I*, 1973, 516.
[5] I. Haiduc, 'The Chemistry of Inorganic Ring Systems,' Part 2, Wiley, London, 1970; A. F. Gapov, N. N. Melńikov, and L. V. Razvodovskaya, *Russ. Chem. Rev.*, 1970, **39**, 20.
[6] V. P. Kukhar', *J. Gen. Chem. U.S.S.R.*, 1970, **40**, 761.
[7] J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2689.

After several days a new doublet (apparent J_{P-H} 34·5 Hz) enclosing a ' hump ' started to appear (Figure), which was connected with a signal at δ 117 p.p.m. in the ^{31}P n.m.r. spectrum. The mass spectrum of the same



^{1}H N.m.r. spectrum of the products of reaction of the compound $(Cl_2P)_2NMe$ with 3 mol equiv. of methylamine: (*a*) immediately after mixing the reagents (the triplet arises from coupling to phosphorus at δ 52 p.p.m. and the doublet of doublets from coupling to phosphorus at δ 52 and 127 p.p.m.); (*b*) after 3 weeks (the new doublet arises by coupling to phosphorus at δ 117 p.p.m.)

mixture indicated that compounds $(ClPNMe)_n$ (n = 2—4) were present, but the most intense molecular ion at *m/e* 339 had a two-chlorine-isotope pattern. This ion may be identified with compound (IV), a probable intermediate in formation of the cage compound $P_4(NMe)_6$ (^{31}P shift, δ 82 p.p.m.), known [5] to be formed from reaction of phosphorus trichloride with excess of

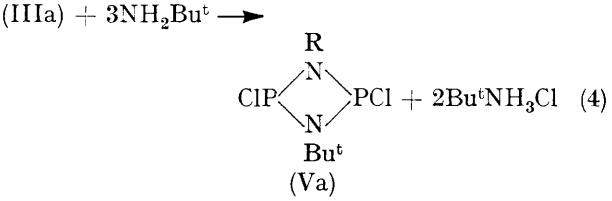


(IV)

methylamine. The credibility of structure (IV) is also advanced by the observation that its arsenic analogue, $As_4(NMe)_5Cl_2$, is known [8] to be formed in the reaction of $As_4(NMe)_6$ with hydrogen chloride. However, in view of difficulties experienced in assigning ^{1}H and ^{31}P n.m.r. signals to such a structure and the possibility of rearrangements occurring within the mass spectrometer (see below), the presence of (IV) and of $(ClPNMe)_{2-4}$ in the reaction products must be regarded as a tentative assignment only.

When R = Et, the products of reaction (3) appeared slightly more stable, and the ^{1}H n.m.r. spectrum of the reaction mixture showed a triplet of quartets, which would be anticipated for the methylene-proton signals in (Ia; R = Et). $^{1}H\{^{31}P\}$ Double-resonance n.m.r. experiments showed that the ^{31}P shift was δ 227 p.p.m. (Table 1), which compares with the very low field shift of δ 211 p.p.m. characterising (Ia; R = Bu^t).[2] Some rather tenuous evidence that (Ia; R = Et) was present as a *cis*-isomer was deduced from the fact that the methylene protons appeared to be magnetically equivalent, as were the methyl protons in (Ia; R = Pr^i).[2] On standing at ambient temperatures the original set of methylene proton signals was replaced by a new, more complex, set at lower field. This mixture was distilled to give a product with two ^{31}P signals at δ 129 and 136 p.p.m. in a 1 : 2 intensity ratio, similar to that obtained from reaction of phosphorus trichloride with ethylamine.[2] Complete ^{1}H decoupling sharpened up these two signals to well defined singlets. The mass spectrum of this mixture gave molecular ions corresponding to (Ia; R = Et) and $(ClPNEt)_3$, with the latter predominating. The ^{31}P shift measurements and the volatility of the mixture suggest that compound (Ia; R = Et) is formed as the result of rearrangements within the spectrometer. It may be noted that the compounds $(ClPNEt)_3$ and $(ClPNEt)_4$ were originally reported [5] to be obtained from reaction of $EtN(SiMe_3)_2$ with phosphorus trichloride.

Cyclisation of compounds (IIIa; R = Me, Et, or Bu^t) was readily effected by t-butylamine, giving for the first time cyclodiphosph(III)azanes with different alkyl substituents [equation (4)]. The size of the R group did



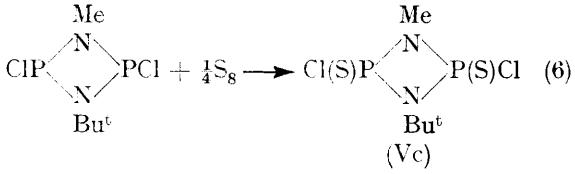
(Va)

not appear to be very important since there was little difference in the ease with which cyclisation occurred when R = Me or Bu^t. Again there was no evidence for the presence of $Cl_2P{\cdot}NR{\cdot}PCl{\cdot}N(H)Bu^t$. The ^{1}H n.m.r. spectrum (Va; R = Et) showed two chemically shifted CH_2 signals in a 1 : 1 intensity ratio indicating,[2] unexpectedly, the presence of a *trans*-isomer, or, less likely, a *cis*-isomer without a mirror plane of symmetry. The possibility that the two signals might arise from a mixture of geometrical isomers is also unlikely since the ^{1}H-decoupled ^{31}P n.m.r. spectrum was a singlet.

The dimethylaminolysis of the dichlorophosphinoyl

[8] H.-J. Vetter, H. Nöth, and W. Jahn, *Z. anorg. Chem.*, 1964, **328**, 144.

and dichlorophosphinothioyl derivatives, $Cl_2P(X)$·NMe·$P(X')Cl_2$ (X = X′ = O; X = X′ = S; X = O, X′ = S), has been investigated,[9] and it has been shown that replacement of chlorine atoms occurs by a non-geminal scheme, similar to that which is dominant in the dimethylaminolysis of $N_3P_3Cl_6$.[10] Since t-butylamine replaces chlorine atoms by a geminal pattern in $N_3P_3Cl_6$,[11] it was of interest to study the reactions of acyclic P^V–N–P^V compounds [12,13] with this amine. The results were closely related to those observed with analogous tervalent phosphorus compounds in that starting material (IIIc; R = Me). It was best obtained as in equation (6). Cyclodiphosph(v)azanes could not



(6)

be identified from reactions with the more reactive primary amines, methylamine and ethylamine, which

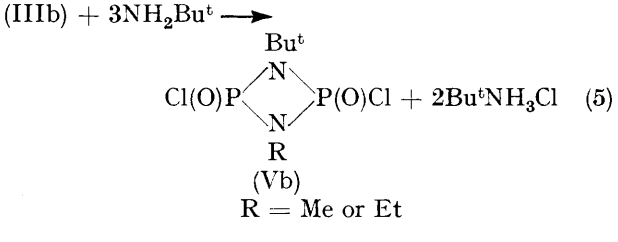
TABLE 1

N.m.r. data

Compound	^{31}P δ/p.p.m.[a]	^1H δ(α-CH) [b]	^1H δ(β-CH) [b]	^1H $^3J_{P-N-C-H}$/Hz	^1H $^4J_{P-N-C-C-H}$/Hz	^1H $^3J_{H-C-C-H}$/Hz
$(Cl_2P)_2NBu^t$ (IIIa)	168·5		1·74		1·0	
$(ClPNBu^t)_2$ (Ia)	210·9		1·34		1·0	
$(ClPNEt)_2$ (Ia)	227·3	3·12	1·27	9·5		7·0
$(ClPNEt)_3$	136 (2) or 129 (1)	3·95	1·52	5·5		7·0
ClP·NMe·PCl·NBu^t (Va)	226	2·72	1·37	11·2	1·0	
ClP·NEt·PCl·NBu^t (Va)	219·5	3·17 [c]	1·39 (Bu^t) 1·26 (Et)	9·5	1·0 (Bu^t)	7·2
Cl(O)P·NMe·P(O)Cl·NBu^t (Vb)	−6·4 (3) −4·1 (1)	2·95	1·61	16·3 (3) 15·7 (1)	0·6	
Cl(O)P·NEt·P(O)Cl·NBu^t (Vb)	−6·2 (4) 4·8 (1)	*ca.* 3·4	1·57 (Bu^t) 1·41 (Et)	16·1 (4) 17·0 (1)		7
Cl(S)P·NMe·P(S)Cl·NBu^t (Vc)	47 (3) 49 (2)	2·96 (3) 2·97 (2)	1·73	17·1 17·1	0·6	
$[Cl(O)PNMe]_2$ (Ib)	−3 (4) 0(1)	2·97		17·0		
$Cl_2P(O)$·NMe·P(O)Cl·N(H)Me (IIb)	14 ($POCl_2$) [d] 14·6					
$Cl_2P(O)$·NMe·P(O)Cl·N(H)Bu^t (II)	*ca.* 15			12·7 14·9		
$Cl_2P(O)$·N(H)Et	16					
$ClP(O)[N(H)Et]_2$	24					
$Cl_2P(O)$·N(H)Pr^i	13					
$ClP(O)[N(H)Pr^i]_2$	19					
$Cl_2P(O)$·N(H)Bu^t	10		1·45		1·2	

[a] Relative to 85% H_3PO_4; figures in parentheses show isomer ratios. [b] Obtained from $CDCl_3$ solutions. [c] Two signals separated by *ca.* 0·5 Hz. [d] $^2J_{P-N-P}$ 16·0 Hz.

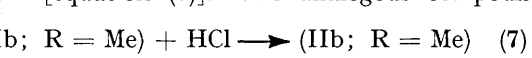
reactions with 2 mol equiv. of t-butylamine gave roughly equimolar quantities of starting materials and cyclodiphosphazanes; 3 mol equiv. of amine gave the same cyclodiphosphazanes in good yield [equation (5)]. The



(5)

dithio-analogue (Vc; R = Me) was obtained only very slowly by this route and even then mixed with the gave insoluble products, although this does not preclude a rapid cyclisation step. The reactions with compounds (IIIb) differed from those with (IIIa) in that small quantities of $Cl_2P(O)$·NR·P(O)Cl·N(H)Bu^t (IIb), were detectable. This shows that the rate of cyclisation, relative to aminolysis, is less than in the case of the tervalent phosphorus compounds.

An acyclic derivative (IIb; R = Me) was however readily isolated following the procedure described by Kukhar' [6] [equation (7)]. The analogous compounds



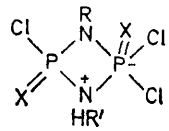
(7)

(Ic) were unreactive under similar conditions.[13] Kukhar' also found that derivatives (IIb) are readily cyclised by

[9] I. Irvine and R. Keat, *J.C.S. Dalton*, 1972, 17; G. Bulloch, R. Keat, and N. H. Tennent, *J.C.S. Dalton*, in the press.
[10] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.
[11] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 5032.
[12] R. Keat, *J. Chem. Soc.* (*A*), 1970, 2732.
[13] R. Keat, *J.C.S. Dalton*, 1972, 2189.

tertiary base, and, as might be anticipated, we found that (IIb; R = Me) is also cyclised by t-butylamine to give (Ib; R = Me). The ready ring cleavage of compounds (Ib) by hydrogen chloride is interesting because (IIb; R = Me) is unreactive to this reagent under similar conditions. The fact that the four-membered phosphorus–nitrogen ring might be expected to have relatively small angles at phosphorus [*cf.* 85·5° in (Ib; R = Bu^t) [14]] means that some of the mechanistic reasoning originally applied to account for the hydrolysis of cyclic phosphates [15] may be important here. Thus we may visualise ring cleavage as proceeding by initial protonation at oxygen, followed by nucleophilic attack of Cl^- at phosphorus to give an intermediate with an approximately trigonal-bipyramidal distribution of bonds about phosphorus. The free energy of activation for formation of this intermediate would be expected to be relatively low. Such an intermediate would not, of course, require a pseudo-rotation step to place a leaving (nitrogen) atom in an axial position. However, it is not yet possible to distinguish this type of mechanism from one in which the approach of the nucleophile is simply less hindered because of a small N–P–N bond angle. Presumably the derivatives (Ia) and (Ic) are unaffected by hydrogen chloride because the initial protonation step is more difficult.

The facility with which ring-closure reactions occurred in this study may also be viewed in terms of formation of the trigonal-bipyramidal intermediate (A). Formation



(A)

of such an intermediate is presumably favoured over one in which a molecule of t-butylamine attacks the $-P(X)Cl_2$ group, because of a relatively small loss of (rotational) entropy.[16] Any unfavourable enthalpy term reflecting ring strain must be overcome by the entropy term. The fact that the N–P–N bond angles are 82·5 and 85·5° in (Ia; R = Bu^t) [17] and (Ib; R = Bu^t) [14] respectively indicates that smaller N–P–N angles are more readily accommodated at tervalent phosphorus, consistent with the observation that the rate of cyclisation relative to aminolysis is greater in the tervalent phosphorus compounds. Although in most cases formation of a four-membered cyclodiphosphazane ring was observed, our results suggest that these are not thermodynamically favoured in the case of cyclodiphosph(III)azanes with small alkyl groups (R = Me or Et). Indeed, formation of the cage compound $P_4(NMe)_6$, and its tentatively identified precursor (IV), are consistent with

TABLE 2

Experimental details

Substrate (Amount/mmol)	Reactant (Amount/mmol)	Reaction conditions [θ_c/°C, Solvent (V/cm^3)]	Subsequent treatment [stirring (t/h) at θ_c/°C]	Product(s) (yield/%), product ratio (isomer ratio)	M.p. (θ_c/°C) or [b.p. (θ_c/°C), P/mmHg]
(IIIa; R = Me) (9)	NH_2Me (30)	−78, CH_2Cl_2 (20)	(0·5) at 20	see text	
(21)	NH_2Bu^t (63)	−78, Et_2O (100)	(0·5) at 20	(IIIa; R = Me), (Va; R = Me) 1 : 1	
(30)	(90)	−78, Et_2O (150)	(0·5) at 20	(Va; R = Me) (52)	[65, 0·4]
(IIIa; R = Et) (25)	NH_2Et (75)	−78, Et_2O (200); also in CH_2Cl_2 at −78		$(ClPNEt)_{2-4}$ (see text)	[100—120, 0·1]
(16)	NH_2Bu^t (48)	−78, Et_2O (100)	(1) at 20	(Va; R = Et) (61)	[46, 0·05]
(IIIa; R = Bu^t) (9)	(27)	−78, Et_2O (60)	(1) at 20	(Ia; R = Bu^t) (88)	see refs. 1 and 2
(IIIb; R = Me) (6)	NH_2Me (18)	−78, Et_2O (100)	(1) at 20	unidentified insoluble products	
(12)	NH_2Bu^t (24)	20, Et_2O (50)	(10) at 20	(IIIb; R = Me), $Cl_2P(O)\cdot NMe\cdot P(O)Cl\cdot N(H)Bu^t$, (Vb; R = Me) (1 : 0·1 : 1	
(17)	(51)	20, Et_2O (60)	(12) at 20	(Vb; R = Me) (57) 3 : 1)	80—85 [130, 0·1]
(IIIb; R = Et) (13)	(39)	20, CH_2Cl_2 (50)	refluxed (24)	(Vb; R = Et) (70) (4 : 1)	40—55
(IIIc; R = Me) (15)	(45)	20, $CHCl_3$ (20)	refluxed (24)	(IIIc; R = Me), (Vc; R = Me) 4 : 1	
(Va); R = Me) (11)	S_8 (2·75)	20 + trace $AlCl_3$	(1) at 150	(Vc; R = Me) (43) (3 : 2)	[84, 0·2]
(IIb; R = Me) (2·5)	NH_2Bu^t (5)	20, CH_2Cl_2 (25)		(Ib; R = Me) (4 : 1)	see ref. 5
PCl_3 (300)	$Bu^tNH_3Cl^-$ (90)	20, $Cl_2CHCHCl_2$ (200)	refluxed (7 weeks)	$(ClPNBu^t)_2$ (47 based on NH_3Bu^tCl)	see refs. 1 and 2
$Cl_2P\cdot N(H)Bu^t$ (100)	PCl_3 (100), Et_3N (100)	−78, Et_2O (1 000)	(1·5)	(IIIa; R = Bu^t) (65)	55
$P(O)Cl_3$ (100)	RNH_2 (300)	−78, Et_2O	refluxed (1)	$Cl_2P(O)\cdot N(H)R$ (R = Me, Et, Pr^i, or Bu^t)	(R = Bu^t) 114—115 (sublimes)
				$ClP(O)[N(H)R]_2$ (R = Me, Et, or Pr^i)	

[14] R. Keat, L. Manojlović-Muir, and K. W. Muir, *Angew. Chem. Internat. Edn.*, 1973, **12**, 311.

[15] R. F. Hudson and C. Brown, *Accounts Chem. Res.*, 1972, **5**, 204.

[16] B. Capon, *Quart. Rev.*, 1964, **18**, 45; M. I. Page, *Chem. Soc. Rev.*, 1973, **2**, 295.

[17] K. W. Muir and J. F. Nixon, *Chem. Comm.*, 1971, 1405.

this suggestion, since they are both built up from a cyclotriphosph(III)azane ring.

The cyclodiphosph(III)azanes are also interesting in that only one of the two possible geometric isomers is obtained in each case. Of these, it is known [17] that (Ia; R = Bu^t) has a *cis*-structure, and the n.m.r. evidence, although not unambiguous, favours a *cis*-structure for (Ia; R = Et and Pr^i). The *trans*-structure suggested for (Va; R = Et), however, indicates that the isomer obtained reflects a very subtle balance of steric and/or electronic factors. By contrast, cyclodiphosph(V)azanes are generally obtained as a mixture of geometrical isomers, which have yet to be identified, and unfortunately, it is not yet clear whether the isomers obtained reflect thermodynamic or kinetic control.

An important difference between the reactions of phosphorus trichloride and phosphoryl chloride with primary amines lies in the ease with which P–N–P units are formed in reactions with phosphorus trichloride. We have examined reactions of phosphoryl chloride with primary amines under conditions where cyclic products are obtained with phosphorus trichloride. Thus 3 mol equiv. of primary amine gave a 1 : 1 mixture of $Cl_2P(O)\cdot N(H)R$ and $ClP(O)[N(H)R]_2$ (R = Me, Et, or Pr^i) at ambient temperatures and t-butylamine gave only $Cl_2P(O)\cdot N(H)Bu^t$. It would appear that these reactions reflect the ease with which the derivatives $Cl_2P\cdot N(H)R$ are dehydrohalogenated relative to $Cl_2P(O)\cdot N(H)R$. The latter compounds are known to eliminate hydrogen chloride to form cyclodiphosph(V)azanes only at higher temperatures.[5]

EXPERIMENTAL

Solvents were dried by conventional means. Phosphorus trichloride, phosphoryl chloride, and t-butylamine were distilled before use. Other amines, obtained commercially, were used without purification. The compounds $(Cl_2P)_2NR$ (IIIa; R = Me or Et),[7] $[Cl_2P(O)]_2NR$ (IIIb; R = Me [12] and Et [18]), $[Cl_2P(S)]_2NMe$,[13] $Cl_2P\cdot N(H)Bu^t$,[1] and $Cl_2P(O)\cdot NMe\cdot P(O)Cl\cdot N(H)Me$ [6] were prepared by literature methods.

TABLE 3

Analytical (%) and mass-spectrometric data

	Found				Calc.			
Compound	C	H	N	*m/e* *	C	H	N	*m/e* *
(Va; R = Me)	25·4	4·9		232	25·8	5·2		232
(Va; R = Et)	28·8	5·5	28·7 †	246	29·1	5·7	28·8 †	246
(Vb; R = Me)	22·7	5·1	10·8	249 ($P - 15$)	22·6	4·5	10·8	264
(Vb; R = Et)	26·0	5·1	10·1	263 ($P - 15$)	25·8	5·1	10·0	278
(Vc; R = Me)	21·6	4·4	8·5	296	20·2	4·1	9·4	296
(IIIa; R = Bu^t)	18·8	3·2	5·6	273	17·5	3·3	5·1	273
$Cl_2P(O)\cdot N(H)Bu^t$	25·4	5·6	7·1	174 ($P - 15$)	25·2	5·3	7·4	189

* For ^{35}Cl-containing ion. † Cl Analysis.

Preparative methods were similar to those previously described [12] and are summarised in Table 2. Analytical data are given in Table 3.

^1H and ^{31}P N.m.r. spectra were obtained on a Jeol C60HL spectrometer at 60 and 24·3 MHz respectively. Selective and power $^1H\{^{31}P\}$ decoupling experiments were accomplished using a Schomandl ND100M frequency synthesiser and a Jeol SDHC unit. Mass spectra were obtained on an A.E.I. MS12 spectrometer.

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[18] M. E. Harman, R. Keat, and D. W. A. Sharp, unpublished work.