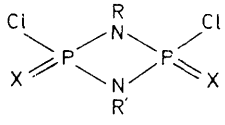
New Observations on the Cyclisation of Compounds containing the P–N–P Skeleton by Primary Amines; an Extension to Diphosphinoylmethanes

By **Gordon Bulloch** and **Rodney Keat,*** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Dichlorophosphino(dichlorophosphinoyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$, reacts with 3 mol equiv. of t-butylamine to give the cyclodiphosphazane $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$. By contrast, $(Bu^tHN)P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$ is the only product isolated from the analogous reaction with $Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$. Similar reactions of $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$ with NH_2Bu^t and NH_2Pr^i give a new class of ring compound, $Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NR$ (R = Pr^i or Bu^t) (1,2,4-azadiphosphetans), but no cyclic products have been identified from analogous reactions with $Cl_2(O)P{\cdot}CH_2{\cdot}CH_2{\cdot}P(O)Cl_2$. Attempted cyclisation of $(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ by NH_2Bu^t gives an acyclic product, $(Bu^tHN)(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)(NHBu^t)$, rather than $(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2){\cdot}NBu^t$. The latter cyclic derivative, obtained by heating $(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)(NHBu^t)$, is resistant to ring opening by $NHMe_2$, whereas ring opening occurred in the attempted dimethylaminolysis of $Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t$. Attempts to prepare pure samples of $Cl_2P{\cdot}CH_2{\cdot}PCl_2$, as a substrate for cyclisation reactions, from the reaction of PCl_3 with $Ph_2P{\cdot}CH_2{\cdot}PPh_2$, have been unsuccessful, and some of the products of these reactions are described.

THE reactions of diphosphinoamines, $Cl_2P{\cdot}NR{\cdot}PCl_2$, and of diphosphinoylamines, $Cl_2(O)P{\cdot}NR{\cdot}P(O)Cl_2$ (R = alkyl), with primary amines were recently shown [1] to result in the formation of cyclodiphosphazanes, (I). It

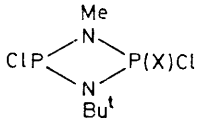


(I) X = lone pair or O; R and R′ = alkyl

was not possible to isolate monoamino-derivatives, $Cl_2(X)P{\cdot}NR{\cdot}P(X)Cl(NHR')$, from these reactions and the only evidence for their formation, in small quantities, was obtained with diphosphinoyl derivatives (X = O). By analogy with results obtained for the formation of carbocyclic compounds,[2] it was suggested [1] that cyclic, rather than acyclic, aminolysis products are obtained as the result of an entropy-controlled intramolecular nucleophilic-displacement reaction. We now report a study of the scope and generality of these reactions, and show that related results can be achieved from the reactions of primary amines with bis(dichlorophosphinoyl)methane, $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$.

RESULTS AND DISCUSSION

The reactions of non-symmetrical compounds of the type $Cl_2P{\cdot}NMe{\cdot}P(X)Cl_2$ (X = O or S) with t-butylamine were examined. This amine was chosen because it frequently gave good yields of cyclodiphosphazanes,[1] which may be related to the fact that it is a good base, but a relatively poor nucleophile (see below). A ^1H n.m.r. spectrum of the products of the reaction of $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ with 3 mol equiv. of NH_2Bu^t in methylene chloride solution was somewhat complex, but after solvent removal two products readily identifiable as isomeric cyclodiphosphazanes, (II; X = O), were obtained, which subsequently rearranged to give one isomer at ambient temperatures over a period of several days.

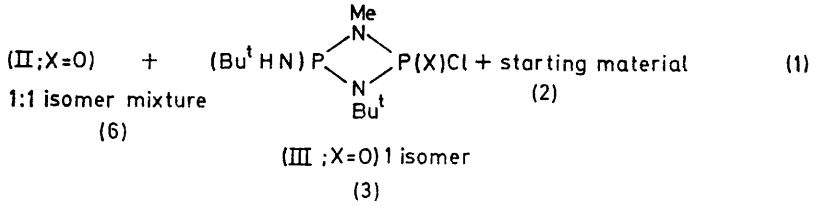


(II)

By combining the results of ^1H-{^{31}P} and ^{31}P-{^1H} n.m.r. spectroscopy it was possible to identify the components in the original reaction mixture, equation (1) (relative proportions in parentheses). Compound (III; X = O) has not been previously identified, and was obtained as the sole product of reaction (2). The isomer of (III; X = O) identified in the cyclisation reaction was

[1] G. Bulloch and R. Keat, *J.C.S. Dalton*, 1974, 2010.
[2] B. Capon, *Quart. Rev.*, 1964, **18**, 45; M. I. Page, *Chem. Soc. Rev.*, 1973, **2**, 295.

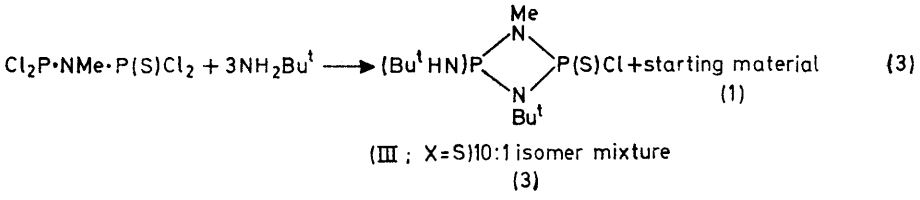
the minor isomer formed here. The reaction of $Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$ with 3 mol equiv. of NH_2Bu^t initially followed a similar course [equation (3)] to that encountered



with the phosphinoyl analogue above, but in this case the products did not react further to form (II; X = S).

$$\text{(II; X = O)} + 2NH_2Bu^t \longrightarrow \underset{\text{1 isomer}}{} \underset{\substack{\text{4 : 1 isomer}\\ \text{mixture}}}{\text{(III; X = O)}} + [NH_3Bu^t]Cl \quad (2)$$

Compound (III; X = S) was also a product of reaction



(4). These results may be contrasted with the finding that good yields of only one isomer of $ClP[\cdot NMe\cdot PCl\cdot]NBu^t$ are obtained from the reaction of $Cl_2P{\cdot}NMe{\cdot}PCl_2$ with 3 mol equiv. of NH_2Bu^t.[1]

$$\text{(II; X = S)} + 2NH_2Bu^t \longrightarrow \underset{\text{5 : 1 isomer mixture}}{} \underset{\substack{\text{1 : 1 isomer}\\ \text{mixture}}}{\text{(III; X = S)}} + [NH_3Bu^t]Cl \quad (4)$$

It is not clear whether the formation of compounds (III) in the reactions of $Cl_2P{\cdot}NMe{\cdot}P(X)Cl_2$ (X = O or S) with NH_2Bu^t is due to: (*a*) the rate of cyclisation [$(Bu^tHN)ClP{\cdot}NMe{\cdot}P(X)Cl_2$ * ⟶ (II)] being less than the rate of aminolysis [(II; X = O or S) ⟶ (III; X = O or S)]; or (*b*) the rate of aminolysis to form $(Bu^tHN)_2P{\cdot}NMe{\cdot}P(X)Cl_2$ (followed by subsequent cyclisation) being greater than the rate of cyclisation [$(Bu^tHN)ClP{\cdot}NMe{\cdot}P(X)Cl_2$ * ⟶ (II)]. The lack of stereospecificity found in the formation of (III; X = S) in reaction (4) compared to the cyclisation (3), and the observation that the two routes leading to the formation of (III; X = O) [products (1) and reaction (2)] result in different isomers predominating, are better accommodated by the cyclisation condition (*b*). On the other hand it seems doubtful whether the dichlorophosphinoyl and dichlorophosphinothioyl groups in the intermediates $(Bu^tHN)ClP{\cdot}NMe{\cdot}P(X)Cl_2$ (X = O or S) possess low enough electrophilicities to hinder the entropy-favoured cyclisation to such an extent as to allow the intermediates $(Bu^tHN)_2P{\cdot}NMe{\cdot}P(X)Cl_2$ (X = O or S) to be formed by further aminolysis.

The fact that (II; X = O) can be obtained pure by solvent evaporation from the initial reaction mixture suggests that the rearrangement (5) occurs fairly readily. This was easily shown to be the case using a sample of (III; X = O), obtained by the direct aminolysis route described above. Compound (II; X = O) was obtained as a 2 : 1 isomer mixture, which eventually formed one isomer on standing over a period of several days at ambient temperatures. Compounds of the general type (II) have previously been identified as products of the controlled oxidation of $ClP[\cdot NMe\cdot PCl\cdot]NBu^t$ (ref. 4) or $ClP[\cdot NBu^t\cdot PCl\cdot]NBu^t$,[5] although different isomer ratios were observed in these cases. The observation of isomerisation of (II; X = O) is interesting because previous studies have shown that the formation of cyclodiphosph(III)azanes, $(ClPNR)_2$, is invariably stereospecific, but that cyclodiphosph(V)azanes are formed as a mixture of *cis* and *trans* isomers.[1,5] It was not clear whether these findings are the result of thermodynamic or kinetic control. In this case it appears that both isomers are kinetically almost equally favoured, but that subsequent isomerisation gives the thermodynamically favoured product. Tervalent phosphorus is known to be configurationally stable at ambient temperatures and the constraint of the cyclodiphosphazane ring might be expected to increase this stability relative to analogous acyclic phosphorus(III) compounds. Isomerisation probably occurs by chloride-ion exchange at P^{III}, for isomerisation is faster in the presence of added $[NH_3Bu^t]Cl$, and because phosphorus(III)–chlorine bonds are known

$$3\text{(III; X = O)} + 2\ Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2 \longrightarrow \underset{\text{5(II; X = O)}}{} + [NH_3Bu^t]Cl \quad (5)$$

* This is the initial product expected from the reaction of $Cl_2P{\cdot}NMe{\cdot}P(X)Cl_2$ with NH_2Bu^t, by analogy with the behaviour of dimethylaminotrimethylsilane.[3]

[3] R. Keat, *J.C.S. Dalton*, 1974, 876.
[4] G. Bulloch and R. Keat, unpublished work.
[5] R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat, and L. Stobbs, *J.C.S. Dalton*, 1973, 1414.

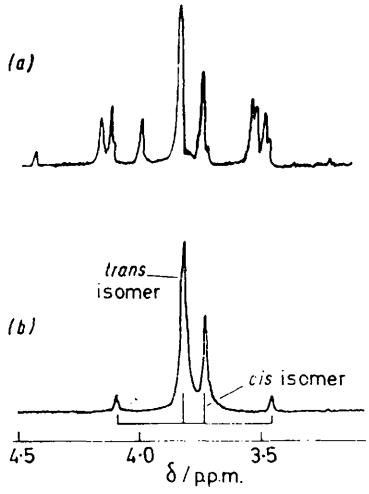
to be more labile than phosphorus(v)–chlorine bonds.[6] In view of these results we decided to recheck previous findings on the cyclisation of $Cl_2P{\cdot}NMe{\cdot}PCl_2$ with NH_2Bu^t by examination of ^1H and ^{31}P n.m.r. spectra at *ca.* −50 °C, immediately after carrying out the reaction at −78 °C. There was no evidence for more than one geometrical isomer.

In order to compare the results of the diphosphino- and diphosphinoyl-amines with the analogous alkanes, $Cl_2(X)P{\cdot}(CH_2)_n{\cdot}P(X)Cl_2$ (X = lone pair or O; n = 1 or 2), we attempted to prepare bis(dichlorophosphino)-methane, $Cl_2P{\cdot}CH_2{\cdot}PCl_2$, but were not successful in obtaining a pure sample. This compound is reported to be obtained from the reaction of $Ph_2P{\cdot}CH_2{\cdot}PPh_2$ with phosphorus trichloride in a sealed tube at 270 °C.[7] In our hands this reaction gave no trace of $Cl_2P{\cdot}CH_2{\cdot}PCl_2$, but, instead, a mixture possibly containing Cl_2PCH_2Cl in addition to the expected chlorodiphenylphosphine and dichlorophenylphosphine. However, $Ph_2P{\cdot}CH_2{\cdot}PPh_2$ undergoes a ready reaction with refluxing PCl_3 (b.p. 76 °C) (0.5 h) [equation (6)]. In addition an unidentified

$$Ph_2P{\cdot}CH_2{\cdot}PPh_2 + PCl_3 \longrightarrow Ph_2P{\cdot}CH_2{\cdot}PCl_2 + PPh_2Cl \quad (6)$$

orange solid was obtained. Displacement of diphenylphosphino-groups was complete (indicated by the appearance of a triplet in the ^1H n.m.r. spectrum) after refluxing with PCl_3 for *ca.* 15 h, but difficulties arose in the separation from PPh_2Cl, and all attempts to effect this resulted in decomposition of the desired product. The ^{31}P shift reported[7] for $Cl_2P{\cdot}CH_2{\cdot}PCl_2$ (δ 187 ± 1) p.p.m.) is *ca.* 13 p.p.m. to low field of that for the compound giving the triplet in the ^1H spectrum. Some clarification of the purification procedure is required, for we believe that difficulties mainly arise by cleavage of the P–C–P bridge.

On the other hand, the preparation of bis(dichlorophosphinoyl)methane and 1,2-bis(dichlorophosphinoyl)-ethane was readily accomplished by a simplified literature method.[8] Reaction of $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$ with NH_2Bu^t in methylene chloride solution (required to dissolve the phosphinoyl compound) gave the new class of ring compound (IV; R = Bu^t),* as a mixture of geometrical isomers [equation (7)]. Similar reaction with 2 mol equiv. of NH_2Bu^t left starting material and compound (IV) only, in a 1 : 2 mol ratio. The compound $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl(NHBu^t)$ was not detected, unlike the analogous reaction with $Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl_2$ from which small quantities of $Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl(NHBu^t)$ were found.[1] The two isomers of (IV; R = Bu^t) were readily identified. The ^1H n.m.r. spectrum of (IV; R = Bu^t) is complex in the methylene region, but ^{31}P decoupling (Figure) showed two groups of signals easily assignable to *cis* and *trans* isomers. If the four-membered ring is assumed to be planar, then the methylene protons will be equivalent in the *trans* isomer, but non-equivalent (and therefore form an AB multiplet) in the *cis* isomer. Integration of these signals shows that the *cis* : *trans*-isomer ratio is 5 : 2. The *cis* isomer was purified by crystallisation from diethyl ether–light petroleum and did not undergo isomerisation at ambient temperatures, which suggests that the observed isomer ratio is the result of kinetic control. The analogous ring compound (IV; R = Pr^i) was obtained in a similar way with an almost identical *cis* : *trans*-isomer ratio, although there was a marked increase in the amount of unidentified insoluble material produced in this reaction, which was impossible to remove completely. Attempts to repeat these reactions with aniline and ethylamine were unsuccessful, a complex mixture of products being obtained.



^1H N.m.r. spectra of a mixture of *cis* and *trans* isomers of $Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t$: (*a*) normal spectrum; (*b*) with ^{31}P decoupling

$$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2 + 3NH_2Bu^t \longrightarrow Cl(O)P\langle CH_2, N(R), P(O)Cl + 2[NH_3Bu^t]Cl \quad (7)$$

(IV; R = Bu^t)

It is very likely that these cyclisation reactions with NH_2Pr^i and NH_2Bu^t are favoured by the relatively small loss in entropy incurred by cyclisation of the intermediate, $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl(NHR)$. It is a feature of the cyclisation of α,ω-halogenoalkylamines, $X(CH_2)_nNH_2$,[2] that the yield of cyclic products, $(CH_2)_nNH$, decreases with increasing n, mainly because of a larger negative

* These compounds are not easily named using the phosphazane nomenclature, but can be classified as 1,2-azadiphosphetans, thus (IV; R = Bu^t) becomes 2,4-dichloro-2,4-dioxo-1-t-butyl-1,2,4-azadiphosphetan.

[6] J. E. Bissey, H. Goldwhite, and D. G. Rowsell, *Org. Magnetic Resonance*, 1970, **2**, 81.

[7] K. Sommer, *Z. anorg. Chem.*, 1970, **376**, 37.

[8] W. Althoff, personal communication.

entropy change when the larger rings are formed. We therefore expected that the reactions of NH_2Bu^t and NH_2Pr^i with 1,2-bis(dichlorophosphinoyl)ethane, $Cl_2(O)P{\cdot}CH_2{\cdot}CH_2{\cdot}P(O)Cl_2$, might give reduced yields of cyclic products if the entropy term is dominant. Reactions with NH_2Bu^t failed to give detectable amounts of ring compound, instead large quantities of a white solid and $[NH_3Bu^t]Cl$ were obtained.

able precursors of the complex mixture of products obtained with these amines. It is worth noting that the amount of insoluble material obtained with a given amine is considerably greater than that observed in the reactions with diphosphinoylamines.[1]

In order to show how the electrophilicity of the phosphinoyl centre affects the cyclisation reactions, we examined the reactions of the dimethylamino-derivatives

TABLE 1

N.m.r. data

Compound	^{31}P [a] $\delta(^{31}P)$ [c] p.p.m.	^{31}P [a] ^2J(P–P) Hz	^1H [b] δ(NMe) p.p.m.	δ(But) p.p.m.	δ(CH_2) p.p.m.	^3J(P–N–C–H) Hz	^4J(P–N–C–C–H) Hz	^2J(P–C–H) Hz
$Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$	170.1 (PIII) 12.9	80 ± 2	3.25			1.5 (PIII) 15.5		
$Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$	167.7 (PIII) 51.4	122 ± 2	2.92			1.2 (PIII) 15.7		
$ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$	134 [d] (PIII) 12.5	12.0	2.91	1.51		10.2 (PIII) 18.7	1.2 (PIII) <0.3	
	135 (PIII) 8.0	36.3	3.13	1.34		8.4 (PIII) 17.3	1.9 (PIII) <0.5	
$(Bu^tHN)P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$	85 [d] (PIII) 10	10 ± 3	2.60	1.31 1.44 (NHBu^t)		9.0 (PIII) 19.6	1.4 <0.3 (NHBu^t)	
	75.5 (PIII) 3.1	7.4	2.73	1.31 1.44 (NHBu^t)		9.0 (PIII) 17.7	1.4 <0.3 (NHBu^t)	
$(Bu^tHN)P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$	101.5 [d] (PIII) 60.5	8.5	2.54	1.30 1.48 (NHBu^t)		9.0 (PIII) 20.5	1.5 <0.3 (NHBu^t)	
	107.5 (PIII) 61.5	8.5	2.68	1.30 1.48 (NHBu^t)		8.9 (PIII) 19.2	1.5 <0.3 (NHBu^t)	
$Ph_2P{\cdot}CH_2{\cdot}PCl_2$	−26 [e] 189 (PCl_2)	±132.5			*ca.* 3.2 [e]			±1.9 ±15.4 (PCl_2)
$Cl_2P{\cdot}CH_2{\cdot}PCl_2$	174 [e]				*ca.* 3.6 [e]			1.56
$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$	22.6				4.18			18.3
$Cl_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)Cl_2$	42.5				3.04			4.5 [f]
$Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t$	6.1 (*cis*)			1.59	3.72 3.92		<0.5	±19.8 ±14.4 16.2 [g]
	6.9 (*trans*)			1.59	3.88		<0.5	16.5
$Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NPr^i$	5.8 (*cis*)			1.52 (Me_2CH)	3.65 3.85		<0.5	16.3 [g]
	7.3 (*trans*)			1.52 (Me_2CH)	3.77		<0.5	17.3
$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$	28.4 [P(O)Cl_2] 29.2	11.6	2.79		3.92 4.09	14.5		*ca.* 19 *ca.* 19 15.3 [g]
$(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ DL	32.0		2.81		3.46	14.2 [h]		18.1
meso	31.8		2.80		3.28 3.42	14.2 [h]		
$(Bu^tHN)(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)(NHBu^t)$	22.9		2.63	1.28	1.73	9.9 [h]	<0.3	16.8
$(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)(NHBu^t)$	30.5 [P(O)$(NMe_2)_2$]	4.1	2.53 2.65			10.2 9.7		
	19.2		2.61	1.25		9.6	<0.5	
$(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2){\cdot}NBu^t$	10.6		2.78	1.35	2.67	10.5 [h]	<0.3	15.3
$(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t$	6.1 11.1	30.0	2.75	1.44		10.7		

[a] Obtained from neat liquids or CH_2Cl_2 solutions except where noted; positive shifts are downfield from H_3PO_4. [b] Obtained from $CDCl_3$ solutions except where noted. [c] Relative to 85% H_3PO_4. [d] Major isomer in cyclisation reaction. [e] Obtained from PCl_3 solutions. [f] $|^2J(P-C-H) + {}^3J(P-C-C-H)|$. [g] $^2J(H-C-H)$. [h] $|^3J(P-N-C-H) + {}^5J(P-C-P-N-C-H)|$.

The observation that NH_2Bu^t gives rise to the highest yields of cyclodiphosphazanes and related compounds indicates that the entropy term is not the only factor controlling cyclisation by primary amines. The function of the free amine in the cyclisation step is to abstract hydrogen chloride, and the ease with which this is carried out is clearly dependent on its base strength. t-Butylamine is a relatively strong base, but a poor nucleophile and, as such, it is likely to be more efficient in abstracting hydrogen chloride than effecting aminolysis at the second dichlorophosphinoyl group. On the other hand, methylamine and ethylamine, being stronger nucleophiles, will be more efficient in producing aminolysis products such as $(RHN)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NHR)$, probably precursors of the cyclic products.

$(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ and $(Me_2N)Cl(O)P{\cdot}NMe{\cdot}P(O)Cl(NMe)_2$ with NH_2Bu^t. The methylene-bridged compound, prepared by dimethylaminolysis of $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$, unexpectedly gave an acyclic product in refluxing chloroform solution [equation (8)],

$$(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2) + 4NH_2Bu^t \longrightarrow (Bu^tHN)(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)(NHBu^t) + 2[NH_3Bu^t]Cl \quad (8)$$

(V)

whereas $(Me_2N)Cl(O)P{\cdot}NMe{\cdot}P(O)Cl(NMe_2)$ was unreactive under the same conditions. To test the possibility that the acyclic product (V) may be formed *via* a facile ring-opening reaction of (VI), we attempted to synthesise

TABLE 2

Experimental details

Substrate (amount/mmol)	Reactants (amount/mmol)	Reaction conditions solvent (V/cm³)	θ_c/°C	Subsequent treatment (t/h)	Products (%) [relative proportions]	M.p. or b.p. (θ_c/°C) [p/mmHg]
$Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ (21)	NH_2But (63)	CH_2Cl_2 (100)	−78	Stirred (½), solvent not evaporated	ClP(NMe·P(O)Cl·NBut [6] (1 : 1),* $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ [2], (ButN)P(NMe·P(O)Cl·NBut [3]	
(21)	(63)	(100)	−78	Stirred (1)	ClP(NMe·P(O)Cl·NBut (46) (after distillation)	102 [0.6]
ClP(NMe·P(O)Cl·NBut (5)	(10)	(25)	−78	Stirred (2)	(ButNH)P(NMe·P(O)Cl·NBut (60) (4 : 1)*	oil
(5 : 1) * (2)	[NH_3But]Cl (Trace)	$CDCl_3$ (2)	25	Shaken	ClP(NMe·P(O)Cl·NBut (one isomer)	
(ButHN)P(NMe·P(O)Cl·NBut (1)	$Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ (Excess)	(2)	25	Shaken (15)	ClP(NMe·P(O)Cl·NBut, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$	
$Cl_2P{\cdot}NMe{\cdot}PCl_2$ (142)	NH_2But (426)	CH_2Cl_2 (200)	−78	Stirred (0.1)	ClP(NMe·PCl·NBut (one isomer, from n.m.r. at −50 °C)	
$Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$ (8)	(24)	(25)	−78	Stirred (1)	(ButHN)P(NMe·P(S)Cl·NBut [3]9(10 : 1) * $Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$ [1] + other products	75—80 [0.03]
ClP(NMe·P(S)Cl·NBut (3)	(6)	(15)	−78	Stirred (2)	(ButHN)P(NMe·P(S)Cl·NBut (75) (1 : 1) *	
$Ph_2P{\cdot}CH_2{\cdot}PPh_2$ (50)	PCl_3 (excess) (350)	Neat; sealed tube	280	Heated (5)	$PPhCl_2$, PPh_2Cl, Cl_2PCH_2Cl + other products	
(13)	(130)	Neat	25	Refluxed (0.5)	$Ph_2P{\cdot}CH_2{\cdot}PCl_2$, PPh_2Cl + other products	
(13)	(130)	Neat	25	Refluxed (15)	$Cl_2P{\cdot}CH_2{\cdot}PCl_2$, PPh_2Cl + other products	
$(PriO)_2(O)P{\cdot}CH_2{\cdot}P(O)(OPri)_2$ (203)	PCl_5 (815)	Neat	50	Heated (2)	$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$ (63), PriCl, $P(O)Cl_3$	103—104
$(PriO)_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)(OPri)_2$ (200)	PCl_5 (805)	Neat	50	Heated (2)	$Cl_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)Cl_2$ (70), PriCl, $P(O)Cl_3$	104—110 (decomp.)
$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$ (51)	NH_2But (153)	CH_2Cl_2 (350)	−78	Refluxed (3)	Cl(O)P(CH₂·P(O)Cl·NBut(49)(5 : 2) *	110 (0.7) (oil, solid on standing)
(8)	(16)	(80)	−78	Stirred (15)	Cl(O)P(CH₂·P(O)Cl·NBut [2], $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$ [1]	
(25)	NH_2Pri (75)	(200)	−78	Refluxed (3)	Cl(O)P(CH₂·P(O)Cl·NPri(35) (5 : 2) *	100 (0.4)
(25)	NH_2Ph (75)	(200)	25	Refluxed (3)	Complex mixture	
(14)	NH_2Et (42)	(170)	−78	Stirred (15)	$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$ + complex mixture	
$Cl_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)Cl_2$ (22)	NH_2But (66)	(350)	0	Refluxed (4)	Insoluble products	
$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$ (20)	$NHMe_2$ (40)	(150)	−78	Stirred (15)	$Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ [1], $(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ [2] (4 : 1)* $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)Cl_2$	
(27)	(108)	(250)	−78	Stirred (15)	$(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ (82) (3 :1)*	
$(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ (8)	NH_2But (24)	$CHCl_3$ (100)	0	Refluxed (20)	(ButHN)$(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)$(NHBut) [3], $(Me_2N)Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl(NMe_2)$ [1]	solid decomp. >90
$(Me_2N)Cl(O)P{\cdot}NMe{\cdot}P(O)Cl(NMe_2)$ (8)	(32)	(100)	0	Refluxed (20)	(ButHN)$(Me_2N)(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)$(NHBut) (75)	136—149
(5)	(20)	(100)	0	Refluxed (20)	No reaction	
Cl(O)P(CH₂·P(O)Cl·NBut (6)	$NHMe_2$ (24)	CH_2Cl_2 (70)	−78	Stirred (1)	$(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)$(NHBut) [5], Cl(O)P(CH₂·P(O)(NMe₂)·NBut [2], $(Me_2N)(O)P(CH_2{\cdot}P(O)(NMe_2){\cdot}NBut$[1]	
Cl(O)P(CH₂·P(O)Cl·NBut (6)	(34)	(70)	−78	Stirred (1)	$(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)$(NHBut) (80)	Oil, decomp. >130 (0.1)
$(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)$(NHBut) (5)	Neat	150	Heated (0.5)	$(Me_2N)(O)P(CH_2{\cdot}P(O)(NMe_2){\cdot}NBut$ (53) (*trans*)	137—139 160 (0.01)	
$Me_2N(O)P(CH_2{\cdot}P(O)(NMe_2){\cdot}NBut$ (2)	(Excess)	$CDCl_3$ (2)	25	Refluxed (1)	No reaction	
(2)	NH_2But (excess)	$CDCl_3$ (2)	25	Refluxed (20)	No reaction	

* Isomer ratio.

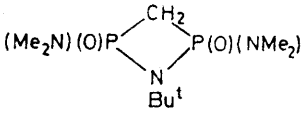
TABLE 3

Analytical data [a]

Compound	Found C	H	N	Cl	m/e [b]	Calc. C	H	N	Cl	m/e [b]
ClP·NMe·P(O)Cl·NBu^t	23.85	5.1	10.9		248	24.1	4.9	11.3		248
(Bu^{t}HN)P·NMe·P(O)Cl·NBu^t	37.0	7.8	14.3	12.1	285	37.8	7.7	14.7	12.4	285
(Bu^{t}HN)P·NMe·P(S)Cl·NBu^t	36.4	8.0	13.9			35.8	7.4	13.9		301
Cl(O)P·CH$_2$·P(O)Cl·NBu^t	24.2	5.1	6.0	27.7	234 (P − 15)	24.0	4.4	5.6	28.4	249
Cl(O)P·CH$_2$·P(O)Cl·NPr^i	20.3	4.1	5.7		220 (P − 15)	20.4	3.8	5.9		235
(Me$_2$N)Cl(O)P·CH$_2$·P(O)Cl(NMe$_2$)	22.2	5.3	9.9	25.1	266	22.5	5.3	10.5	26.6	266
(Bu^{t}HN)(Me$_2$N)(O)P·CH$_2$·P(O)(NMe$_2$)(NHBu^t)	46.0	10.0	16.2		340	45.9	10.1	16.5		340
(Me$_2$N)$_2$(O)P·CH$_2$·P(O)(NMe$_2$)(NHBu^t)					312					312
(Me$_2$N)(O)P·CH$_2$·P(O)(NMe$_2$)·NBu^t	40.2	8.9	15.6		267	40.5	8.7	15.7		267

[a] Elemental analysis figures are given in %. [b] For ions containing ^{35}Cl.

(VI) from (IV; R = Bu^t) with the results in equation (9). Compound (VI) was obtained as a pure *trans* isomer on



(VI)

heating the acyclic compound (VII) as shown below, but failed to react with NH$_2$Bu^t or NHMe$_2$ in refluxing chloroform solution, thus proving that (V) is not formed *via*

(IV; R = Bu^t) + 5NHMe$_2$ → (*cis* isomer)

(Me$_2$N)$_2$(O)P·CH$_2$·P(O)(NMe$_2$)(NHBu^t) + 2[NH$_2$Me$_2$]Cl

(VII)

↓ Heat

(VI) (9)

the ring compound (VI). When reaction (9) was performed using less than 5 mol equiv. of NHMe$_2$, examination of the reaction mixture by ^{1}H and ^{31}P n.m.r. indicated the presence of the 1,2,4-azadiphosphetan (Me$_2$N)(O)P·CH$_2$·P(O)Cl·NBu^t, showing that at least part of the reaction leading to the formation of (VII) proceeds *via* a ring opening of this monodimethylamino-derivative of (IV; R = Bu^t). The ease with which ring opening occurs in reaction (9) is unexpected in view of previous studies of the amine-induced ring opening of cyclodiphosphazanes, which, with the exception of the cleavage of [ClP(S)(NMe)]$_2$ [9] (or a methylamino-derivative) by NH$_2$Me, generally require relatively forcing conditions.[10]

EXPERIMENTAL

Solvents were dried by conventional means. Ethanol was removed from chloroform by contact with basic alumina. Phosphorus trichloride, t-butylamine, i-propylamine, and aniline were distilled before use. Phosphorus pentachloride, ethylamine, and dimethylamine were obtained commercially and used without further purification. The compounds Cl$_2$P·NMe·P(O)Cl$_2$,[11] Cl$_2$P·NMe·P(S)Cl$_2$,[11] ClP·NMe·P(S)Cl·NBu^t,* Cl$_2$P·NMe·PCl$_2$,[12] Ph$_2$P·CH$_2$·PPh$_2$,[13] (Pr^{i}O)$_2$(O)P·(CH$_2$)$_n$·P(O)(OPr^i)$_2$ (n = 1 or 2) [14] [*cf.* preparation of Cl$_2$(O)P·(CH$_2$)$_n$·P(O)Cl$_2$], and (Me$_2$N)ClP(O)·NMe·P(O)Cl(NMe$_2$) [15] were prepared by literature methods. Preparative methods are summarised in Table 2, analytical data are given in Table 3, and n.m.r. data are in Table 1.

Hydrogen-1 and ^{31}P n.m.r. spectra were obtained on a Jeol C60HL spectrometer at 60 and 24.3 MHz respectively. Selective and noise ^{31}P and ^{1}H decoupling was accomplished using a Schomandl ND100M frequency synthesiser and a Jeol SDHC unit. A ^{1}H spectrum of (Me$_2$N)Cl(O)P·CH$_2$·P(O)Cl(NMe$_2$) was obtained on a Varian HR-220 spectrometer. Mass spectra were recorded on an A.E.I. MS12 spectrometer.

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* Prepared by a method similar to that used for ClP·NBu^t·P(S)Cl·NBu^t (ref. 5).

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