Some Oxidation Reactions of Aminocyclodiphosph(III)azanes

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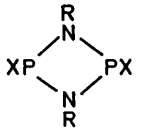
The reactions of *cis* and *trans* isomers of the aminocyclodiphosph(III)azane, $Me_2NPNBu^tP(NMe_2)NBu^t$ with t-butyl hydroperoxide, sulphur, selenium, tellurium, and methyl iodide give the oxidation products, $Me_2N(Z)PNBu^tP(NMe_2)NBu^t$ (Z = S, Se, Te, or MeI) and $Me_2N(Z)PNBu^tP(Z)(NMe_2)NBu^t$ (Z = O, S, or Se), *cis* and *trans* isomers being isolated in each case (except where Z = Te). No reaction occurs with dimethyl sulphoxide.

A series of sulphides and selenides of $R_2NPNR^1P(NR_2)NR^1$ (R_2 = Et_2 or C_5H_{10}, R^1 = Bu^t; and R_2 = Me_2, R^1 = Ph), $MeNP(NBu^t)_2PNMe(CH_2)_2$, and $ClPNBu^tP(NMe_2)NBu^t$ have also been obtained by analogous routes.

trans Isomers of $Me_2NPNBu^tP(NMe_2)NBu^t$ are more reactive than the analogous *cis* isomers, and it has been established that the oxidation of both isomers by sulphur or selenium occurs with retention of configuration at phosphorus. Exchange of selenium and of tellurium between phosphorus atoms has been observed in some derivatives, and in one case identification of the products of exchange enabled structural assignments to be made.

The chlorocyclodiphosph(v)azanes $Cl(Y)PNBu^tP(Z)(Cl)NR$ (R = Bu^t; Y = Z = O or S) react very slowly with dimethylamine even under forcing conditions. However, the latter compounds (R = Me, Y = lone pair, Z = O or S) are readily aminolysed by dimethylamine at the P^{III} atom. Selected ^1H and ^{31}P n.m.r. and i.r. data are reported and their relevance to structural assignments discussed.

THE controlled oxidation of cyclodiphosph(III)azanes (1) to give the compounds (2) and (3) (R = Pr^i or Bu^t; X = Cl; Z = O or S) was first reported [1] in 1973, using dimethyl sulphoxide and elemental sulphur respectively.



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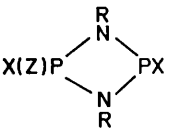

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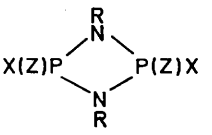


(3)

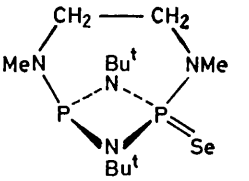
Oxidation of cyclodiphosph(III)azanes has since been effected by dimethyl sulphoxide,[2] t-butyl hydroperoxide,[3] elemental oxygen,[4] sulphur,[3-7] selenium,[3,6,8] tellurium,[8,9] alkyl halides,[4,6] azides,[3,4] diketones,[10,11] 2-(*o*-hydroxyphenylimino)-2-phenylacetophenone,[12] and metal carbonyls.[13,14] Reactions with elemental sulphur are very convenient and have been widely investigated. Cyclodiphosph(v)azanes, with four co-ordinated phosphorus, have been obtained by several other routes and their chemistry has been reviewed elsewhere.[15] Here we describe the synthesis of oxides, sulphides, selenides, and a telluride of aminocyclodiphosph(III)azanes, with special emphasis on the effects of geometrical isomerism on the reactivity of compounds (1) and (2), as well as the stereochemistry of oxidation reactions.

RESULTS

Attempts to oxidise *cis*-(1; R = Bu^t, X = NMe_2) with dimethyl sulphoxide (dmso) were unsuccessful, even at 70—80 °C in benzene solution. However, oxidation to the dioxide was readily accomplished using t-butyl hydroperoxide [equation (i)]. The reaction was stereospecific,

$$(1;\ R = Bu^t,\ X = NMe_2) \xrightarrow{Bu^tOOH} (3;\ R = Bu^t,\ X = NMe_2,\ Z = O) \quad \text{(i)}$$

for *cis* and *trans* isomers of (1; R = Bu^t, X = NMe_2) gave different isomeric forms of (3). Treatment of *cis*-(1; R = Bu^t, X = NMe_2) with 1 or 2 mol equivalents of elemental sulphur or of selenium in benzene solution resulted in a smooth, stereospecific, stepwise addition, affording (2) or (3) (R = Bu^t, X = NMe_2, Z = S or Se) respectively. The mixed-oxidation-state cyclodiphosphazanes, (2), were less reactive than (1), generally requiring heating to complete the reaction. Analogous reactions with sulphur were carried out on *trans*-(1; R = Ph, X = NMe_2) and *cis*-(1; R = Bu^t, X = NEt_2), and elemental selenium on *cis*-(1; R = Bu^t, X = NEt_2 or NC_5H_{10}). The monoselenide (4) was obtained similarly.

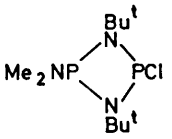


(4)

Reaction of (1; R = Bu^t, X = NMe_2) with elemental tellurium gave a monotelluride (2; R = Bu^t, X = NMe_2, Z = Te), but no ditelluride, even after extended reaction times in refluxing benzene solution. Furthermore, the same isomer was obtained, irrespective of which isomer of the starting material was used. The tellurium in this derivative can readily be displaced by elemental sulphur in a stereospecific reaction to give (2; R = Bu^t, X = NMe_2, Z = S). Methyl iodide and (1; R = Bu^t, X = NMe_2) gave two isomeric mono-quaternary salts, phosphorus being the site of quaternisation in both cases (^1H n.m.r.). It is significant that reactions of a 1 : 1 mixture of isomers of (1; R = Bu^t, X = NMe_2) (total 1 mol equivalent) with sulphur, selenium, or MeI (0.5 mol equivalent) result in the formation of *trans*-mono-oxidation products [2; R = Bu^t, X = NMe_2, Z = S, Se, or MeI (as phosphonium iodide)] from the *trans* isomer, leaving the *cis* isomer unchanged.

In connection with the observed lack of reactivity of dimethylamino-derivatives (1; R = Bu^t, X = NMe_2) to

dmso some oxidation reactions of (5) with the latter reagent were studied. Unexpectedly, 1 mol equivalent of dmso gave the starting material and (6) as a mixture of isomers,



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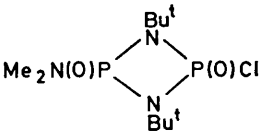

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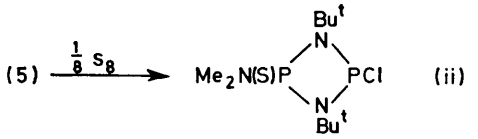
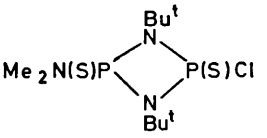


(7)

there being no indication which phosphorus atom was most reactive. However, the outcome of the reaction of (5) with sulphur was more informative [equation (ii)].



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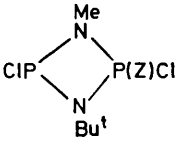

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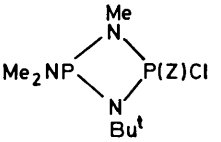


(10)

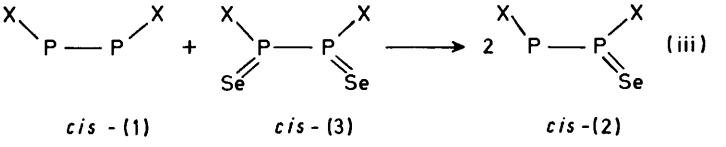
Selenium is relatively labile in the diselenides (3; R = Bu^t, X = NMe_2, Z = Se). Thus equimolar mixtures of this diselenide (*cis* or *trans* isomers) and (1; R = Bu^t, X = NMe_2) rapidly give (2; R = Bu^t, X = NMe_2, Z = Se) in deuteriochloroform solution at ambient temperatures. A knowledge of the isomer of (2) formed can be used to make structural assignments since the reactions are stereospecific (see below).

The possibility of preparing aminocyclophosph(v)azanes by displacement of chlorine from the compounds (3; R = Bu^t, X = Cl, Z = O or S) was briefly studied. By contrast with the analogous phosphorus(III) compound (1; R = Bu^t, X = Cl), there was no reaction with dimethylamine at ambient temperatures, and even a sealed-tube reaction of (3; R = Bu^t, X = Cl, Z = S) with excess of dimethylamine only gave a low yield of (8). It was also found that dimethylaminolysis of the mixed-oxidation state compounds (9; Z = O or S) occurs exclusively at the phosphorus(III) atom leading to the compounds (10; Z = O or S).

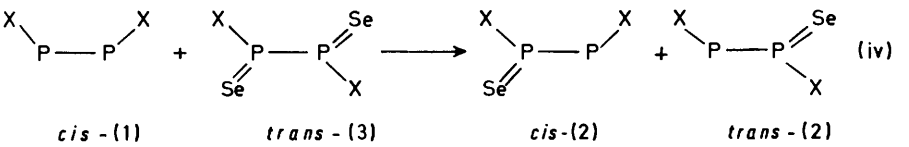
DISCUSSION

Structural Assignments.—The results of an *X*-ray crystallographic examination [7,16] of the disulphide (3; R = Bu^t, X = NMe_2, Z = S), m.p. 214 °C, obtained by oxidation of *cis*-(1; R = Bu^t, X = NMe_2) by elemental sulphur, play a key role in our structural assignments. This disulphide was shown to have a mutual *cis* arrangement of dimethylamino-groups and the molecular symmetry is close to C_{2v}. The other isomer of (3), m.p. 255—256 °C, was shown to have crystallographic C_i symmetry, only consistent with a *trans* structure.

The assignment of structures to the mono-oxidation products (2; R = Bu^t, X = NMe_2, Z = S, Se, or Te) is based on a number of results. First, it was shown by ^1H-{^{31}P} double resonance that rapid equilibration (<2 min) by intermolecular exchange occurs on mixing solutions of (1; R = Bu^t, X = NMe_2) and (3; R = Bu^t, X = NMe_2, Z = Se), leading to (2; R = Bu^t, X = NMe_2, Z = Se). The results are summarised in equations (iii) and (iv), where the molecules are viewed in the plane of the P_2N_2 ring and the NBu^t groups are omitted for clarity (X = NMe_2 throughout). In reaction (iii), only one monoselenide, (2; R = Bu^t, X = NMe_2, Z = Se), is produced, whilst in reaction (iv) a 1 : 1 mixture of geometrical isomers of (2) is obtained. The former result implies that both reactants have the same (*cis*) configuration, and the latter result that the reactants have opposite configurations. It would also appear reasonable to assume that the monoselenide produced in reaction (iii) must be *cis*; in fact this isomer is also obtained from *cis*-(1; R = Bu^t, X = NMe_2) and 1 mol equivalent of elemental selenium.



cis-(1) *cis*-(3) *cis*-(2)



cis-(1) *trans*-(3) *cis*-(2) *trans*-(2)

Secondly, vibrational spectroscopy proved to be of limited value for structural assignments to compounds (2) and (3), except where empirical correlations were

possible (see below). The i.r. spectra of the oxidation products of (1; R = Bu^t, X = NMe_2) generally featured a strong band in the region 870—930 cm^{-1}, which can be assigned to the P–N–P asymmetric stretching mode of the cyclodiphosphazane ring (Table 1). This band

TABLE 1

Values of ν_{asym}(P–N–P) in compounds of the type $Me_2N(X)\overline{PNBu^tP(Y)NMe_2}NBu^t$ *

X	Y	ν_{asym}(P–N–P)/cm^{-1} *cis* isomer	ν_{asym}(P–N–P)/cm^{-1} *trans* isomer
Lone pair	Lone pair	872, 862	880
Te	Lone pair		884
Se	Lone pair	879	890
S	Lone pair	884	897
Se	Se	898	904
S	S	905	912
O	O	919	930

* All spectra run as Nujol mulls.

occurs at lower energy in the *cis* relative to the *trans* isomer of (1; R = Bu^t, X = NMe_2). In every case the isomer of (2) or (3) arising from *cis*-(1; R = Bu^t, X = NMe_2) shows a band at lower energy than the analogous isomer arising from *trans*-(1), suggesting that oxidation of (1) and (2) occurs with retention of configuration at phosphorus. Comparison of the general features of the i.r. spectra in the range 400—1 000 cm^{-1} for *cis*- and *trans*-(3; R = Bu^t, X = NMe_2, Z = O, S, or Se) readily enables structural assignments to the latter group of compounds to be made on an empirical basis. The use of i.r. and Raman spectra for such assignments was ambiguous, with both *cis* and *trans* isomers showing coincidences in the 600—950 cm^{-1} range. The lower symmetry of the mixed-oxidation-state cyclodiphosphazanes (2) precludes a structural assignment by this method.

Thirdly, ^{1}H and ^{31}P n.m.r. data (Table 2) are consistent with the structural assignments above. It has been established [17] that *cis* isomers of (1; R = Bu^t, X = amino) have ^{31}P shifts that are upfield of the shifts for the corresponding *trans* isomers. Assuming that the structural assignments to the cyclodiphosph(v)azanes above are correct, then the same trend applies to the oxidation products (2) and (3), except in the case of oxides, (3; R = Bu^t, X = NMe_2, Z = O). It is of interest that the chemical-shift differences between isomeric forms of (1) (60—95 p.p.m.) are considerably larger than those between isomeric forms of (2), or of (3) (generally 25 p.p.m. for P^{III} and P^V). Although the *PNP* spin–spin couplings were more positive for *cis* than for *trans* isomers of (1),[18] there is no clear evidence of a similar relationship for the mono-oxidation products, (2). Torsional barriers about P–N bonds are generally larger in *trans*, than in *cis* isomers of (1), and the same is true of compounds (2) and (3).[19] Selenium-77 n.m.r. data for the selenides in Table 2 are reported elsewhere.[20]

Stereochemistry of Oxidation Reactions.—As indicated above, the oxidation of cyclodiphosphazanes (1) ⟶ (2) ⟶ (3) by sulphur, selenium, and methyl iodide occurs with retention of configuration at phosphorus. Overall retention of configuration occurs in the oxidation of (1; R = Bu^t, X = NMe_2) to (3; R = Bu^t, X = NMe_2, Z = O) and of (1; R = Me, X = Bu^t) to (3; R = Me, X = Bu^t, Z = S).[5,21] The addition of elemental sulphur or selenium to optically active tertiary phosphines also proceeds with retention of configuration at phosphorus, and in the case of the chalcogens involves nucleophilic attack of phosphorus on S_8 [22] or Se_8 [23] ring systems. The latter point is consistent with the reaction of (5) with sulphur at the electron-rich phosphorus atom to give (7), although this reaction is less stereospecific than those of (1; R = Bu^t, X = NMe_2 or NEt_2), since a 1 : 1 mixture of isomers was produced. Attempted reactions with dmso held some surprises. Since *cis*-(1; R = Bu^t, X = Cl) was readily oxidised by this reagent,[1,2] and *cis*-(1; R = Bu^t, X = NMe_2) was not, oxidation of (5) at the PCl centre might have been expected. However, a 1 : 1 mixture of (5) and (6) was obtained.

Two possible mechanisms for the reactions of dmso with phosphorus(III) compounds have been proposed by Shaw and co-workers.[24] The first step is either nucleophilic attack by phosphorus on sulphur as in the case of tris(dimethylamino)phosphine which is a good electron donor and poor acceptor, or electrophilic attack of phosphorus on oxygen as with phosphorus trichloride which has marked acceptor properties. The interpretation of the reaction of (5) with dmso is difficult, for it is not clear whether oxidation occurs initially at the PCl or $PNMe_2$ end of the molecule. It may be the case, therefore, that (1; R = Bu^t, X = Cl), being a good acceptor, is readily susceptible to nucleophilic attack by the oxygen atom of dmso whereas the dimethylamino-derivatives (1; R = Bu^t, X = NMe_2), being worse acceptors, but not good enough electron donors, react very slowly or not at all.

In contrast to the action of selenium on *cis*- or *trans*-(1; R = Bu^t, X = NMe_2), tellurium produced only the *trans*-monotelluride (2; R = Bu^t, X = NMe_2, Z = Te) which shows tellurium–exchange effects. Its structure is assigned by comparison of its i.r. spectra and ^{31}P n.m.r. shifts with *trans*-(2; R = Bu^t, X = NMe_2, Z = S or Se). Rapid exchange of tellurium has also been observed in tertiary phosphine–tertiary phosphine telluride mixtures [25] and in *cis*-(2; R = Me, X = Bu^t, Z = Te).[9] The latter compound is interesting in that the *cis* form [obtained from *cis*-(1; R = Me, X = Bu^t)] is quite stable and that a ditelluride, (3; R = Me, X = Bu^t, Z = Te), may also be obtained.[9] Tellurium is clearly much more labile than selenium or sulphur in these systems as neither the *cis* nor the *trans* isomers of (2; R = Bu^t, X = NMe_2, Z = S or Se) exhibited exchange effects in their ^{1}H n.m.r. spectra at temperatures up to *ca.* 140 °C. At *ca.* 160 °C, however, the P–Se bond does become labile in *o*-dichlorobenzene solution, the *cis* isomer completely isomerising to the *trans*. It therefore appears that it is the lability of the phosphorus–tellurium bond which precludes the form-

TABLE 2

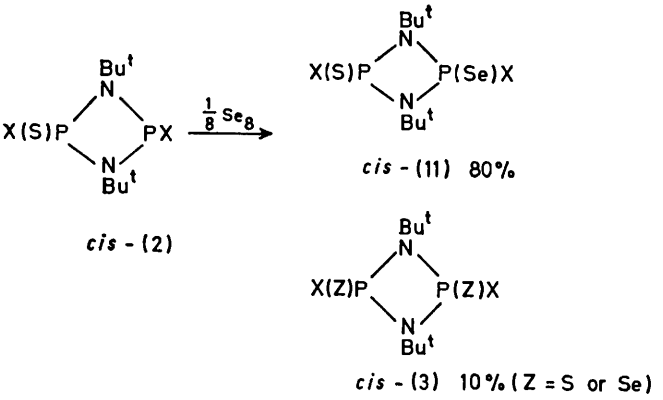
Hydrogen-1 and ^{31}P n.m.r. data [a]

Compound	^{31}P δ(P) [b]/ p.p.m.	^{31}P $^{2}J(PNP)$/ Hz	^{1}H δ(PNCH)/ p.p.m.	^{1}H $^{3}J(PNCH)$ [c]/ Hz	^{1}H δ(Bu^{t})/ p.p.m.	^{1}H $^{4}J(PNCCH)$/ Hz
cis } (3; R = Bu^{t}, X = NMe_2, Z = S)	44.8		2.93	11.8	1.44	0.5
trans }	53.8		2.92	12.0	1.38	0.5
cis } (3; R = Bu^{t}, X = NMe_2, Z = Se)	39.8		2.92	12.8	1.47	0.6
trans }	48.9		3.01	12.8	1.46	0.6
cis } (3; R = Bu^{t}, X = NMe_2, Z = O)	4.0 [d]		2.72	10.5	1.30	0.4
trans }	1.6 [d]		2.78 [e]	10.5	1.31	0.5
cis-(2; R = Bu^{t}, X = NMe_2, Z = S)	91.4(P^{III})	11.2	2.64(P^{III})	9.0	1.30	<0.5
	49.0		2.90	11.6		*ca.* 0.5
trans-(2; R = Bu^{t}, X = NMe_2, Z = S)	103.6(P^{III}) [f]	11.2	2.72(P^{III}) [g]	3.4	1.23	1.1
			2.57(P^{III}) [g]	14.3		
	68.9		*ca.* 2.65 [g]	*h*		0.6
cis-(2; R = Bu^{t}, X = NMe_2, Z = Se)	90.0(P^{III})	9.4	2.68	8.3 [g]	1.36	⩽0.3
	36.2		2.99	12.0		⩽0.5
trans-(2; R = Bu^{t}, X = NMe_2, Z = Se)	111.7(P^{III})	10.1	2.78(P^{III}) [f,g]	3.0	1.23	1.0
			2.56(P^{III})	13.9		
	61.0		*ca.* 2.65 [g]	*h*		0.5
trans-(2; R = Bu^{t}, X = NMe_2, Z = Te)	127.7(P^{III})	*h*, *i*	2.83 [i]	10.3 [i]	1.29	0.75
	16.7		2.83	10.3		0.75
cis-(11; X = NMe_2)	48.5(S)	36.7	2.94(S)	12.3	1.50	*ca.* 0.4
	40.5(Se)		2.97(Se)	12.8		*ca.* 0.4
cis-(2; R = Bu^{t}, X = NMe_2, Z = MeI)	86.1(P^{III})	5.2	2.82(P^{III}) [g]	15.7	1.35	<0.3(P^{III})
			2.66(P^{III})	3.3		*ca.* 0.3(P^{+})
	30.3		3.02	11.3	2.38 [j]	14.8 [k]
trans-(2; R = Bu^{t}, X = NMe_2, Z = MeI)	123.5(P^{III})	6.0	2.83(P^{III}) [g]	14.6	1.31	<0.5
			2.68(P^{III})	3.7		
	51.5		3.07 [g]	10.0		⩽0.5
			2.78	9.4	2.69 [j]	13.6 [k]
trans-(3; R = Ph, X = NMe_2, Z = S)	49.7		3.06	13.2		
trans-(2; R = Ph, X = NMe_2, Z = S)	99.5(P^{III})		2.88(P^{III})	9.1		
	64.5		2.87	12.0		
cis-(3; R = Bu^{t}, X = NEt_2, Z = S)	47.8		3.40	14.0	1.47	*ca.* 0.4
					1.15(Et)	7.2 [l]
cis-(3; R = Bu^{t}, X = NEt_2, Z = Se)	38.2		3.41	14.4	1.15	*ca.* 0.4
					1.15(Et)	7.3 [l]
cis-(2; R = Bu^{t}, X = NEt_2, Z = S)	87.4(P^{III})		3.07 [g]	*h*	1.40	<0.4
					1.12(Et)	6.7 [l]
	47.0(P^{V})		3.44	13 ± 2	1.40	*ca.* 0.4
					1.17(Et)	6.5 [l]
cis-(2; R = Bu^{t}, X = NEt_2, Z = Se)	87.2(P^{III})	8.0	3.01 [g]	*h*	1.41	0.4
					1.12(Et)	6.8 [l]
	34.7		3.38	13 ± 2	1.41	*ca.* 0.4
					1.16(Et)	6.6 [l]
cis-(11; X = NEt_2)	47.4(S)	33.6	*ca.* 3.4	*h*	1.49	*ca.* 0.4
					1.15(Et)	7.2 [l]
	38.6(Se)		*ca.* 3.4	*h*	1.15(Et)	7.2 [l]
cis-(3; R = Bu^{t}, X = NC_5H_{10}, Z = Se)	39.0		3.47	*h*	1.55	⩽0.3
cis-(2; R = Bu^{t}, X = NC_5H_{10}, Z = Se)	86.6(P^{III})	7.2	3.03	*h*	1.39	<0.3
	35.6		3.44	*h*		*ca.* 0.3
(4)	97.5(P^{III})	20.6	2.69(N*Me*)	13.8	1.36	⩽0.6
			ca. 3.15	*h*		
	66.1		3.00(N*Me*)	13.1		⩽0.4
			ca. 3.25	*h*		
(7)	150.2(*P*Cl)	22.6			1.38	<0.4
	77.2		*ca.* 2.9 [g]	12.0		⩽0.4
			2.51	10.7		
	155.8(*P*Cl)	30.9			1.38	<0.4
	63.3		2.88	12.1		⩽0.4
(6)	0.3	55.9	2.74	11.9	1.41	⩽0.5
	−1.6					⩽0.5
	[P(O)Cl]					
	−2.5	59.5	2.80 [g]	10.0	1.41	⩽0.5
	−5.3		2.72	11.5		
	[P(O)Cl]					⩽0.5
(10) (Z = O)	80.5(P^{III})	−8 ± 2 [d]	2.68(NMe)	9.1(P^{III})	1.34	0.4
	2.4			17.4		0.4
	101.2(P^{III})	*h*	2.63(NMe)	8.5(P^{III})	1.33	<0.4
	5.3			17.6		<0.4
(10) (Z = S)	113.9(P^{III})	−12 ± 2 [d]	2.68(NMe)	8.7(P^{III})	1.41	<0.4
	61.4			18.6		<0.4
	110.9(P^{III})	−10 ± 4 [d]	2.73(NMe)	9.0(P^{III})	1.41	<0.4
	55.1			18.8		<0.4

[a] For $CDCl_3$ or CH_2Cl_2 solutions at *ca.* 33 °C unless stated otherwise. [b] Downfield ^{31}P chemical shifts are positive relative to external 85% H_3PO_4. [c] More correctly, $^{3}J(PNCH) + {}^{5}J(PNPNCH)$ for symmetrical cyclodiphosph(v)azanes. These couplings are positive. [d] Obtained by ^{1}H-{^{31}P} double resonance. [e] Signal broadened as a result of slow rotation about the exocyclic P–N bond. [f] In C_6H_5Cl solution. [g] Two N-methyl signals due to restricted rotation at *ca.* 33 °C. [h] Not measured. [i] Signals broadened due to tellurium exchange. [j] δ(PC*H*). [k] $^{2}J(PCH)$. [l] $^{3}J(HCCH)$.

ation of more than one isomer of (2; R = Bu^t, X = NMe_2, Z = Te).

Attempted synthesis of the mixed chalcogen derivative (11; X = NMe_2, Y = S, Z = Se) from *cis*-(2; R = Bu^t, X = NMe_2, Z = S) was hampered by scrambling of the chalcogen atoms, producing a mixture of the sulphide–selenide, disulphide, and diselenide species. Similarly, reaction of (2; R = Bu^t, X = NEt_2, Z = Se) with sulphur gave (11; X = NEt_2, Y = Se, Z = S) (50%) along with (3; R = Bu^t, X = NEt_2, Z = S or Se), but the latter three products were not separated.



A different situation arises on addition of 1 mol equivalent of sulphur to *trans*-(2; R = Bu^t, X = NMe_2, Z = Te), tellurium being displaced and *trans*-(2) and *trans*-(3; R = Bu^t, X = NMe_2, Z = S) being produced. This provides an alternative route to the *trans*-monosulphide, as the *trans*-monotelluride may be made from thermodynamically stable *cis*-(1; R = Bu^t, X = NMe_2).

It is significant that reactions of a 1 : 1 mixture of isomers of (1; R = Bu^t, X = NMe_2) (total 1 mol equivalent) with sulphur, selenium, or MeI (0.5 mol equivalent) result in the formation of the *trans*-monooxidation products, (2; R = Bu^t, X = NMe_2, Z = S, Se, or MeI), from the *trans* isomer leaving the *cis* isomer unchanged. Such dramatic differences in chemical reactivity resulting from geometrical isomerism in inorganic ring systems are unique. For example, in cyclophosph(v)azenes small differences in reactivity could only be indirectly inferred from observed reaction patterns.[26] What causes these differences in reactivity is not clear but the results do parallel the higher basicity of *trans*-(1; R = Bu^t, X = NMe_2) relative to the analogous *cis* isomer and the fact that the lowest energy bands in the photoelectron spectra are *ca.* 0.5 eV lower in energy in the *trans* isomer.[17] Both these observations are in accordance with a mechanism involving nucleophilic attack by phosphorus on sulphur, selenium, or the carbon atom in methyl iodide.

It is worth noting that $n_P \rightarrow \sigma_{P-N}^*$ bonding interactions across the cyclodiphosph(III)azane ring, if important, would predict greater thermal stability for the *cis* isomer of (1; R = Bu^t, X = NMe_2) and greater nucleophilicity at phosphorus in the analogous *trans* isomer. *Ab initio* molecular-orbital calculations show[27] that a related $n \rightarrow \sigma^*$ interaction can be used to rationalise chemical differences between geometrical isomers of compounds formed from the first-row elements, and that $n_O \rightarrow \sigma_{P-O}^*$ bonding effects are important in phosphorus–oxygen compounds.[28]

It was found that on adding elemental sulphur or selenium (0.5 mol equivalent) to a 1 : 1 mixture of *cis*- and *trans*-(2; R = Bu^t, X = NMe_2, Z = S or Se) that the *trans* isomer again reacted more rapidly. However, in this instance the difference in reactivity between the isomers (as followed by ^{1}H n.m.r.) was not so marked, some of the *cis* isomer reacting before complete removal of the elemental chalcogen.

The lack of reactivity of the cyclodiphosph(v)azanes (3; R = Bu^t, X = Cl, Z = O or S) to dimethylamine may be partly steric in origin for the related compound Cl(O)PNBu^{t}P(S)(Cl)NMe, undergoes fairly ready dimethylaminolysis at the P(O)Cl centre.[29] Dimethylaminolysis of (9) at the PCl centre is to be expected in view of the ease of formation of dimethylaminocyclodiphosph(III)azanes,[6,30] and of dimethylaminolysis studies on acyclic P^{III}–N–P^V compounds,[31] although in the latter case a rearrangement of the dimethylamino-group to the P^V atom was also observed. There was no evidence for this occurring in the case of compounds (10).

EXPERIMENTAL

Experimental methods and spectroscopic techniques used have been described previously.[1,6,30] Literature methods[30] were employed for the synthesis of the aminocyclodiphosph(III)azanes, (1; R = Bu^t, X = amino) and ClPNBu^{t}P(NMe_2)NBu^t, the substrates for the oxidation reactions, and for the chlorocyclodiphosph(v)azanes (3; R = Bu^t, X = Cl, Z = O or S).[1]

The oxidation reactions are described in detail below. Analytical data for new compounds are given in Table 3.

2-cis-4-*Bis*(*dimethylamino*)-2,4-*dioxo*-1,3-*di*-t-*butylcyclodiphosph*(v)*azane*, *cis*-(3; R = Bu^t, X = NMe_2, Z = O).—A solution of t-butyl hydroperoxide (3.3 g, 37 mmol) in benzene (20 cm^3) was added dropwise to 2-*cis*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (5.2 g, 18 mmol) in benzene (35 cm^3) at *ca.* 0 °C. The mixture was heated under reflux for 5 min, allowed to cool, and the solvent and t-butyl alcohol removed leaving a light yellow solid. This was washed with pentane (30 cm^3) and crystallised from light petroleum (b.p. 40—60 °C)–methylene chloride (4 : 1) to give the product (2.6 g, 44%) as white air-stable needles, m.p. 194—196 °C.

The *trans* isomer was prepared similarly from 2-*trans*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane in 53% yield as colourless needles (which became white on exposure to air), m.p. 205 °C.

Attempted Preparations of (3; R = Bu^t, X = NMe_2, Z = O) —2,4-Dichloro-2,4-dioxo-1,3-di-t-butylcyclodiphosph(v)-azane (0.60 g, 2.0 mmol) was mixed with dimethylamine (0.40 g, 8.9 mmol) in methylene chloride (35 cm^3) at −10 °C. The solution was brought to ambient temperature and stirred (3 h). Examination of the reaction mixture by ^{1}H n.m.r. spectroscopy indicated that no reaction had taken place. In another experiment, dimethyl sulphoxide (0.83 g,

TABLE 3
Analytical data

Compound	Analysis (%) [a] C	H	N	*m/e* [b]
cis (3; R = Bu^t, X = NMe_2, Z = S)	40.4	8.45	15.35	356
	(40.45)	(8.4)	(15.7)	(356)
trans (3; R = Bu^t, X = NMe_2, Z = S)	40.5	8.3	15.7	356
	(40.45)	(8.4)	(15.7)	(356)
cis (3; R = Bu^t, X = NMe_2, Z = Se)	32.1	6.7	12.5	452
	(32.0)	(6.7)	(12.4)	(452)
trans (3; R = Bu^t, X = NMe_2, Z = Se)	32.25	6.6	12.5	452
	(32.0)	(6.7)	(12.4)	(452)
cis (3; R = Bu^t, X = NMe_2, Z = O)	44.4	9.2	17.5	324
	(44.4)	(9.3)	(17.3)	(324)
trans (3; R = Bu^t, X = NMe_2, Z = O)	44.65	9.0	17.2	324
	(44.4)	(9.3)	(17.3)	(324)
cis (2; R = Bu^t, X = NMe_2, Z = S)	44.7	9.0	17.5	324
	(44.4)	(9.3)	(17.3)	(324)
trans (2; R = Bu^t, X = NMe_2, Z = S)	44.5	9.3	17.3	324
	(44.4)	(9.3)	(17.3)	(324)
cis (2; R = Bu^t, X = NMe_2, Z = Se)	38.6	8.1	14.7	372
	(38.8)	(8.1)	(15.1)	(372)
trans (2; R = Bu^t, X = NMe_2, Z = Se)	39.1	7.9	14.75	372
	(38.8)	(8.1)	(15.1)	(372)
trans-(2; R = Bu^t, X = NMe_2, Z = Te)	34.5	7.3	13.2	422
	(34.3)	(7.15)	(13.35)	(422)
cis-(11; R = Bu^t, X = NMe_2, Y = Se, Z = S)	36.0	7.15	13.5	404
	(35.7)	(7.4)	(13.9)	(404)
cis (2; R = Bu^t, X = NMe_2, Z = MeI)	36.4	7.9	12.7	
	(35.9)	(7.6)	(12.9)	
trans (2; R = Bu^t, X = NMe_2, Z = MeI)	35.1	7.7	12.9	
	(35.9)	(7.6)	(12.9)	
trans-(3; R = Ph, X = NMe_2, Z = S)	48.4	5.35	14.1	396
	(48.5)	(5.55)	(14.1)	(396)
trans-(2; R = Ph, X = NMe_2, Z = S)	52.5	6.1	15.5	364
	(52.75)	(6.0)	(15.4)	(364)
cis-(3; R = Bu^t, X = NEt_2, Z = S)	46.3	9.1	13.5	412
	(46.6)	(9.2)	(13.6)	(412)
cis-(3; R = Bu^t, X = NEt_2, Z = Se)	37.7	7.5	11.5	508
	(37.9)	(7.5)	(11.1)	(508)
cis-(2; R = Bu^t, X = NEt_2, Z = S)	50.4	10.2	14.7	380
	(50.5)	(10.0)	(14.7)	(380)
cis-(2; R = Bu^t, X = NEt_2, Z = Se)	44.7	8.8	13.4	428
	(45.0)	(8.9)	(13.1)	(428)
cis-(11; R = Bu^t, X = NEt_2, Y = Se, Z = S)				460
				(460)
cis-(3; R = Bu^t, X = NC_5H_{10}, Z = Se)	40.6	7.2	10.6	532
	(40.75)	(7.2)	(10.6)	(532)
cis-(2; R = Bu^t, X = NC_5H_{10}, Z = Se)	47.6	8.6	12.8	452
	(47.9)	(8.4)	(12.4)	(452)
(4)	39.0	7.85	15.2	370
	(39.0)	(7.6)	(15.2)	(370)
(7) [c]	38.1	7.75	13.6	315
	(38.0)	(7.6)	(13.3)	(315)
(6)				315
				(315)
(10) (Z = O)				257
				(257)
(10) (Z = S)	30.6	7.1	14.5	273
	(30.7)	(6.6)	(15.35)	(273)

[a] Calculated values are given in parentheses. [b] Calculated for ions containing ^{35}Cl, ^{80}Se, or ^{130}Te where appropriate. [c] 1 : 1 Mixture of isomers analysed.

10.6 mmol) was added to a solution of 2-*cis*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (1.55 g, 5.3 mmol) in benzene (60 cm^3) at room temperature. The mixture was refluxed (24 h) whereupon examination by ^1H n.m.r. spectroscopy indicated that no reaction had occurred.

2-cis-4-*Bis*(*dimethylamino*)-1,3-*di-t-butyl*-2,4-*dithioxocyclodiphosph*(v)*azane*, *cis*-(3; R = Bu^t, X = NMe_2, Z = S).—To 2-*cis*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (3.2 g, 11 mmol) in benzene (60 cm^3) at ambient temperature was added flowers of sulphur (0.70 g, 22 mmol). After an initial mild exothermic reaction the mixture was stirred (4 h) at 60 °C by which time all the sulphur had dissolved. Concentration of the benzene solution afforded the product (2.9 g, 73%) as colourless octahedral crystals, m.p. 214 °C.

trans-(3; R = Bu^t, X = NMe_2, Z = S).—2-*trans*-4-Bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (1.1 g, 3.8 mmol) and flowers of sulphur (0.24 g, 7.6 mmol) in benzene (30 cm^3) on similar treatment gave the product (0.9 g, 66%) as colourless needles, m.p. 255—256 °C.

Attempted Preparations of (3; R = Bu^t, X = NMe_2, Z = S) —Dimethylamine (1.6 g, 36 mmol) was mixed with 2,4-dichloro-1,3-di-t-butyl-2,4-dithioxocyclodiphosph(v)azane (2.9 g, 8.6 mmol) in diethyl ether (60 cm^3) at −78 °C. The solution was allowed to warm to ambient temperature and stirred (3 h). Examination of the product by ^1H n.m.r. spectroscopy showed that no reaction had occurred. Another experiment in which the above dithioxocyclodiphosph(v)azane (2.7 g, 8.0 mmol) was heated (16 h) with excess of dimethylamine (*ca.* 20 g) in a sealed tube at 85 °C provided evidence after work-up for the starting material and traces of 2-*chloro*-4-*dimethylamino*-1,3-*di-t-butyl*-2,4-*dithioxocyclodiphosph*(v)*azane*, (8), identified by mass spectroscopy [Found: *m/e*, 347. Calc.: *m/e*, 347 (^{35}Cl)].

2-*Chloro*-4-*dimethylamino*-1-*methyl*-2-*oxo*-3-*t-butylcyclodiphosphazane*, (10; Z = O).—2,4-Dichloro-1-methyl-2-oxo-3-t-butylcyclodiphosphazane (2.9 g, 12 mmol) was mixed with dimethylamine (1.10 g, 24.4 mmol) in diethyl ether (110 cm^3) at −78 °C. The reaction was stirred (1 h) after warming to ambient temperature. The almost clear viscous liquid obtained on work-up was not purified further, but ^1H-{^{31}P} n.m.r. showed that this liquid almost completely consisted of (10; Z = O) (isomer ratio 4 : 1), identified also by mass spectroscopy (Table 3).

The compound (10; Z = S) was obtained similarly in 36% yield, with b.p. 60—64 °C, 0.03 mmHg,* as a clear viscous liquid (isomer ratio 4 : 1).

cis- *and* trans-2,4-*Bis*(*dimethylamino*)-2,4-*diselenoxocyclodiphosph*(v)*azanes*, (3; R = Bu^t, X = NMe_2, Z = Se).—Finely powdered elemental selenium (3.39 g, 42.8 mmol) was added to a 1 : 1 mixture of *cis*- and *trans*-2,4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azanes (6.25 g, 21.4 mmol) in benzene (50 cm^3) at ambient temperature. The mixture was refluxed (2 d), traces of unchanged selenium and the solvent were removed, and the off-white residue crystallised from methylene chloride affording *cis*- and *trans*-(3; R = Bu^t, X = NMe_2, Z = Se) (7.4 g, 77%) as colourless crystals. The *cis* and *trans* forms were separated by fractional crystallisation from benzene (the *trans* isomer being the less soluble): *cis* isomer, m.p. 253—255 °C; *trans* isomer, m.p. 264 °C.

2-cis-4-*Bis*(*dimethylamino*)-1,3-*di-t-butyl*-2-*thioxocyclodiphosphazane*, *cis*-(2; R = Bu^t, X = NMe_2, Z = S).—To a rapidly stirred solution of 2-*cis*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (6.5 g, 22 mmol) in benzene (80 cm^3) at ambient temperature was added flowers of sulphur (0.71 g, 22 mmol). After 6 h the solvent was removed and the white solid residue crystallised from pentane–methylene chloride (10 : 1) to give the product (3.6 g, 50%) as colourless needles, m.p. 73—75 °C.

The compound (2; R = Bu^t, X = NMe_2, Z = Se) was prepared similarly as white needles (54%), m.p. 102—104 °C.

trans-(2; R = Bu^t, X = NMe_2, Z = S).—To a 1 : 4 mixture of *cis*- and *trans*-2,4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azanes (6.20 g, 21.2 mmol) in

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

benzene (50 cm^3) at ambient temperature was added flowers of sulphur (0.54 g, 17.0 mmol). A mildly exothermic reaction occurred and the mixture was stirred (1 h). Removal of the solvent left an oily white solid which was carefully washed with cold pentane (*ca.* 2 cm^3) and then crystallised from light petroleum (b.p. 40—60 °C)–pentane (1 : 1) to yield the product (3.3 g, 59% based on sulphur) as white needles, m.p. 127—129 °C.

The compound *trans*-(2; R = Bu^t, X = NMe_2, Z = Se) was prepared similarly as white needles (69%), m.p. 126—127 °C.

trans-(2; R = Bu^t, X = NMe_2, Z = Te).—(*a*) To a solution of 2-*cis*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (3.30 g, 11.3 mmol) in benzene (10 cm^3) at ambient temperature was added finely ground tellurium (1.44 g, 11.3 mmol). There appeared to be no immediate reaction, but the tellurium dissolved after heating under reflux (4 h), and the solution turned green. Removal of the solvent and crystallisation of the residue from light petroleum (b.p. 40—60 °C)–methylene chloride (4 : 1) afforded the pure product (1.40 g, 29%) as pale yellow crystals, m.p. 120 °C (decomp.). The compound is stable on exposure to light and air, but slowly decomposes in solution over extended periods of time.

(*b*) To a solution of 2-*trans*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (4.5 g, 15 mmol) in benzene (15 cm^3) at ambient temperature was added finely ground tellurium (1.2 g, 9 mmol). The solution immediately turned green, was stirred (2 h), and on removal of the solvent and after work-up afforded the product (2.3 g, 60%).

On refluxing this compound with an equimolar amount of tellurium in benzene for 3 d there was no evidence (^1H n.m.r.) of a ditelluride species.

2-cis-4-*Bis*(*dimethylamino*)-2-*selenoxo*-1,3-*di-t-butyl*-4-*thioxocyclodiphosph*(v)*azane*, *cis*-(11; X = NMe_2, Y = S, Z = Se).—To 2-*cis*-4-bis(dimethylamino)-1,3-di-t-butyl-2-thioxocyclodiphosphazane (6.7 g, 21 mmol) in benzene (100 cm^3) at ambient temperature was added powdered selenium (1.7 g, 21 mmol). The mixture was refluxed (24 h) and shown (^1H n.m.r.) to consist of a *ca.* 8 : 1 : 1 mixture of *cis*-(11; X = NMe_2, Y = S, Z = Se) and the analogous *cis*-(3; R = Bu^t, X = NMe_2, Z = S) and *cis*-(3; R = Bu^t, X = NMe_2, Z = Se) respectively. The mixture was separated after work-up by careful crystallisation from light petroleum (b.p. 40—60 °C)–methylene chloride (3 : 1) giving the product (11) (X = NMe_2, Y = S, Z = Se) (3.9 g, 46%) as colourless crystals, m.p. 236 °C.

Attempted Preparation of 2,4-*Bis*(*dimethylamino*)-2-*telluroxo*-1,3-*di-t-butyl*-4-*thioxocyclodiphosph*(v)*azane*, (11; X = NMe_2, Y = Te, Z = S).—Sulphur (0.102 g, 3.20 mmol) was added at ambient temperature to a solution of 2-*trans*-4-bis(dimethylamino)-2-telluroxo-1,3-di-t-butylcyclodiphosphazane (1.35 g, 3.20 mmol) in benzene (15 cm^3). The solution immediately turned black due to deposition of elemental tellurium. On refluxing (60 h) there was no evidence for the recombination of tellurium, and ^1H n.m.r. spectroscopy indicated that the solution consisted mainly of the *cis*-(2) and *cis*-(3) (R = Bu^t, X = NMe_2, Z = S) derivatives in a *ca.* 6 : 1 ratio respectively. Proton n.m.r. signals from the starting material (if present) may be obscured by those of the other species in solution.

2-cis-4-*Bis*(*dimethylamino*)-2-*methyl*-1,3-*di-t-butylcyclodiphosphazanium Iodide*, *cis*-(2; R = Bu^t, X = NMe_2, Z = MeI).— 2-*cis*-4-Bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (4.47 g, 15.3 mmol) and methyl iodide (8.5 g, 60 mmol) were mixed in benzene (25 cm^3) at ambient temperature. The mixture warmed slightly and was stirred (6 h) during which time a white flocculent precipitate appeared. This was filtered off and crystallised from benzene to yield the product (4.00 g, 60%) as white needles, m.p. 132—134 °C.

trans-(2; R = Bu^t, X = NMe_2, Z = MeI).—To a 1 : 3 mixture of *cis*- and *trans*-2,4-bis(dimethylamino)-1,3-t-butylcyclodiphosph(III)azanes (1.20 g, 4.11 mmol) in benzene (5 cm^3) at ambient temperature was added methyl iodide (0.44 g, 3.10 mmol). Almost immediately there was a vigorous exothermic reaction and the production of a copious white precipitate. This was filtered off and washed with benzene (3 × 10 cm^3) to yield the pure product (1.16 g, 86% based on methyl iodide), m.p. 150—153 °C. Crystallisation proved difficult owing to the very poor solubility of the compound in most common organic solvents. Proton n.m.r. spectroscopy indicated that the filtrate consisted almost entirely of 2-*cis*-4-bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)azane, (1; R = Bu^t, X = NMe_2).

Attempted Preparation of 2,4-*Bis*(*dimethylamino*)-2,4-*dioxo*-1,3-*diphenylcyclodiphosph*(v)*azane*, (3; R = Ph, X = NMe_2, Z = O).—Dimethyl sulphoxide (0.2 g, 2.6 mmol) was added to a solution of 2-*trans*-4-bis(dimethylamino)-1,3-diphenylcyclodiphosph(III)azane (0.6 g, 1.8 mmol) in benzene (5 cm^3). The mixture was refluxed (24 h) and studied by ^1H n.m.r. spectroscopy, which indicated that no reaction had taken place.

2-trans-4-*Bis*(*dimethylamino*)-1,3-*diphenyl*-2,4-*dithioxocyclodiphosph*(v)*azane*, (3; R = Ph, X = NMe_2, Z = S).—Sulphur (0.48 g, 15 mmol) was added to a solution of 2-*trans*-4-bis(dimethylamino)-1,3-diphenylcyclodiphosph(III)azane (2.5 g, 7.5 mmol) in benzene (100 cm^3) at ambient temperature. After reflux (6 h) the solution became cloudy. The mixture was allowed to cool and the solvent removed, affording the pure *compound* (2.7 g, 92%) as a fine white powder, m.p. 302—305 °C, only sparingly soluble in most common organic solvents.

2-trans-4-*Bis*(*dimethylamino*)-1,3-*diphenyl*-2-*thioxocyclodiphosphazane*, (2; R = Bu^t, X = NMe_2, Z = S).—2-*trans*-4-Bis(dimethylamino)-1,3-diphenylcyclodiphosph(III)azane (2.57, 7.74 mmol) in benzene (100 cm^3) was mixed with sulphur (0.25 g, 7.8 mmol) at ambient temperature. The mixture was refluxed (2 h) and after work-up and crystallisation from benzene afforded the product (1.90 g, 68%) as white crystals, m.p. 219 °C.

2-cis-4-*Bis*(*diethylamino*)-1,3-*di-t-butyl*-2,4-*dithioxocyclodiphosph*(v)*azane*, (3; R = Bu^t, X = NEt_2, Z = S).—To 2-*cis*-4-bis(diethylamino)-1,3-di-t-butylcyclodiphosph(III)-azane (4.68 g, 13.45 mmol) in benzene (60 cm^3) was added sulphur (0.86 g, 26.9 mmol). The mixture was warmed slightly, stirred at ambient temperature (0.5 h), and refluxed (2 h). Removal of the solvent and crystallisation of the residue from light petroleum (b.p. 40—60 °C) afforded the pure product (3.85 g, 69%) as white needles, m.p. 169 °C.

The compound *cis*-(3; R = Bu^t, X = NEt_2, Z = Se) was prepared similarly as colourless needles (59%), m.p. 219—221 °C.

2-cis-4-*Bis*(*diethylamino*)-1,3-*di-t-butyl*-2-*thioxocyclodiphosphazane*, (2; R = Bu^t, X = NEt_2, Z = S).—As above, sulphur (0.69 g, 21.6 mmol) and 2-*cis*-4-bis(diethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (7.5 g, 21.6 mmol) were mixed with rapid stirring (0.5 h) at ambient temperature in benzene solution (60 cm^3). Removal of the solvent left a brownish low-melting solid. This was washed

with cold pentane (1 cm³) and crystallised from pentane giving the product (3.82 g, 47%) as colourless needles, m.p. 93—95 °C.

The compound *cis*-(2; R = Bu^t, X = NEt_2, Z = Se) was prepared similarly in refluxing benzene (2 h) as colourless needles (79%), m.p. 101—102 °C.

Attempted Preparation of 2-cis-4-*Bis(diethylamino)*-2-*selenoxo*-1,3-*di-t-butyl*-4-*thioxocyclodiphosph*(v)*azane*, (11; X = NEt_2, Y = Se, Z = S).—Sulphur (0.41 g, 12.8 mmol) was added at ambient temperature to a solution of *cis*-(2; R = Bu^t, X = NEt_2, Z = S) (5.5 g, 12.9 mmol) in benzene (60 cm³). The mixture was stirred (0.5 h) at 60 °C. Removal of the solvent and work-up yielded a white solid (5.6 g) which was shown by ^{31}P n.m.r. spectroscopy to consist of a 2 : 1 : 1 mixture of (11; X = NEt_2, Y = Se, Z = S), *cis*-(3; R = Bu^t, X = NEt_2, Z = S), and *cis*-(3; R = Bu^t, X = NEt_2, Z = Se) respectively. Attempts to isolate (11; X = NEt_2, Y = Se, Z = S) by fractional crystallisation from a variety of solvents, solvent mixtures, and by thin-layer chromatography were unsuccessful.

2-cis-4-*Dipiperidino*-2,4-*diselenoxo*-1,3-*di-t-butylcyclodiphosph*(v)*azane*, (3; R = Bu^t, X = NC_5H_{10}, Z = Se).—To a solution of 2-*cis*-4-dipiperidino-1,3-di-t-butylcyclodiphosph(III)azane (1.56 g, 4.19 mmol) in benzene (25 cm³) at ambient temperature was added finely powdered elemental selenium (0.66 g, 8.37 mmol). The mixture was refluxed with rapid stirring (1 h), allowed to cool to ambient temperature, the solvent removed, and the white solid residue crystallised from methylene chloride–pentane (1 : 1) to give the product (1.1 g, 50%) as colourless prisms, m.p. 214—215 °C.

2-cis-4-*Dipiperidino*-2-*selenoxo*-1,3-*di-t-butylcyclodiphosphazane*, (2; R = Bu^t, X = NC_5H_{10}, Z = Se).—Similarly, a solution of 2-*cis*-4-dipiperidino-1,3-di-t-butylcyclodiphosph(III)azane (1.48 g, 3.97 mmol) and elemental selenium (0.313 g, 3.97 mmol) in benzene (50 cm³) was refluxed (1 h). After work-up, crystallisation from pentane afforded the product (1.4 g, 78%) as colourless crystals, m.p. 110 °C.

2,5-*Dimethyl*-1-*selenoxo*-7,8-*di-t-butyl*-2,5,7,8-*tetra-aza*-1,6-*diphosphabicyclo*[4.1.1]*octane*, (4).—Finely powdered selenium (2.0 g, 25 mmol) was added at ambient temperature to a solution of 2,5-dimethyl-7,8-di-t-butyl-2,5,7,8-tetra-aza-1,6-diphospha(III)bicyclo[4.1.1]octane (7.2 g, 25 mmol) in methylene chloride (10 cm³). An exothermic reaction occurred and the solution came to reflux. After stirring (0.5 h), the reaction had gone to completion (^{1}H n.m.r.). Traces of unchanged selenium were filtered off and the solvent evaporated leaving a cloudy oil which was crystallised from pentane–methylene chloride (1 : 1) and recrystallised from pentane to yield (4) (2.9 g, 32%) as colourless needles, m.p. 80—82 °C.

2-*Chloro*-4-*dimethylamino*-1,3-*di-t-butyl*-4-*thioxocyclodiphosphazane*, (7).—Sulphur (0.64 g, 20 mmol) was added at ambient temperature to a solution of 2-chloro-4-dimethylamino-1,3-di-t-butylcyclodiphosph(III)azane (5) (5.6 g, 20 mmol) in benzene (100 cm³). The solution was heated (3 h) with rapid stirring at 70 °C. Removal of the solvent left a colourless oil which was purified by distillation under reduced pressure to give (7) (1.5 g, 24%), b.p. 98—100 °C (0.02 mmHg). Examination of the product by ^{1}H-{^{31}P} and ^{31}P n.m.r. spectroscopy indicated that a 1 : 1 mixture of isomers was present both before and after purification.

2-*Chloro*-4-*dimethylamino*-2,4-*dioxo*-1,3-*di-t-butylcyclodiphosph*(v)*azane*, (6).—To a stirred solution of 2-chloro-4-dimethylamino-1,3-di-t-butylcyclodiphosph(III)azane (5) (3.43 g, 12.1 mmol) in methylene chloride (50 cm³) at −78 °C was slowly added dimethyl sulphoxide (0.94 g, 12.1 mmol) in methylene chloride (30 cm³). The solution was allowed to warm to ambient temperature after which time the methylene chloride and dimethyl sulphide were removed under reduced pressure and collected in a trap held at −78 °C. The oily residue was shown by ^{1}H-{^{31}P} n.m.r. spectroscopy to consist of a 1 : 1 mixture of (6) and starting material. Partial purification was effected by distillation under reduced pressure, yielding 2-chloro-4-dimethylamino-1,3-di-t-butylcyclodiphosph(III)azane, (5) (1.36 g, 40% recovery), b.p. 70—80 °C (0.1 mmHg) [lit.,[30] 55—65 °C (0.03 mmHg)]. The distillation residue now consisted mainly of (6), which ^{1}H-{^{31}P} n.m.r. spectroscopy showed to be a 1 : 1 mixture of isomers both before and after distillation. Further identification of these isomers was limited to mass spectroscopic data (Table 3).

Reactions involving exchange of chalcogens, and the relative reactivity of geometrical isomers of (1; R = Bu^t, X = NMe_2), were followed by ^{1}H n.m.r. spectroscopy. The identity of the products was checked by ^{1}H-{^{31}P} double resonance, and by comparison with the ^{1}H n.m.r. spectra of authentic compounds.

We thank the S.R.C. for a studentship (to D. G. T.), Dr. G. Bulloch for carrying out the aminolysis of mixed-oxidation state cyclodiphosphazanes, and Dr. D. S. Rycroft for obtaining the 40.5-MHz ^{31}P n.m.r. spectra.

[9/842 *Received*, 30*th May*, 1979]

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