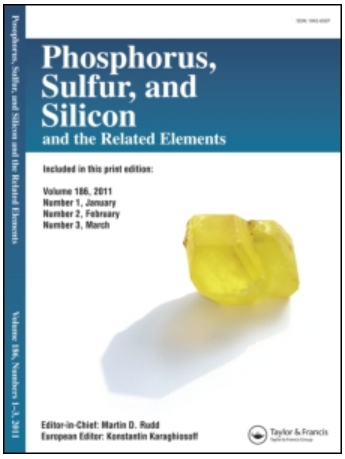

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THE STRUCTURES AND MODE OF FORMATION OF SOME CYCLODIPHOSPH(V)AZANES AND THEIR *cis-trans* ISOMERISATION

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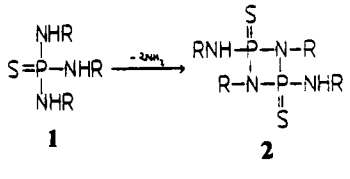
Methods of preparation and likely reaction mechanisms of the formation of $[PhP(S)NR]_2$ from $PhP(S)Cl_2$ and NH_2R are discussed. These cyclodiphosph(V)azanes were investigated by means of N.M.R. spectroscopy and X-ray crystallography. The initial reaction products appear to be the *trans*-isomers. *Cis–trans* isomerisation is discussed.

INTRODUCTION

The methods of preparation and possible reaction mechanisms for the formation of cyclodiphosph(V)azanes, $[PhP(S)NR]_2$, are discussed. These cyclodiphosphazanes and their monomeric precursors, $PhP(S)(NHR)_2$, have been investigated using n.m.r. spectroscopy and their properties related to known crystallographic structural data.

THERMOLYSIS REACTIONS

The thermal condensation of phosphorothioic tri(monoalkylamides), $P(S)(NHR)_3$ (**1**), under an inert atmosphere, with (i) unbranched, and (ii) α-branched alkyl groups gives a partial conversion to 1,3-dialkyl-2,4-di(alkylamino)-2,4-dithiocyclodiphosph(V)azanes, $[(RNH)P(S)NR]_2$ (**2**), (e.g. R = ME, Et, Pr^n, Pr^i, Bu^n, CH_2Ph, Pe^c, Hex^c).[1] (Figure 1).



1 **2**

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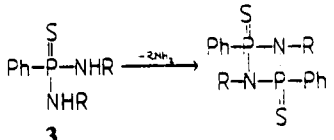
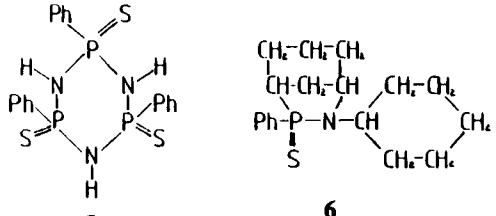
By contrast, the corresponding reaction of phenylphosphonothioic di(monoalkylamide), $PhP(S)(NHR)_2$ (**3**), leads to a variety of different products.[2-10] When R = Me, Et, Pr^n, Bu^n, Bu^i, Pr^c, CH_2Ph, the corresponding 1,3-dialkyl-2,4-diphenyl-2,4-dithiocyclodiphosph(V)azane, $[PhP(S)NR]_2$ (**4**), is obtained. The *trans*-form predominates[2,5,7,9,10] but the *cis*-isomer has also been obtained.[4,5,7,8] (Figure 2).



3 **4**

When R = H, Pr^i, Bu^s, Bu^t, the dealkylated cyclotriphosph(V)azane, $[PhP(S)NH]_3$ (**5**), is the product;[5,10] whilst with R = Hex^c, a most unusual fused bicyclic compound is formed,[6,10] (**6**). (Figure 3).



5 **6**

The thermolysis of phenylphosphonothioic di(monoarylamides),

$$PhP(S)(NHC_6H_4X)_2 \quad (X = H;\ o\text{-},\ m\text{-},\ p\text{-Me},\ o\text{-},\ m\text{-},\ p\text{-OMe})$$

leads to the corresponding cyclodiphosph(V)azanes, $[PhP(S)NHC_6H_4X]_2$. The pure products have been assigned *trans*-structures (based on ^1H n.m.r. evidence), but in some cases the *cis*-isomer was detected (^{31}P n.m.r., infra-red spectroscopy, t.l.c.) in crude reaction mixtures.[11,12]

SOLUTION REACTIONS

We have now developed a solution method for the synthesis of cyclodiphosph(V)azanes which allows the isolation of hitherto unavailable cyclodiphosph(V)azanes with α-branched alkyl carbon atoms. [The anomalous behaviour of the cyclopropylamine derivatives should be noted. Although branched at the α-carbon atom, the di(cyclopropylamide) gives the normal cyclodiphosph(V)azane by the thermolysis route]. The reaction of phenylphosphonothioic dichloride, $PhP(S)Cl_2$, with alkylamines, NH_2R (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i,

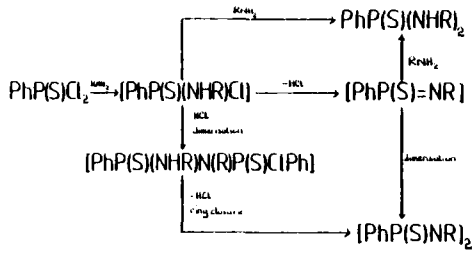


FIGURE 1 Suggested mechanistic schemes for the formation of cyclodiphosph(V)azanes and di(monoalkylamides)

Bu^s, Bu^t, Pe^{neo}, CH_2Ph, Hex^c), in polar, non-aqueous solvents at room temperature yields phenylphosphonothioic di(monoalkylamides), $PhP(S)(NHR)_2$, and 1,3-dialkyl-2,4-diphenyl-2,4-dithiocyclodiphosph(V)azanes, $[PhP(S)NR]_2$. All compounds had satisfactory elemental analysis and mass spectrometric molecular mass. The formation of the cyclodiphosph(V)azane is enhanced when low stochiometric amounts of amine are used. The cyclodiphosph(V)azanes obtained in this way are isomerically pure derivatives and n.m.r. spectroscopy shows them to be the *trans*-isomer. Thus, the ^1H n.m.r. spectrum of $[PhP(S)NPr^i]_2$ shows two methyl group environments due to their intrinsic asymmetry[4,5,10] and a similar non-equivalence is observed in the ^{13}C n.m.r. spectra of compounds having *gem*-dimethyl groups.

Monitoring the reaction of phenylphosphorothioic dichloride and isopropylamine by ^{31}P n.m.r. spectroscopy, at room temperature, only shows signals due to the starting material, $PhP(S)Cl_2$, the di(monoalkylamide), $PhP(S)(NHPr^i)_2$, and the cyclodiphosph(V)azane, $[PhP(S)NPr^i]_2$. The reaction proceeds very quickly under a variety of concentration conditions. Following the same reaction at -80 °C showed the formation of at least three intermediates, which were low in concentration (as indicated by peak height) and were very short-lived, during the reaction. The absorptions appeared as single lines implying that the intermediates contained only one phosphorus atom or more than one phosphorus atom, but in identical environments. Mechanistic proposals have been made for reactions of this type previously[13] and a typical scheme is shown in Figure 1. However, there is no ^{31}P n.m.r. evidence, at the present time, to support the existence of the "linear dimer" or "trigonal phosphorus" intermediates and these investigations are continuing.

STRUCTURE OF CYCLODIPHOSPHAZANES

The structure of the cyclodiphosph(V)azane ring has been investigated by various physico-chemical methods, but X-ray diffraction analysis has proved to be the most informative. *Trans*-cyclodiphosph(V)azanes, $[PhP(S)NR]_2$ (R = Me[9,14], Et[5], Ph[14], C_6H_4Me-*o*,[15] C_6H_4OMe-*o*[15]), which contain four-coordinate phosphorus atoms are characterised by a centrosymmetric structure with a planar four-membered $(P—N)_2$ ring, and the phenyl group attached to phosphorus eclipses the P = S bond. In *cis*-$[PhP(S)NEt]_2$,[5] the $(P—N)_2$ ring is puckered and the phenyl groups suffers a

TABLE I

^{31}P n.m.r. chemical shifts for $P(S)(NHC_6H_4X)_3$, $PhP(S)(NHC_6H_4X)_2$ and $[PhP(S)NC_6H_4X]_2$

X =	$P(S)(NHC_6H_4X)_3$ Me	OMe	$PhP(S)(NHC_6H_4X)_2$ Me	OMe	$[PhP(S)NC_6H_4X]_2$ Me	OMe
ortho-	43.6	46.6	52.6	51.9	77.1	72.9
meta-	42.3	41.9	51.5	51.4	67.3	67.0
para-	43.9	46.3	52.3	53.1	68.1	70.8

torsion angle of approximately 35°, in order to relieve interaction due to steric crowding.

Of particular interest is the effect of *ortho*-substituents on the structure of *N*-aryl cyclodiphosph(V)azanes.[15] The *N*-phenyl ring in *trans*-$[PhP(S)NPh]_2$[14] lies planar with the $(P—N)_2$ ring whereas in $[PhP(S)NC_6H_4Me\text{-}o]_2$ steric crowding is relieved by rotation about the C—N bond making the aryl group almost perpendicular to the $(P—N)_2$ ring. In $[PhP(S)NC_6H_4OMe\text{-}o]_2$, the aryl group remains planar to the $(P—N)_2$ ring, but steric crowding is relieved by bending of the C—N bond. This effect is also observed in the considerable ^{31}P n.m.r. chemical shift differences of these compounds, viz. $[PhP(S)NC_6H_4X]_2$ (X = *o*-, *m*-, *p*-Me, δ = 77.1, 67.3, 68.1 p.p.m.; X = *o*-, *m*-, *p*-OMe, δ = 72.9, 67.0, 70.8 p.p.m.) compared with the chemical shifts in a series of *N*-aryl derivatives of $P(S)Cl_3$ and $PhP(S)Cl_2$ (Table I).

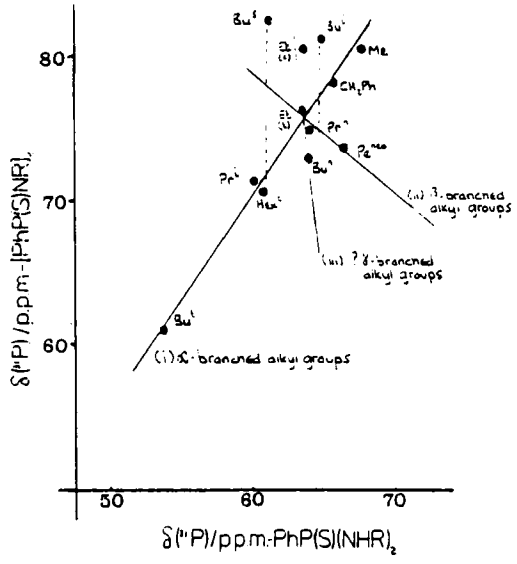


FIGURE 2 Graph of ^{31}P n.m.r. chemical shift of $PhP(S)(NHR)_2$ (R = alkyl) against ^{31}P n.m.r. chemical shift of $[PhP(S)NR]_2$. [δ (p.p.m.); w.r.t. 85% H_3PO_4; solvent–$CDCl_3$; downfield shifts positive].

N.M.R. SPECTROSCOPY

A plot of ^{31}P n.m.r. chemical shifts for $[PhP(S)NR]_2$ (R = alkyl) against those of the monomeric precursors, $PhP(S)(NHR)_2$, reveals three relationships which correspond to the nature of the alkyl substituent (Figure 2). Two distinct curves are observed corresponding to (i) α-branched alkyl carbons, and (ii) β-branched alkyl carbons. A third, more tentative curve, appears to correspond to γ-branching in the alkyl substituent. The plots for R = *cis*-Et, Bu^i and Bu^s appear to be anomalous in that they do not fall in the expected positions on the straight lines. Extrapolation of the points to the "di(monoalkylamide) curves" gives the predicted position showing that the anomaly is due to the cyclic dimer molecule. In analogous plots for $P(S)(NHR)_3$ (R = alkyl) and the corresponding cyclodiphosph(V)azanes, $[(RNH)P(S)NR]_2$, the position of the Bu^i derivatives is also anomalous.

We have also found a linear relationship between (^{31}P) shifts and (^{13}C-1) shifts (C-1 is the *ipso*-carbon atom of the P-phenyl group) for $PhP(S)(NHR)_2$(R = alkyl), Figure 3, and for $[PhP(S)NR]_2$ (R = alkyl), Figure 4. Again, the plot for R = Bu^i appears anomalous.

^1H and ^{13}C n.m.r. confirm the *trans*-structure of $[PhP(S)NBu^i]_2$ and the different behaviour of this anomalous compound may possibly be explained by the asymmetric alkyl groups causing either $(P—N)_2$ ring buckling, and/or rotation of the phenyl substituent, by analogy with the known structure of *cis*-$[PhP(S)NEt]_2$ where ring buckling and rotation of the phenyl substituent occurs. This possibility is under investigation using X-ray crystallography.

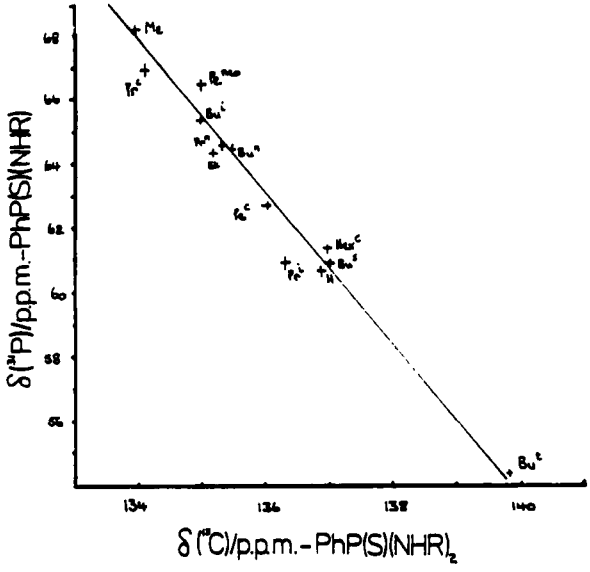


FIGURE 3 Graph of δ (^{31}P) against δ (^{13}C-1) for $PhP(S)(NHR)_2$ (R = alkyl). [δ (p.p.m.); solvent–$CDCl_3$].

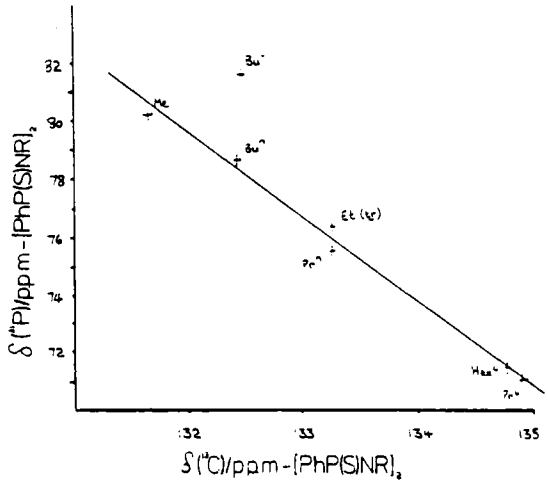


FIGURE 4 Graph of δ (^{31}P) against δ (^{13}C-1) for $[PhP(S)NR]_2$ (R = alkyl). [δ (p.p.m.); solvent–$CDCl_3$].

cis / *trans* ISOMERISATION

As a general rule, the formation of *cis*-cyclodiphosph(V)azanes appears to be temperature dependent. The formation of $[PhP(S)NR]_2$ (R = Et, Ph), by thermolysis (180–260 °C), leads to a mixture of *cis*- and *trans*-isomers (*cis*-isomers have also been detected in other systems) although the *trans*-isomers predominate. The formation of the cyclodiphosph(V)azanes by solution methods at room temperature (and below) leads to the *trans*-isomers only, whilst reactions carried out at the boiling point of the solvent give, additionally, some *cis*-isomers, particularly if the solvent is non-polar and if a tertiary base is present.

Pure *trans*- or *cis*-$[PhP(S)NEt]_2$ show the formation of the other isomer when boiled in nitrobenzene for six to eight hours. Preliminary studies show that the equilibrium ratio of *trans*-:*cis*-isomers after conversion is 6 : 1 and the conditions and equilibrium governing this interconversion are under investigation.

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