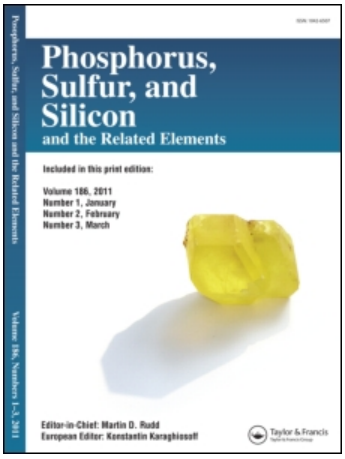

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PHOSPHORUS-NITROGEN COMPOUNDS. PART XLIV.[1] CYCLODIPHOSPH(V)AZANES DERIVED FROM TRI-ALKYLPHOSPHOROTHIOIC TRIAMIDES

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N,N',N''-Tri-alkylphosphorothioic triamides, $P(S)(NHR)_3$, R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Ch_2Ph, cyclopentyl and cyclohexyl, decompose at 190–240°C to give cyclodiphosph(V)azanes, $[RHNP(S)NR]_2$. The ^1H nmr spectra of the cyclic dimers are reported; *trans*-structures are assigned to the products R = Et, Pr^n, Bu^n, Bu^i, and CH_2Ph.

INTRODUCTION

The thermal decomposition reaction of P-phenyl-*N,N'*-diethylphosphonothioic diamide, $PhP(S)(NHEt)_2$, has been reported in an earlier study.[2] The *cis*- and *trans*-isomers of the cyclodiphosph(V)azane, $[PhP(S)NEt]_2$, were obtained. Structures were assigned to these isomers on the basis of proton nmr spectroscopy. Other phenylphosphonothioic diamides containing an α-CH_2 group also decompose at 200–225°C but only cyclodiphosphazanes with *trans*-structures have been isolated.[3,4]

In 1915, Michaelis[5] reported the thermal decomposition reactions of three triamides, $P(S)(NHR)_3$ (R = Et, Pr^n, Bu^i) and obtained products which he formulated as, P(S)(NR)NHR. Bock and Wiergrabe[6] heated the triamides, $P(S)(NHR)_3$, (R = Pr^n, Bu^i) at 280°C; the single product obtained in good yield from each reaction was assigned a cyclodiphosphazane structure on the basis of molecular weight measurements in solution. We report here the thermal decomposition reactions of several triamides of this type. The nmr spectra of the products are also described.

EXPERIMENTAL AND RESULTS

Tri-alkylphosphorothioic triamides, $P(S)(NHR)_3$, were prepared by the reaction of thiophosphoryl chloride and alkylamines (1:6 stoichiometry) in organic solvents. The compounds isolated were: $P(S)(NHMe)_3$ mp 109–110°C, lit.[6] mp 108° (yield 73%); $P(S)(NHEt)_3$ mp 66°, lit.[7] mp 68° (87%); $P(S)(NHPr^n)_3$ mp 72°, lit.[6] mp 75° (89%); $P(S)(NHPr^i)_3$ mp 93° (11%). (Found: C, 45.4; H, 10.3; N, 17.5. Calc. for $C_9H_{24}N_3PS$: C, 45.6; H, 10.1; N, 17.7); $P(S)(NHBu^n)_3$ mp 53°, lit.[7] mp 54° (54%); $P(S)(NHBu^i)_3$ mp 79°, lit.[6] mp 78° (45%); $P(S)(NHBu^s)_3$ mp 94° (23%). (Found: C, 51.2; H, 11.2; N, 15.3. Calc. for $C_{12}H_{30}N_3PS$: C, 51.6; H, 10.8; N, 15.1); $P(S)(NHC_5H_9)_3$ mp 164° (20%). (Found: C, 54.1; H, 9.4; N, 13.2. Calc. for $C_{15}H_{30}N_3PS$: C, 54.1; H, 9.5; N, 13.3); $P(S)(NHC_6H_{11})_3$ mp 143°, lit.[8] mp 144° (86%); $P(S)(NHCH_2Ph)_3$ mp 127° lit.[9] mp 126° (47%). The cyclodiphosphazanes $[RNHP(S)NR]_2$, R = Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, are also formed in small quantities (5–20%), along with their corresponding triamides (Table 1); one experiment is described in detail below.

Reaction of Thiophosphoryl Chloride with Isopropylamine

A solution of thiophosphoryl chloride (16.9 g, 0.1 mole), in dry benzene (200 ml) was added dropwise to a stirred solution of isopropylamine (35.4 g, 0.6 mole) in dry benzene (200 ml) at room temperature. After 2 h, the precipitate (isopropylamine hydrochloride) was filtered off and the filtrate evaporated to dryness. The residue was dissolved in cold methanol. The methanol insoluble portion was recrystallized from benzene/light petroleum (60–80°) (1:1) to give trans-*1,3-di-isopropyl-2,4-di-isopropylamino-2,4-dithiocyclodiphosphazane,* mp 225° (2.4 g, 18%).

The methanol soluble portion was evaporated to dryness and the resulting oil was recrystallized from ethyl acetate to give *N,N',N''*-tri-isopropylphosphorothioic triamide, mp 93°, lit.[7] mp 225°† (2.7 g, 10.4%).

The preparations of cyclodiphosphazanes by thermal decomposition of the respective triamides are summarized in Table 1. A typical experiment is described below.

Thermolysis of N,N',N''-Trismethylphosphorothioic triamide

Trismethylphosphorothioic triamide (3.06 g, 0.02 mole) was melted in a pyrex tube under an atmosphere of dry nitrogen. The

†It now seems clear that the mp given for this triamide in the earlier literature[7] is actually that of its cyclodiphosphazane.

temperature was raised slowly to 220–230° and maintained for 5 h. The melt was cooled and chromatographed on silica gel [eluant: benzene/chloroform (7:3)] to give: (*a*) 1,3-dimethyl-2,4-bismethylamino-2,4-dithiocyclodiphosphazane, mp 219°, lit.[10] mp 220–225° (0.74 g, 15.2%), which was recrystallized from chloroform/light petroleum (60–80°) (1:1), (*b*) *N,N',N''*-trismethylphosphorothioic triamide (1.2 g, 39.2%), mp and mixed mp 109–110°.

TABLE I
Physical and analytical data

Thermolysis of $P(S)(NHR)_3$					Found %						Calculated %				
Temp. °C	Time (h)	Product	mp °C	% yield[a]	C	H	N	P	S	Formula	C	H	N	P	S
230	5	$[MeHNP(S)NMe]_2$	219	39	19.7	6.0	23.0	25.4	25.9	$C_4H_{14}N_4P_2S_2$	19.7	6.0	23.0	25.4	25.9
205	8	$[EtHNP(S)NEt]_2$	191[b]	21	32.2	7.4	18.5	20.2	20.5	$C_8H_{22}N_4P_2S_2$	32.0	7.3	18.7	20.3	20.7
190	6	$[Pr^nHNP(S)NPr^n]_2$	156[c]	14 (5)	40.2	8.4	15.6	17.1	17.8	$C_{12}H_{30}N_4P_2S_2$	40.0	8.5	15.6	17.2	17.9
190	4	$[Pr^iHNP(S)NPr^i]_2$	228	24 (18)	39.6	8.1	15.4								
205	6	$[Bu^nHNP(S)NBu^n]_2$	113	6 (8)	46.9	9.0	13.4	15.2	15.7	$C_{16}H_{38}N_4P_2S_2$	46.6	9.2	13.6	15.0	15.5
200	5	$[Bu^iHNP(S)NBu^i]_2$	150[d]	21 (18)	46.3	9.1	13.3	15.3	15.6						
190	6	$[Bu^sHNP(S)NBu^s]_2$	165	17 (22)	47.0	9.4	13.5	14.9	15.7						
240	4	$[PhCH_2HNP(S)NCH_2Ph]_2$	203	19	61.2	5.5	10.2	11.3	11.8	$C_{28}H_{30}N_4P_2S_2$	61.3	5.5	10.3	11.3	11.7
205	4	$[C_5H_9NHP(S)NC_5H_9]_2$	237	24	52.1	8.2	12.2	13.5	13.9	$C_{20}H_{38}N_4P_2S_2$	52.2	8.3	12.2	13.5	13.9
205	6	$[C_6H_{11}NHP(S)NC_6H_{11}]_2$	228	15	55.8	8.9	10.8	12.0	12.5	$C_{24}H_{46}N_4P_2S_2$	55.8	8.9	10.9	12.0	12.5

[a] The yields of cyclodiphosphazane isolated from the reaction of $PSCl_3$ and amine in an organic solvent are given in brackets.
[b] lit.[5] mp 169°.
[c] lit.[6] mp 157°.
[d] lit.[6] mp 151°.

TABLE II
^1H nmr data ($CDCl_3$, 100 MHz)

Compound	δ_{NH}	$\delta_{\alpha\text{-}CH_2}$	δ_{CH_3}	$^3J(P-H)$	Structure
$[MeHNP(S)NMe]_2$	3.3	—	2.68[a], 2.68[b]	14.5[a], 15.0[b]	
$[EtHNP(S)NEt]_2$	3.2	3.19[a]; 3.16[b]; 2.96[a]	1.28, 1.15	14.5[a]; 14.5[b] 14.5[a]; 15.0[c]	*trans*
$[Pr^nHNP(S)NPr^n]_2$	3.2	3.05[a], 2.93[b], 2.78[a]	0.95, 0.91	13.8[a], 11.0[b], 13.8[a], 15.0[c]	*trans*
$[Pr^iHNP(S)NPr^i]_2$	3.1	—	1.48, 1.45; 1.24 (1) (1) (2)	—	
$[Bu^nHNP(S)NBu^n]_2$	3.2	2.9[d]			*trans*
$[Bu^iHNP(S)NBu^i]_2$[e]	3.3	3.02[a]; 2.8[b]; 2.66[a]	1.03, 0.97; 0.93 (1) (1) (2)	16.5[a], 11.0[b] 19.5[a]; 14.5[c]	*trans*
$[Bu^sHNP(S)NBu^s]_2$	[f]	—	1.35[g], 1.34[g]	—	
$[PhCH_2HNP(S)NCH_2Ph]_2$	3.2	3.99[a]; 3.70[b]	—	13.9[a], 16.0[a]; 9.5[b]	*trans*

[a] Proton(s) in alkyl group attached to a *ring* nitrogen atom.
[b] Proton(s) in alkyl group attached to an *exocyclic* nitrogen atom.
[c] $^2J(H-H)$.
[d] Approximate centre of very complex overlapping multiplets.
[e] 220 MHz
[f] Assignment uncertain.
[g] CH_3CH-

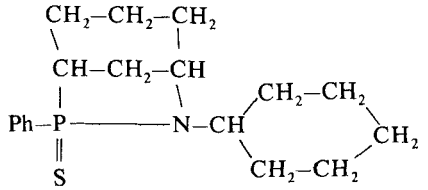
DISCUSSION

The thermal decomposition of trialkylphosphorothioic triamides takes place in the temperature range 190–240°C to give a cyclodiphosphazane and an alkylamine. Yields of product are only modest and about half the starting material is recovered unchanged.

$$2P(S)(NHR)_3 \rightarrow [RHNP(S)NR]_2 + 2RNH_2$$

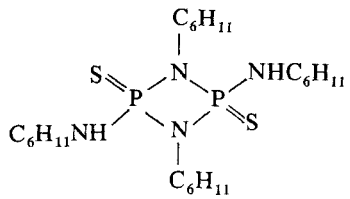
There are two interesting contrasts with the thermal decomposition reactions of phenylphosphonothioic diamides, $PhP(S)(NHR)_2$. In the latter system, dealkylation always occurs when the alkyl substituent has chain-branching at the α-carbon atom (e.g., R = Pr^i, Bu^s, Bu^t).[4] The only ring compound obtained in these examples is the dealkylated cyclotriphosphazane, $N_3H_3P_3Ph_3S_3$. The thermal decomposition of the cyclohexyl derivative, $PhP(S)(NHC_6H_{11})_2$, gives the bicyclic derivative[11] (**1**) and not a cyclodiphosphazane (**2**), as observed in the present work with $P(S)(NHC_6H_{11})_3$. The reasons for this difference in behaviour remain obscure.

$PhP(S)(NHC_6H_{11})_2 \longrightarrow$



(1)

$P(S)(NHC_6H_{11})_3 \longrightarrow$



(2)

It has been shown previously that the *cis* and *trans*-isomers of the cyclodiphosphazane, $[PhP(S)NEt]_2$ can easily be distinguished by ^1H nmr spectroscopy.[2] These structures were later confirmed by X-ray crystallography.[12] The methylene protons of the *cis*-isomer are effectively equivalent under conditions of fast rotation around the nitrogen–carbon bond; the analogous protons of the *trans*-isomer remain non-equivalent irrespective of the rate of rotation. Consequently, the $-CH_2-$ signal is very much more complex for the *trans*-dimer than for its *cis*-isomer.†

The cyclodiphosphazanes, $[RHNP(S)NR]_2$ (R = Et, Pr^n, Bu^n, Bu^i, CH_2Ph) also possess α-CH_2- protons. A careful scrutiny of their ^1H nmr spectra permits a structural assignment by utilizing the principles outlined above. Figure 1 illustrates the NCH_2- signal observed in the spectrum of the n-propyl dimer. The spectrum is complex owing to the overlap of lines arising from

$$\equiv P{-}NCH_2 \quad \text{and} \quad \equiv P{-}\underset{\displaystyle CH_2}{N}{-}P \equiv$$

units. The former should give rise to two triplets; the appearance of the latter depends on whether the two protons are equivalent (i.e., a *cis*-structure) or non-equivalent (i.e., a *trans*-structure). Nine lines are expected if the methylene protons are equivalent (coupling to two phosphorus nuclei and two β-CH_2 protons); thirty-six lines can be predicted for non-equivalent $-CH_2$ protons (a four line AB spectrum with coupling to two phosphorus nuclei and two β-CH_2 protons). At least twenty-five lines‡ are observed for these α-CH_2 protons and a *trans*-structure is clearly indicated. The data obtained from a complete analysis of the α-CH_2 region of the spectrum of *trans*-$[Pr^nNHP(S)NPr^n]_2$ are given in Table 2. Similar analyses were possible for the α-CH_2 region of $[EtNHP(S)NEt]_2$ and $[Bu^iNHP(S)NBu^i]_2$ and in both cases the presence of non-equivalent methylene protons indicates *trans*-structures. The numerous lines observed in the α-CH_2 region of the spectrum of the dimer, $[Bu^nNHP(S)NBu^n]_2$ can also only be interpreted as arising from a *trans*-disposition of substituents. However, in this case the overlap of signals does not permit an analysis of the chemical shifts and coupling constants to be made with the same degree of confidence.

The α-CH_2 region of the spectrum of the benzyl compound, $[PhCH_2NHP(S)NCH_2Ph]_2$, is comparatively straight-forward as β-CH_2 protons are absent (Figure 2). The doublet at δ 3.70 is asigned to

†See Ref. 2 for a more detailed discussion and illustrations of spectra.

‡The number of lines observed is less than that anticipated owing to fortuitous numerical relationships between coupling constants and chemical shifts of the type described in Part XXXIII of this series (see also Table 2).

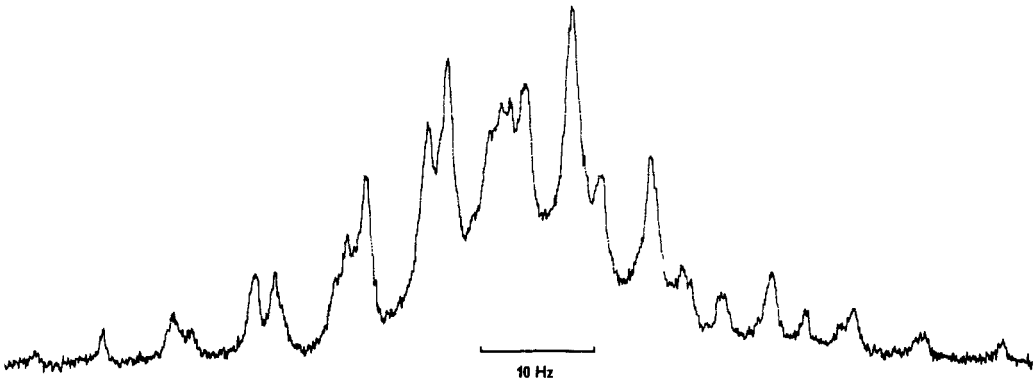


FIGURE 1 The $-NCH_2$ region of the ^1H nmr spectrum of $[Pr^nNHP(S)NPr^n]_2$.

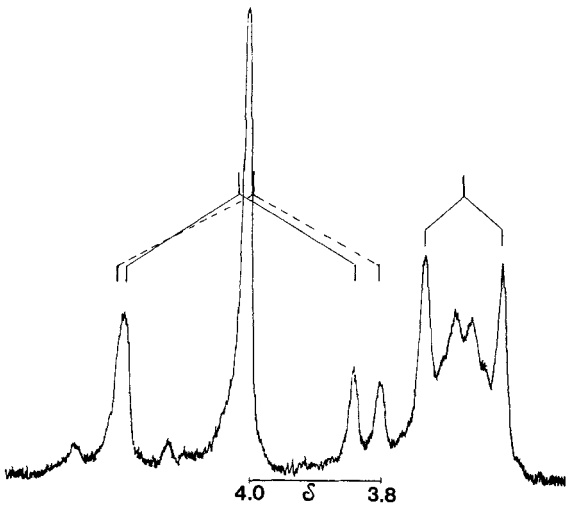


FIGURE 2 The methylene region of the ^1H nmr spectrum of $[PhCH_2NHP(S)NCH_2Ph]_2$.

the $-CH_2$ protons of the $\equiv P-NHCH_2-$ group. The poorly resolved signals in the centre of this doublet are due to virtual coupling.† This phenomenon is a characteristic feature of complex-spin systems and occurs frequently in the spectra of acyclic organophosphorus compounds (e.g., $\{PhP(O)[N(CH_2Ph)_2]\}_2O$)[13] and cyclophosphazene derivatives [e.g., nongeminal $N_3P_3Cl_4(NHCH_2Ph)_2$.][14] The low field methylene signal in the spectrum of $[PhCH_2NHP(S)NCH_2Ph]_2$ is essentially two overlapping triplets (Figure 2), although lines of low intensity are also apparent in this region of the spectrum and suggest that the two methylene protons are in slightly different chemical environments (i.e., an AB system that is very close to A_2). The couplings of these non-equivalent methylene protons to the ring phosphorus nuclei differ by ~2 Hz. A similar feature is observed in the spectrum of the isobutyl dimer and is probably the result of a steric effect. It seems likely that the benzyl dimer also possesses a *trans*-structure and that the coincidence of chemical shifts of the methylene protons is accidental. This conclusion implies that the shielding (or deshielding) effects of a thiophosphoryl group and a benzylamino substituent are very similar.

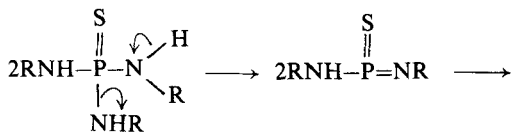
The methyl dimer, $[MeNHP(S)NMe]_2$, has been reported previously by two other groups.[10,15] Holmes and Forstner were unable to obtain an nmr spectrum owing to the insolubility of their product.[15] However, our sample was reasonably soluble in deuteriochloroform and its spectrum consisted of a doublet with intense virtual coupling ($MeNHP\equiv$) and a triplet for the methyl substituent on the ring nitrogen atom. These methyl protons cannot exhibit intrinsic assymmetry, hence it is not clear whether this derivative has a *cis*- or a *trans*- structure.

The chemical shifts of the terminal methyl group(s) of the triamides, $P(S)(NHR)_3$, are: R = Et (1.18), Pr^n (0.90), Pr^i (1.20) and Bu^i (0.95). These data suggest that the methyl signal at highest field in the spectra of the cyclodiphosphazanes (Table II) should be assigned to the methyl protons of the group attached to the exocyclic nitrogen atom (i.e., $\equiv PNHR$). The spectra of the isopropylamino- and isobutylamino-derivatives contain three methyl doublets in the ratio 1 : 1 : 2. This observation indi-

†Similar virtual coupling effects are observed in the spectra of all the other cyclodiphosphazanes containing α-CH_2 groups reported here and create an additional problem in the analysis. (see Figure 1). In each case, these broad humps are associated with the $\equiv PNHCH_2R$ groups.

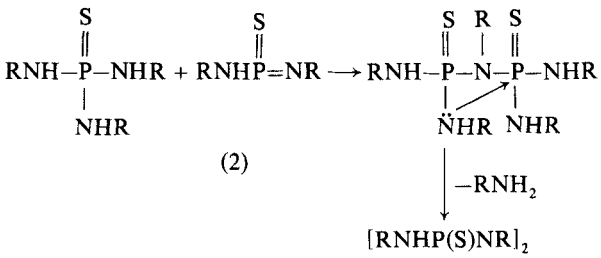
cates that the terminal methyl groups of the alkyl chain attached to the ring nitrogen atom are non-equivalent.

There are several possible hypotheses for the formation of cyclodiphosphazanes by the thermal decomposition method. One of the simplest involves the initial formation of a three coordinate phosphorus (V) compound by a β-elimination step. Dimerization of the latter would give the cyclodiphosphazane:



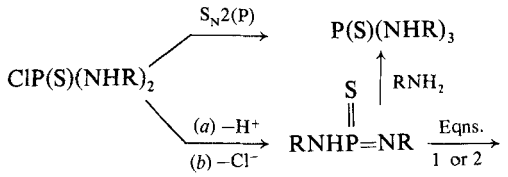
$[RNHP(S)NR]_2$ (1)

Three coordinate phosphorus (V) compounds have been isolated recently, *viz.*, $(Me_3C)(Me_3Si(N-P(S)=NCMe_3$[16] and $(Me_3Si)_2N-P(=NSiMe_3)_2$.[17] The dimerization of the latter to a cyclodiphosphazane[18] provides some experimental support for the feasibility of the hypothesis outlined in Eq. (1). Alternatively reaction with the triamide would give a linear species which could cyclise by internal nucleophilic attack:



(2)

Some reactions of thiophosphoryl chloride and primary amines give mixtures of triamides and cyclodiphosphazanes (Table I). The yield of the latter is enhanced for the amines containing branched chains. It can be assumed that both these competing reactions involve a common intermediate, *viz.*, $ClP(S)(NHR)_2$. The relative yields of the products would then be influenced by the competing processes illustrated in Eq. 3.



$[RNHP(S)NR]_2$

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