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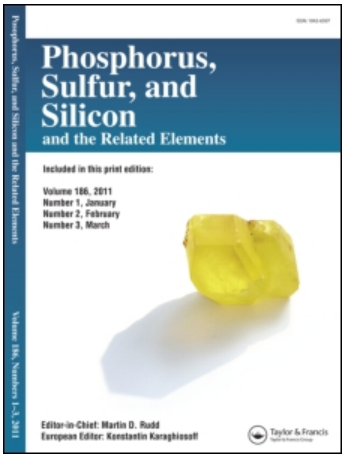

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PHOSPHORUS-NITROGEN COMPOUNDS. PART XLVI.[1] CYCLODIPHOSPHAZANES DERIVED FROM PHENYLPHOSPHONOTHIOIC DIAMIDES

Peter J. Argent[a]; James D. Healy[a]; Ezzeldine H. Ibrahim[ab]; Robert A. Shaw[a]; Michael Woods[a]
[a] Department of Chemistry, Birkbeck College (University of London), London, U.K. [b] Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt

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PHOSPHORUS-NITROGEN COMPOUNDS. PART XLVI.[1] CYCLODIPHOSPHAZANES DERIVED FROM PHENYLPHOSPHONOTHIOIC DIAMIDES‡

PETER J. ARGENT, JAMES D. HEALY, EZZELDINE H. IBRAHIM,†
ROBERT A. SHAW* and MICHAEL WOODS

Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX, U.K.

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P-Phenyl-*N*,*N*'-dialkyl(aryl)phosphonothioic diamides, $PhP(S)(NHR)_2$, R = Me, Pr^n, Bu^n, Bu^i, cyclopropyl, CH_2Ph, Ph, *o*- and *p*-MeC_6H_4, *o*-, *m*- and *p*-$MeOC_6H_4$ and *o*- and *p*-ClC_6H_4, decompose at 160–260°C to give cyclodiphosph(V)azanes, $[PhP(S)NR]_2$. The diamides, $PhP(S)(NHR)_2$, R = H, Pr^i, Bu^s and Bu^t, decompose on heating to give the cyclotriphosphazane, $[PhP(S)NH]_3$. The ^1H nmr spectra of the cyclic dimers are discussed: *trans*-structures are assigned to all the products.

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INTRODUCTION

Earlier parts of this series have discussed the formation of cyclodiphosph(V)azanes from the thermal decomposition reactions of tri-alkylphosphorothioic triamides,[2] $P(S)(NHR)_3$, and of *P*-phenyl-*N*,*N*'-diethylphosphonothioic diamide,[3] $PhP(S)(NHEt)_2$. In this paper we report the thermolyses of an extensive range of phenylphosphonothioic diamides.

EXPERIMENTAL AND RESULTS

Phenylphosphonothioic diamides, $PhP(S)(NHR)_2$, were prepared by the reaction of phenylphosphonothioic dichloride (Aldrich Chemical Co.) and aliphatic or aromatic amines (1 : 4 stoichiometry) in organic solvents. The compounds are listed in Table I. Thermal decomposition reactions were carried out in pyrex tubes (20 × 2.5 cm.) under an atmosphere of dry nitrogen or vacuum (0.05 mm Hg.). After each experiment, the cooled residue was examined by tlc. The mixture of cyclodiphosphazane and unreacted diamide was usually separated by column chromatography using silica gel. Three typical experiments are described below and the remainder are summarized in Table II.

Thermolysis of P-*phenyl*-N,N'-*di-isobutylphosphonothioic diamide* (*VI*)

Phenyl-di-isobutylphosphonothioic diamide (2.84 g, 0.01 mole) was slowly melted under an atmosphere of nitrogen. The temperature was then gradually raised to

† Permanent address: Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.
* Author to whom all correspondence should be addressed.
‡ Dedicated in friendship to Professor Leopold Horner on the occasion of his 70th birthday.

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TABLE I

Preparation of Phenylphosphonothioic diamides, $PhP(S)(NHR)_2$

Compound	No.	mp °C	Solvent	Temp °C	Yield %	Found % C	H	N	S	Formula	Calculated % C	H	N	S
$PhP(S)(NH_2)_2$	(I)	43	$CHCl_3$	25[a]	95	41.8	5.2	16.2	18.5	$C_6H_9N_2PS$	41.8	5.2	16.2	18.5
$PhP(S)(NHMe)_2$	(II)	68	$CHCl_3$	25[a]	80	47.8	6.5	14.0	16.1	$C_8H_{13}N_2PS$	48.0	6.5	14.0	16.0
$PhP(S)(NHPr^n)_2$	(III)	54	$CHCl_3$	25	79	56.1	8.3	10.7	12.6	$C_{12}H_{21}N_2PS$	56.3	8.2	10.9	12.6
$PhP(S)(NHPr^i)_2$	(IV)	51	Et_2O	25	70	56.3	8.2	10.8	12.4					
$PhP(S)(NHBu^n)_2$	(V)	47	C_6H_6	25	90	59.1	8.9	9.8	11.1	$C_{14}H_{25}N_2PS$	59.2	8.5	9.9	11.3
$PhP(S)(NHBu^i)_2$	(VI)	84	$C_6H_5CH_3$	25	44	59.4	8.6	9.7	11.4					
$PhP(S)(NHBu^s)_2$	(VII)	liq	Et_2O	25	9	59.3	8.8	9.8	11.1					
$PhP(S)(NHBu^t)_2$	(VIII)	103	CCl_4	25	63	59.1	8.8	9.8	11.2					
$PhP(S)(NHC_3H_5)_2$	(IX)	119	C_6H_6	25	95	57.0	6.9	11.1	12.7	$C_{12}H_{17}N_2PS$	57.1	6.8	11.1	12.7
$PhP(S)(NHC_6H_{11})_2$	(X)	109	C_6H_6	25	90	64.2	8.6	8.1	9.4	$C_{18}H_{29}N_2PS$	64.3	8.6	8.3	9.5
$PhP(S)(NHCH_2Ph)_2$	(XI)	80	$CHCl_3$	25	85	68.2	5.9	8.3	9.4	$C_{20}H_{21}N_2PS$	68.1	6.0	8.0	9.1
$PhP(S)(NHPh)_2$	(XIII)	180	$CHCl_3$	58	90	66.7	5.2	8.6		$C_{18}H_{15}N_2PS$	66.7	5.2	8.6	
$PhP(S)(NHC_6H_4Me\text{-}o)_2$	(XIV)	122	$CHCl_3$	58	82	67.9	5.7	7.8		$C_{20}H_{21}N_2PS$	68.2	5.7	7.9	
$PhP(S)(NHC_6H_4Me\text{-}p)_2$	(XV)	179	$CHCl_3$	58	88	67.9	5.7	7.9						
$PhP(S)(NHC_6H_4OMe\text{-}o)_2$	(XVI)	139	C_6H_6[b]	80	89	62.5	5.2	7.3		$C_{20}H_{21}N_2O_2PS$	62.5	5.2	7.3	
$PhP(S)(NHC_6H_4OMe\text{-}m)_2$	(XVII)	122	C_6H_6[b]	80	82	62.3	5.2	7.3						
$PhP(S)(NHC_6H_4OMe\text{-}p)_2$	(XVIII)	121	C_6H_6	80	79	62.4	5.2	7.2						
$PhP(S)(NHC_6H_4Cl\text{-}o)_2$	(XIX)	119	C_6H_6[b]	80	80	54.8	3.8	7.1		$C_{18}H_{15}Cl_2N_2PS$	55.1	3.8	7.1	
$PhP(S)(NHC_6H_4Cl\text{-}p)_2$	(XX)	190	C_6H_6[b]	80	82	55.0	3.8	7.1						

[a] Reactants mixed initially at *ca* −78°.
[b] Et_3N added.

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TABLE II

Preparation of some cyclodiphosph(V)azanes, $[PhP(S)NR]_2$

Monomeric Precursor	Thermolysis Temp. °C	Time h	Product	mp °C	% yield	Found % C	H	N	Formula	Calculated % C	H	N
(I)	250	6	$[PhP(S)NH]_3$	260	72	47.6	4.2	8.9	$C_{18}H_{18}N_3P_3S_3$	46.5	3.9	9.0
(II)	195	6	$[PhP(S)NMe]_2$	175–215[a]	25	49.7	4.8	8.2	$C_{14}H_{16}N_2P_2S_2$	49.6	4.9	8.1
(III)	160	24	$[PhP(S)NPr^n]_2$	137	27	54.5	6.3	7.0	$C_{18}H_{24}N_2P_2S_2$	54.8	6.1	7.1
(IV)	180–200	12	$[PhP(S)NH]_3$	260	33							
(V)	210	12	$[PhP(S)NBu^n]_2$	94–96	15	56.3	6.5	6.6	$C_{20}H_{14}N_2P_2S_2$	56.8	6.6	6.6
(VI)	220	2	$[PhP(S)NBu^t]_2$	195	12	56.8	6.7	6.6				
(VII)	200–220	6	$[PhP(S)NH]_3$	260	26							
(IX)	200	7	$[PhP(S)NC_3H_5]_2$	208	20	53.9	5.3	7.3	$C_{18}H_{20}N_2P_2S_2$	54.5	5.1	7.2
(X)	205	14	[b]	184	1	67.7	8.1	4.3	$C_{18}H_{26}NPS$	67.7	8.2	4.4
(XI)	210	6	$[PhP(S)NCH_2Ph]_2$	213[c]	15	63.5	5.0	5.8	$C_{26}H_{24}N_2P_2S_2$	63.7	4.9	5.7
(XII)[d]	220–240	5	$[PhP(S)NCH_2Ph]_2$	213	26							
(XIII)	315	6	$[PhP(S)NPh]_2$	268[e]	58	62.6	4.2	6.0	$C_{24}H_{20}N_2P_2S_2$	62.3	4.3	6.0
(XIV)	250	7	$[PhP(S)NC_6H_4Me\text{-}o]_2$	232–238	42	63.4	4.9	5.7	$C_{26}H_{24}N_2P_2S_2$	63.7	4.9	5.7
(XV)	250	8	$[PhP(S)NC_6H_4Me\text{-}p]_2$	280	30	63.6	4.9	5.7				
(XVI)	260	5	$[PhP(S)NC_6H_4OMe\text{-}o]_2$	239	55	59.6	4.8	5.5	$C_{26}H_{24}N_2O_2P_2S_2$	59.8	4.6	5.4
(XVII)	230	5	$[PhP(S)NC_6H_4OMe\text{-}m]_2$	188	64	59.7	4.8	5.5				
(XVIII)	250	4	$[PhP(S)NC_6H_4OMe\text{-}p]_2$	228	62	59.6	4.7	5.4				
(XIX)	250	5	$[PhP(S)NC_6H_4Cl\text{-}o]_2$	221	46	54.1	3.4	5.3	$C_{24}H_{18}Cl_2N_2P_2S_2$	54.3	3.4	5.3
(XX)	250	5	$[PhP(S)NC_6H_4Cl\text{-}p]_2$	222	52	54.2	3.5	5.3				

[a] lit.[4] mp 216–217°; *trans*-structure.[5]
[b] The product is a bicyclic compound whose structure was reported earlier.[6]
[c] lit.[4] mp 213.5–214.5°.
[d] $PhP(S)[N(CH_2Ph)_2](NHEt)$ prepared by lit.[7] method, mp 81°.
[e] lit.[8] mp 265°.

215–225°C and maintained for 2 h. The melt was cooled, dissolved in benzene and chromatographed on silica gel [eluant: light petroleum bp 80–100°C/benzene (5 : 4)] to give: (*a*) trans-*1,3-di-isobutyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane,* mp 195° (0.31 g, 11.7%), which was recrystallised from light petroleum, (*b*) unreacted diamide (VI) mp and mixed mp 84° (1.13 g, 40%).

Thermolysis of P-*phenyl*-N,N′-*di-tert-butylphosphonothioic diamide* (*VIII*)

Phenyl-di-tert-butylphosphonothioic diamide (2.84 g, 0.01 mole) was heated in an atmosphere of nitrogen at 200–220° for 8 h. After cooling, the residual oil was shaken with tetrachloromethane and left to stand. A precipitate was obtained which after recrystallisation from 1,2-dichloroethane gave colourless crystals of 2,4,6-trithio-2,4,6-triphenylcyclotriphosphazane, mp 260° (0.40 g, 25%) [m/e obs. 465; $(C_{18}H_{18}N_3P_3S_3)^+$ requires m/e 465].

Thermolysis of P-*Phenyl*-N,N′-*di*-p-*chlorophenylphosphonothioic diamide* (*XX*)

Phenyl-di-*p*-chlorophenylphosphonothioic diamide (7.86 g, 0.02 mole) was melted under vacuum and the temperature was raised to 250°. A vapor was observed throughout the experiment (5 h) which condensed in the cooler part of the pyrex tube and in the liquid air trap before the vacuum pump. This condensate was identified as *p*-chloroaniline, mp 70°. The residue from the thermolysis was chromatographed [eluant:benzene] to give: (*a*) trans-*1,3-di*-p-*chlorophenyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane,* mp 222° (2.76 g, 52%), (*b*) a trace of unreacted diamide, (XX), mp 190° and (*c*) *p*-chloroaniline.

DISCUSSION

Phenylphosphonothioic diamides, $PhP(S)(NHR)_2$, R = Me, Et[3], Pr^n, Bu^n, Bu^i, cyclo-Pr, CH_2Ph, Ph, *o*- and *p*-MeC_6H_4, *o*-, *m*- and *p*-$MeOC_6H_4$ and *o*- and *p*-ClC_6H_4, undergo decomposition on heating to give cyclodiphosph(V)azanes.

$$2PhP(S)(NHR)_2 \longrightarrow [PhP(S)NR]_2 + 2RNH_2 \qquad (1)$$

The mixed diamide, $PhP(S)[N(CH_2Ph)_2](NHEt)$ (XII) decomposes to give the *N*-benzyl cyclodiphosphazane, $[PhP(S)NCH_2Ph]_2$. In general, diamides with aryl substituents require temperatures *ca.* 50°C higher than their alkyl analogues to undergo this cyclisation reaction.

In principle, cyclodiphosph(V)azanes containing four-coordinate phosphorus can exist as two geometric isomers. The major product (30%) obtained by heating the diamide, $PhP(S)(NHEt)_2$ is the *trans*-cyclodiphosphazane, $[PhP(S)NEt]_2$ although a modest yield (12%) of the *cis*-isomer was also isolated.[3] In the current study, only one cyclodiphosphazane has been isolated from each reaction although tlc[9] indicates the probable presence of a second isomer when R = Pr^n or Bu^n.[10]

Proton nmr data for the cyclodiphosph(V)azanes, $[PhP(S)NR]_2$, R = Me, Et, Pr^n, Bu^n, Bu^i, CH_2Ph are given in Table III. The multiplicity of the signals arising from the $>NCH_2$ protons is only consistent with a *trans*-structure for these derivatives: α-methylene protons of a *trans*-isomer remain non-equivalent irrespective of the rate of rotation around the nitrogen-carbon bond.[2,3] The $>NCH_2$ region of the spectrum of the *N*-isobutyl compound, $[PhP(S)NBu^i]_2$ is shown in Figure 1. The

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TABLE III

^{1}H nmr data ($CDCl_3$, 100 MHz) for some *N*-Alkylcyclodiphosph(V)azanes

Compound	$^{\delta}\alpha$-CH_2	$^3J(P\text{-}H)$	$^{\delta}CH_3$	Structure
$[PhP(S)NMe]_2$		14.0	2.52	*trans*[a]
$[PhP(S)NEt]_2$[b]	3.10, 2.79	14.5, 16.5 14.0[c]	0.98	*trans*
$[PhP(S)NPr^n]_2$	3.11, 2.68	16.0, 18.0 14.0[c]	0.64	*trans*
$[PhP(S)NBu^n]_2$	3.17, 2.64	15.2, 17.8 14.4[c]	0.61	*trans*
$[PhP(S)NBu^i]_2$[d]	3.03, 2.34	16.0, 19.0 14.0[c]	0.71, 0.68	*trans*
$[PhP(S)NCH_2Ph]_2$	4.22, 3.80	14.0, 18.8 15.5[c]		*trans*

[a] X-ray structure.[5]
[b] Prepared by lit.[3] method.
[c] $^2J(H\text{-}H)$.
[d] 220 MHz.

non-equivalence of the α-CH_2 protons is so pronounced that this region of the spectrum may be analyzed on first order considerations. Molecular models suggest that these very different $\geq NCH_2$ environments arise from the branching of the isobutyl chain.

The above nmr criterion for structural assignment is clearly inapplicable for the *N*-arylcyclodiphosphazanes (Table II). It has been suggested[3] that the characteristic doublet of multiplets arising from the *ortho*-protons† of the PhP≡group may pro-

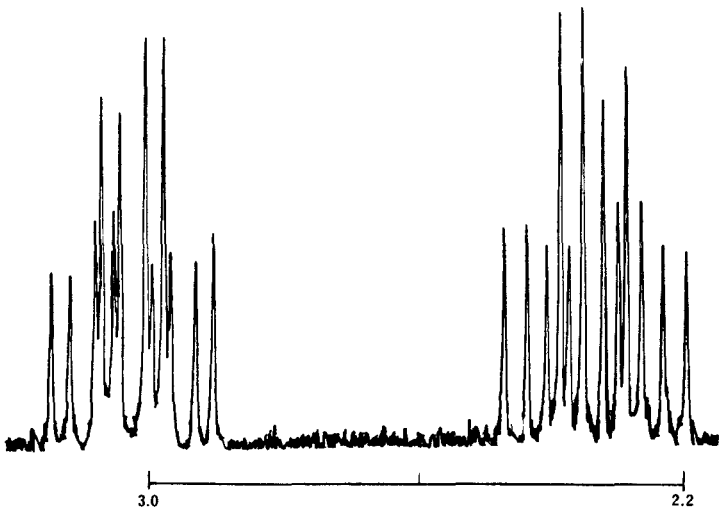

FIGURE 1 The NCH_2 region of the ^{1}H nmr spectrum of $[PhP(S)NBu^i]_2$.

† The resonance of *meta*- and *para*- protons of the PhP≡group of the *N*-arylcyclodiphosphazanes reported here occurs as a multiplet [center *ca.* 7.5($CDCl_3$) or *ca.* 7.0(C_6D_6)] and well separated from the *ortho*-proton resonance. These aryl resonances are similar to those observed for many triarylphosphine sulfides (R. A. Shaw and M. Woods, unpublished results).

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vide some structural information for the cyclodiphosphazanes, $[PhP(S)NR]_2$. The high π-electron density of the *P*-phenyl substituents would be expected to give a preferred orientation so that their planes are perpendicular to that of the cyclodiphosphazane ring.[3,12] Consequently, an isomer of *cis*-stereochemistry would have *ortho*-aromatic protons that are in the vicinity of one P=S group whereas those of a *trans*-isomer are reasonably close to two thiophosphoryl groups and a pronounced deshielding effect is anticipated.

It has been established previously[3] that for *trans*-$[PhP(S)NEt]_2$ a downfield shift occurs for the *ortho*-protons of the PhP≡group relative to the resonance position of the *ortho*-protons of *cis*-$[PhP(S)NEt]_2$ *or* $PhP(S)(NHEt)_2$. Table IV summarises the data obtained for the *N*-arylcyclodiphosphazanes and their respective diamides and provides some evidence, albeit not unequivocal, for their *trans*-stereochemistry. Further support for this assignment comes from the predicted absence of coincidences in the infrared and Raman spectra[13,14] of *N*-arylcyclodiphosphazanes.

The almost exclusive formation of *trans*-isomers in these decomposition reactions is not easy to explain in terms of a simple mechanistic hypothesis. Obviously one (or more) phosphorus-nitrogen bonds must be broken at some stage. We suggest that formation of a reactive, three coordinate phosphorus(V) species, *viz.*, PhP(S)=NR, by a β-elimination step is most probable. Reaction of this species with diamide followed by internal nucleophilic attack would give the cyclodiphosphazane.

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TABLE IV

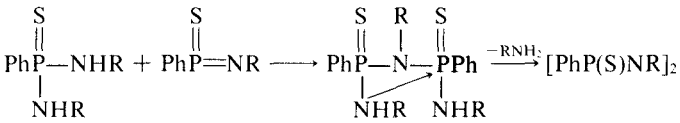
The chemical shift (in p.p.m.) of *ortho*-protons of the PhP≡group in the proton nmr spectrum of N-arylcyclodiphosph(V)azanes and their precursors.

	Compound	Solvent[a] $CDCl_3$ *ortho*-protons[b]	Solvent[a] C_6D_6 *ortho*-protons[b]
	$PhP(S)(NHPh)_2$ (XIII)		8.0
	$[PhP(S)NPh]_2$		8.5
ortho	$PhP(S)(NHC_6H_4Me)_2$ (XIV)	8.0	
	$[PhP(S)NC_6H_4Me]_2$	8.7	
para	$PhP(S)(NHC_6H_4Me)_2$ (XV)	8.0	
	$[PhP(S)NC_6H_4Me]_2$	8.6	
ortho	$PhP(S)(NHC_6H_4OMe)_2$ (XVI)		8.1
	$[PhP(S)NC_6H_4OMe]_2$		8.9
meta	$PhP(S)(NHC_6H_4OMe)_2$ (XVII)	8.0	
	$[PhP(S)NC_6H_4OMe]_2$	8.6	
para	$PhP(S)(NHC_6H_4OMe)_2$ (XVIII)		7.9
	$[PhP(S)NC_6H_4OMe]_2$		8.8
ortho	$PhP(S)(NHC_6H_4Cl)_2$ (XIX)		8.0
	$[PhP(S)NC_6H_4Cl]_2$		8.9
para	$PhP(S)(NHC_6H_4Cl)_2$ (XX)		7.9
	$[PhP(S)NC_6H_4Cl]_2$		8.8
	$PhP(S)(NHEt)_2$	8.0	8.0
trans-	$[PhP(S)NEt]_2$	8.4	8.6
cis-	$[PhP(S)NEt]_2$[c]	8.0	8.0

[a] Owing to the poor solubility of these derivatives, it has not been possible to obtain spectra in only one solvent.

[b] Measured as centre of symmetrical multiplet.

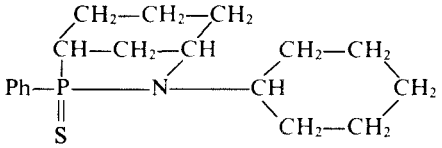
[c] Prepared by lit.[3] method.



(2)

The cyclization of a linear phosphorus-nitrogen compound was originally suggested by Norris and Jonassen for the formation of cyclodiphosphazanes from phosphorothioic triamides.[15] Holmes and Forstner[16] noted that there seemed no apparent reason why trimeric phosphazanes should not also be formed similarly by a further reaction of a linear compound with the parent amide. It is possible though that cyclodiphosph(V)azanes may be favored both kinetically and thermodynamically. It is interesting to note that very few cyclophosph(V)azanes are known with more than four atoms in the ring systems and many of these involve cyclophosphazene precursors.[12] A further difficulty with the mechanism depicted by Eq. (2) is that the internal nucleophilic attack ought to give rise to approximately equal amounts of *cis*- and *trans*-isomers. It is possible that *cis*-isomers are more labile and that ring rupture occurs, followed by recyclization to the more stable *trans*-isomer but the high thermal stability of the cyclodiphosphazane ring[4] (and particularly the *N*-aryl derivatives,[13]) would suggest otherwise. Arguments for the formation of *trans*-cyclodiphosph(V)azanes (and the consequent lack of *cis*-isomers) based on steric factors also lack conviction. Perhaps, as we considered earlier,[2] direct dimerization[17] of the postulated three-coordinate intermediate, PhP(S)=NR, remains a plausible alternative.

An additional feature occurs in the thermolyses of compounds containing an α-branched alkyl group which further complicates the mechanistic picture. The diamides, $PhP(S)(NHR)_2$ R = Pr^i, Bu^s and Bu^t, decompose on heating with elimination of alkene to give a cyclo*tri*phosphazane, $[PhP(S)NH]_3$. This compound is also obtained by heating the ammono derivative, $PhP(S)(NH_2)_2$. The phosphorus nmr spectrum of this dealkylated trimer is of the AB_2 type as would be expected for a six-membered phosphorus-nitrogen ring. Another cyclotriphosphazane, $N_3Me_3P_3O_3(OMe)_3$, also has a ^{31}P nmr spectrum of the AB_2 type[18] and has been shown by X-ray analysis to have a distorted boat structure.[19]



Many of the foregoing observations can be rationalized if β-elimination of the alkyl group attached to nitrogen is postulated. This would explain the instability of the secondary and tertiary *N*-alkyl groups at these thermolysis temperatures; it would also provide a rational way of explaining the formation of the unusual product obtained in the thermolysis of *P*-phenyl-*N*,*N*'-dicyclohexylphosphonothioic diamide (X).[6] Elimination of cyclohexene and ammonia, followed by the recombination of the former with a reactive phosphorus-nitrogen intermediate, could yield the above fused bicyclic system.[6]

All the reactions discussed here would thus have a common mechanistic feature.

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