Phosphorus–Nitrogen Compounds. Part XXXVI.[1] Alkylthio- and Arylthio-cyclotetraphosphazatetraenes

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The reaction of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, with sodium thiolates gives the tetrathiocyclotetraphosphazatetraenes, $N_4P_4Cl_4(SR)_4$, and the organic disulphides, R_2S_2. The only exception to the above replacement pattern is the reaction with sodium isobutanethiolate when a trisubstituted derivative, $N_4P_4Cl_5(SBu^i)_3$, is detected. More forcing reaction conditions do not lead to higher thiolated cyclotetraphosphazatetraenes; instead ring scission and formation of trithiophosphites and trithiophosphates is observed. The tetrathio-derivatives, $N_4P_4Cl_4(SR)_4$, have geminal structures and spectroscopy suggests that the thio-groups have a 2,2,6,6-arrangement.

THE reaction of sodium thiolates with hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, was discussed in Part XXI.[1] The degree of chlorine replacement is largely determined by the nature of the solvent and the reaction temperature. The observed replacement pattern was exclusively geminal. When sodium alkanethiolates are used the bis-, tetrakis-, and hexakis-derivatives, $N_3P_3Cl_{6-n}(SAlk)_n$ (n = 2, 4, or 6), are the major products. The reaction of the hexachloride, $N_3P_3Cl_6$, with sodium benzenethiolate (NaSPh), however, yields only bis- and hexakis-derivatives, $N_3P_3Cl_{6-n}(SPh)_n$ ($n = 2$ or 6). Recent studies[3] indicate that reactions of hexachlorocyclotriphosphazatriene with other sodium arenethiolates do not necessarily conform to the benzenethiol pattern.[2]

Tetra-alkylthio- and tetra-arylthio-cyclotetraphosphazatetraenes are prepared from octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (I), by the sodium thiolate method by use of diethyl ether as the reaction solvent. Some of these compounds were listed in a preliminary communication.[4] Lead thiolates, which are useful reagents for the preparation of mononuclear thio-esters of phosphorus,[5,6] are insufficiently reactive for use with cyclophosphazenes. The reactions with sodium thiolates are heterogeneous and a considerable excess of the thiolate is required. Preparations involving primary alkanethiolates (R = Et, Pr^n, Bu^n) are carried out at room temperature (48 h) and the tetrathio-derivatives, $N_4P_4Cl_4(SR)_4$, are obtained in yields of 40—60%. For arenethiolates (R = Ph, p-MeC_6H_4, p-ClC_6H_4) reflux conditions (10 h) are required. The yields of product, $N_4P_4Cl_4(SR)_4$, are somewhat less than with the alkanethiolates and are only slightly increased after prolonged heating under reflux.

No other cyclotetraphosphazatetraenes are isolated in any of the above experiments, even when widely differing molar ratios of reactants are employed. Significant amounts of the organic disulphides, R_2S_2 are always formed, making the purification of the products difficult and tedious. A similar tendency towards disulphide formation has also been noticed in the thiolysis of hexachlorocyclotriphosphazatriene,[2] $N_3P_3Cl_6$, and of phosphoryl and thiophosphoryl chlorides,[5] but this feature is absent from thiolyses of phosphorus(III) compounds.[6]

In the reaction of sodium isobutanethiolate with $N_4P_4Cl_8$ (I), the tris-derivative $N_4P_4Cl_5(SBu^i)_3$ is detected by mass spectrometry, as well as some of the organic disulphide. This is the only reaction of the tetramer (I) with a branched-chain thiolate in which we have observed the formation of any thiolated cyclophosphazene derivatives. In contrast, several branched-chain thio-derivatives of $N_3P_3Cl_6$ are known.[2] The structure of $N_4P_4Cl_5(SBu^i)_3$ is not clear from the available evidence.

In the reaction of sodium thiolates with hexachlorocyclotriphosphazatriene,[2] higher boiling solvents were successfully utilised for the synthesis of fully thiolated derivatives $N_3P_3(SR)_6$. More forcing reaction conditions are found to be unsatisfactory in the present work. Thus, when sodium ethanethiolate is heated (30 h) in boiling tetrahydrofuran with the octachloride (I) an intractable gum is obtained. When identical conditions with sodium n-propane- or n-butane-thiolate are used, colourless oils are obtained containing phosphorus and sulphur, but no nitrogen and chlorine. These oils were identified by mass spectrometry as mixtures of trithiophosphites, $P(SR)_3$, and trithiophosphates, $P(O)SR_3$ (R = Pr^n or Bu^n), with the former predominating. Similar mononuclear phosphorus products are obtained from the reaction with sodium benzenethiolate. Reactions in boiling dimethylformamide (homogeneous reaction conditions) give viscous oils which contain trithiophosphites(ates) but no cyclophosphazatetraene derivatives.

The alkylthio-derivatives prepared are insoluble in water and reasonably stable to hydrolysis. The compounds can be distilled under vacuum only after preliminary purification procedures (appreciable decomposition occurs during the first distillation). The ethyl and n-propyl derivatives are subsequently obtained as solids. The arylthio-derivatives are colourless crystalline solids stable to both heat and hydrolysis.

Evidence for the geminal replacement pattern in the ethanethioalcoholysis of octachlorocyclotetraphosphazatetraene is obtained from ^{31}P n.m.r. spectroscopy.[7] It was not possible to obtain good spectra for all our compounds but data for three of them are in Table 1. The spectra show either two triplets with very low $^2J_{P-P}$ coupling or two broad lines. The ratio of signals is always 1 : 1 which indicates a geminal arrangement of

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[1] Part XXXV, S. K. Das, R. A. Shaw, and B. C. Smith, *J.C.S. Dalton*, 1973, 1883.

[2] A. P. Carroll and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 914.

[3] R. A. Shaw and M. Woods, unpublished results.

[4] A. P. Carroll and R. A. Shaw, *Chem. and Ind.*, 1962, 1908.

[5] R. A. Shaw and M. Woods, *Phosphorus*, 1971, **1**, 41.

[6] R. A. Shaw and M. Woods, *Phosphorus*, 1971, **1**, 191.

[7] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Chem. and Ind.*, 1962, 1909.

substituents. However, there are two possible geminal tetrakis-isomers (II) or (III) $N_4P_4Cl_4(SR)_4$, and it is not easy to ascertain the precise structure of our derivatives solely on the basis of the available ^{31}P data.

A comparison of the i.r. and Raman spectra of $N_4P_4Cl_4(SR)_4$ (R = Et and Ph) suggests a symmetrical disposition of substituents (see Experimental section for details). The very small number of minor coincidences in the spectra indicates that the molecule is approximately centrosymmetric and therefore probably has the 2,2,6,6-configuration (see Figure). The evidence is by no means definitive as the other geminal isomer (2,2,4,4) is not available for a comparative study.

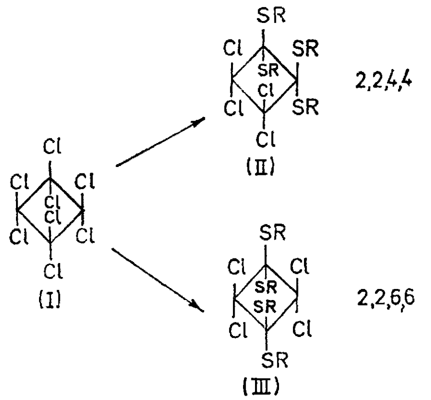
TABLE 1

^{31}P and ^{1}H N.m.r. data

Compound	δ/p.p.m.[a] $\equiv P(SR)_2$	δ/p.p.m.[a] $\equiv PCl_2$	$^2J_{P-P}$/Hz	$\tau(NMe_2)$ [b]	$^3J^*_{P-N-Me}$/Hz	$^4J_{P-H}$ [d]/Hz CCl_4	$^4J_{P-H}$ [d]/Hz C_6D_6	$^7J_{P-H}$ [e]/Hz CCl_4	$^7J_{P-H}$ [e]/Hz C_6D_6
$N_4P_4Cl_4(SEt)_4$	−28·6 [c]	+9·7 [c]	11·8 [c]						
$N_4P_4Cl_4(SPh)_4$	−22·9	+9·5	17·6						
$N_4P_4Cl_4(S{\cdot}C_6H_4{\cdot}Cl\text{-}p)_4$	−19·9	+10·3	f			g	2·3		
$N_4P_4Cl_4(S{\cdot}C_6H_4{\cdot}Me\text{-}p)_4$						2·3	2·3	2·6	2·7
$N_4P_4(SEt)_4(NMe_2)_4$				7·44	11·2				
$N_4P_4(SPh)_4(NMe_2)_4$				7·67	11·2				
$N_4P_4(S{\cdot}C_6H_4{\cdot}Cl\text{-}p)_4(NMe_2)_4$				7·63	11·1	2·0	2·0		
$N_4P_4(S{\cdot}C_6H_4{\cdot}Me\text{-}p)_4(NMe_2)_4$				7·66	11·2	2·0	2·0	2·0	2·0

[a] Measured in $CDCl_3$ with 85% H_3PO_4 as external reference. [b] Measured in CCl_4 wih tetramethylsilane as internal standard. [c] Data from ref. 7. [d] Coupling to *ortho*-protons. [e] Coupling to *para*-methyl protons. [f] Insufficient resolution. [g] Insufficient separation of the AB quartet.

Geminal isomers of tetrachlorotetrathiocyclotetraphosphazatetraene *



* The eight-membered N_4P_4 ring is shown for clarity as a square, the corners representing phosphorus atoms

The i.r. spectra of the chloro-derivatives, $N_4P_4Cl_4(SR)_4$, show a broad phosphorus–nitrogen absorption band in the region 1280—1370 cm^{-1}. The position of this band is characteristic of the cyclotetraphosphazatetraene ring.[8,9] In the examples studied this band always appears as a doublet with a splitting of *ca.* 70 cm^{-1}. The P=N region of the i.r. spectra of the dimethylamino-derivatives, $N_4P_4(NMe_2)_4(SR)_4$, is complex and at least three distinct peaks are discernible. The overall band position moves to lower energy (1190—1300 cm^{-1}) (see Table 2).

The mass spectra of these compounds are very complex and no attempt has been made to analyse them in detail. Fragmentation occurs almost exclusively by loss of substituent groups [SR and/or Cl(NMe_2)]. The fragmentation of the tetrameric ring on electron impact is not observed until most substituent groups have been lost, and therefore the major fragments containing two phosphorus atoms have $m/e < 150$. Thus, it is not possible to gather any conclusive structural information from these spectra.

A more detailed structural assessment can be attempted from the ^{1}H n.m.r. spectra of the dimethylamino-derivatives, $N_4P_4(NMe_2)_4(SR)_4$. The chemical shift and the apparent phosphorus–hydrogen coupling constants ($^3J^*_{P-H}$) for the dimethylamino-protons are given in Table 1. The shielding of the dimethylamino-protons is more pronounced in the arylthio-derivatives than in the ethylthio-compound. Similar shielding has been observed in the spectra of dimethylaminophenoxy-[10] and dimethylaminophenyl[1] derivatives and is presumably associated with the shielding effect of the ring-current of the aryl groups. The resonance of the dimethylamino-protons of $N_4P_4(SR)_4(NMe_2)_4$ derivatives appears as a clean doublet without any virtual coupling, $^3J^*_{P-H}$ 11·1—11·2 Hz. The appearance and extent of virtual coupling in the spectra of dimethylamino-tetramer derivatives has been reported elsewhere.[11] The general

TABLE 2

I.r. data [a]

Compound	P=N Stretching frequency/cm^{-1}
$N_4P_4Cl_8$	1315
$N_4P_4(SEt)_4Cl_4$	1258, 1278
$N_4P_4(S{\cdot}C_6H_4{\cdot}Me\text{-}p)_4Cl_4$	1297, 1370
$N_4P_4(SPh)_4Cl_4$	1305, 1345
$N_4P_4(S{\cdot}C_6H_4{\cdot}Cl\text{-}p)_4Cl_4$	1282, 1357
$N_4P_4(SEt)_4(NMe_2)_4$	1180, 1245, 1275
$N_4P_4(S{\cdot}C_6H_4{\cdot}Me\text{-}p)_4(NMe_2)_4$	1185, 1215, 1297
$N_4P_4(SPh)_4(NMe_2)_4$	1190, 1251, 1306
$N_4P_4(S{\cdot}C_6H_4{\cdot}Cl\text{-}p)_4(NMe_2)_4$	1190, 1245, 1288

[a] Peaks are quoted as the centre of broad bands and should be regarded as accurate to ±5 cm^{-1}.

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[8] R. A. Shaw, *Chem. and Ind.*, 1959, 54.

[9] *E.g.*, H. R. Allcock, *Chem. Rev.*, 1972, **72**, 320—322.

[10] D. Dell, B. W. Fitzsimmons, R. Keat, and R. A. Shaw, *J. Chem. Soc.*, 1966, 1680.

[11] G. J. Bullen, P. E. Dann, V. B. Desai, B. C. Smith, R. A. Shaw, and M. Woods, *Phosphorus*, 1973, **3**, 67.

conclusion is that virtual coupling is minimal or nonexistent for compounds with identical substituents on the distant phosphorus atoms (2,6) and pronounced for those with identical substituents on near phosphorus atoms (2,4). This hypothesis has also elucidated the structures[12] of the two geminal tetrameric derivatives, $N_4P_4Ph_4(NMe_2)_4$. Hence, the absence of virtual coupling from the spectra of the derivatives $N_4P_4(SR)_4(NMe_2)_4$ indicates a 2,2,6,6-structure.

The ^1H n.m.r. spectra of the derivatives, $N_4P_4(S{\cdot}C_6H_4{\cdot}X\text{-}p)_4Y_4$ (X = Me or Cl, Y = NMe_2 or Cl) also show long-range spin–spin coupling between phosphorus and hydrogen nuclei over seven (*p*-methyl group) and four (*ortho*-protons) bonds (see Table 1). Although there are a few examples in the literature of seven-bond interactions between phosphorus and hydrogen nuclei in mononuclear phosphorus compounds,[13-15] this is the first time such effects have been reported in cyclophosphazenes. The $^7J_{P\text{-}H}$ value of 2·6 Hz observed for the *p*-tolylthio-derivative, $N_4P_4(S{\cdot}C_6H_4{\cdot}Me\text{-}p)_4Cl_4$, is comparable with those reported[15] for some mononuclear phosphorus(v) compounds containing *p*-tolylthio-groups. Similar direct long-range coupling was observed[3] in the spectra of some geminal $N_3P_3(S{\cdot}C_6H_4{\cdot}X\text{-}p)_2(NMe_2)_4$ derivatives but not in the spectra of geminal $N_3P_3(SR)_4(NMe_2)_2$ (R = *para*-substituted aromatic group). We believe that this difference is significant; these spectra will be assessed in detail elsewhere. For the moment it is sufficient to point out that a 2,2,6,6-structure for the tetrathio-derivatives $N_4P_4(SR)_4(NMe_2)_4$ is analogous to the bisthiocyclotriphosphazatriene $N_3P_3(SR)_2(NMe_2)_4$ in that each $\equiv P(SR)_2$ grouping is linked through nitrogen on either side to a $\equiv P(NMe_2)_2$ group. As the observed n.m.r. spectra can be correlated for these two sets of derivatives, we believe that the long-range coupling effects observed also strongly favour 2,2,6,6-structures. Thus, for a number of reasons based on different physical methods, we conclude that the compounds $N_4P_4Cl_4(SR)_4$ (III) and their derivatives have a 2,2,6,6-arrangement of substituents. The crystal structure of $N_4P_4Cl_4(SPh)_4$ is under investigation.

Reactions conducted under milder conditions led only to very small yields of tetrathio-compound and substantial amounts of starting material (I). Using similar rationalisations[2] as in the trimer series, one would expect initial formation of the geminal bis-derivative, $N_4P_4Cl_6(SR)_2$ (no non-geminal chlorothio-derivative of the cyclic phosphazenes is known at present[2,3]). This bis-geminal intermediate, which we have been unable to detect, appears to be very reactive and rapid replacement of two more chlorine atoms takes place to give the observed tetrakis-derivatives (III). Fully substituted derivatives, $N_4P_4(SR)_8$, were not obtained, and the use of more forcing reaction conditions (*e.g.*, higher boiling solvents) led to the formation of mononuclear phosphorus–sulphur esters, $P(SR)_3$ and $P(O)(SR)_3$ (the latter arising by rapid oxidation[5] of the former). The precise mechanism for this ring scission is uncertain and we have been unsuccessful in isolating any residues containing nitrogen. It is not clear whether either (*a*) octakis-compounds $N_4P_4(SR)_8$ are formed initially under more forcing conditions and then decompose, or (*b*) ring scission occurs at an earlier stage. In contrast, fully substituted derivatives of the trimeric phosphazene, $N_3P_3(SR)_6$, are stable and are prepared without undue difficulty.[2] Ring scission reactions are also observed when hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazatetraene are treated with certain organometallic reagents.[16]

The geminal replacement pattern for thioalcoholysis of cyclochlorophosphazenes is maintained in the tetrameric series. In contrast to the trimeric system, the degree of substitution of the products is independent of the aliphatic or aromatic character of the organic part of the nucleophile. The geminal replacement of chlorine atoms by alkanethiolate (or benzenethiolate) in hexachlorocyclotriphosphazatrienes was rationalised[2] with reference to Pearson's principle of 'hard' and 'soft' acids and bases.[17] The isolation of all five possible geminal fluoroethylthiocyclotriphosphazatrienes, $N_3P_3F_{6-n}(SEt)_n$ [n = 1—5], by Niecke, Glemser, and Roesky[18] appears to support our previous hypothesis.[2] Although fluorine is a smaller atom than chlorine, it is also a harder one and consequently a $\equiv P(SR)F$ group, although less sterically hindered, will provide a phosphorus centre that is harder than in $\equiv P(SR)Cl$. The replacement of the second fluorine atom by another SR group should be slower than in the analogous chlorine species if softness is the major factor. Consequently, the intermediate compounds, $N_3P_3F_{6-n}(SEt)_n$ (n = 1, 3, or 5), will be less reactive and hence easier to isolate. Even so, the thiolate attacks a P(SR)F group in preference to a $\equiv PF_2$ group, as indicated by the absence of non-geminal isomers.

At present there does not appear to be any obvious theory as to the preferential 2,2,6,6-orientation of alkyl-(aryl)thio-groups observed in the tetrameric series. This replacement pattern is not unique to thiolyses. Paddock *et al.*[19] have studied the methylation of the octafluoride $N_4P_4F_8$ with methyl-lithium. Here, in contrast to our work, the geminal disubstituted derivative $N_4P_4F_6Me_2$ can be isolated; the third and fourth methyl groups displace preferentially (although not exclusively) at the antipodal phosphorus, giving rise to a 2,2,6,6-structure, $N_4P_4F_4Me_4$. Both structures, $N_4P_4F_6Me_2$ and $N_4P_4F_4Me_4$, have been confirmed[20] by *X*-ray analysis.

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[12] M. Biddlestone, G. J. Bullen, P. E. Dann, S. S. Kirshnamurthy, R. A. Shaw, and M. Woods, *Phosphorus*, 1973, **3**, 179.

[13] K. Khaleeluddin and J. M. W. Scott, *Chem. and Ind.*, 1966, 1034.

[14] C. E. Griffin and M. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4427.

[15] R. A. Shaw and M. Woods, *Phosphorus*, 1972, **2**, 61.

[16] M. Biddlestone and R. A. Shaw, *J. Chem. Soc.* (*A*), 1969, 178; 1970, 1750; 1971, 2715; *Phosphorus*, 1973, **3**, 95.

[17] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[18] E. Niecke, O. Glemser, and H. W. Roesky, *Z. Naturforsch.*, 1969, **24**b, 1187.

[19] N. L. Paddock, T. N. Ranganathan, and S. M. Todd, *Canad. J. Chem.*, 1971, **49**, 164.

[20] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 569.

EXPERIMENTAL

Octachlorocyclotetraphosphazatetraene was recrystallised to constant m.p. (124 °C) from light petroleum (b.p. 60—80 °C). Other reagents and solvents were purified as before.[2] Sodium thiolates were prepared from the thiol and sodium hydride. This method of preparation is more convenient and much swifter than use of metallic sodium. The preparation of $N_4P_4Cl_4(SEt)_4$ and $N_4P_4Cl_4(SPh)_4$ has been described in detail.[21] Other experiments describing different isolation procedures are given below and a summary of all the experiments is in Table 3. Analyses and physical properties are in Table 4.

TABLE 3

Reaction conditions and yields of products

Reaction solvent	Reactant ratio (moles)		Experimental conditions	Yields $N_4P_4Cl_4(SR_4)$ (%) and remarks
Ether	NaSEt (10)	$N_4P_4Cl_8$ (1)	Room temp. 48 h	58
Ether	$NaSPr^n$ (10·5)	$N_4P_4Cl_8$ (1)	Room temp. 48 h	55
Ether	$NaSBu^n$ (9)	$N_4P_4Cl_8$ (1)	Room temp. 48 h	41
Ether	$NaSBu^s$ (9·5)	$N_4P_4Cl_8$ (1)	Room temp. 72 h	Starting material only
Ether	$NaSBu^s$ (9·5)	$N_4P_4Cl_8$ (1)	Reflux 48 h	Starting material only
Ether	$NaSBu^t$ (12)	$N_4P_4Cl_8$ (1)	Reflux 50 h	Starting material only
Ether	NaSPh (10)	$N_4P_4Cl_8$ (1)	Reflux 10 h	42
Ether	NaSPh (10·5)	$N_4P_4Cl_8$ (1)	Reflux 30 h	63
Ether	NaS·C_6H_4·Me-*p* (10)	$N_4P_4Cl_8$ (1)	Reflux 10 h	29
Ether	NaS·C_6H_4·Cl-*p* (10)	$N_4P_4Cl_8$ (1)	Reflux 10 h	40
Ether	$NaSBu^i$ (9)	$N_4P_4Cl_8$ (1)	Room temp. 72 h	$N_4P_4Cl_5(SBu^i)_3$ detected in the oily product by mass spectrometry
Benzene	$NaSPr^i$ (9·5)	$N_4P_4Cl_8$ (1)	Reflux 35 h	Oily semi-solid formed which decomposed on distillation
Tetrahydrofuran	NaSEt (9·5)	$N_4P_4Cl_8$ (1)	Room temp. 30 h	42
Tetrahydrofuran	NaSEt (12)	$N_4P_4Cl_8$ (1)	Reflux 30 h	Intractable gum
Tetrahydrofuran	$NaSPr^n$ (12)	$N_4P_4Cl_8$ (1)	Reflux 30 h	Colourless oil containing P and S, but no N, Cl. Mass spectrometry indicates mixture of $(Pr^nS)_3P$ and $(Pr^nS)_3P{=}O$
Tetrahydrofuran	$NaSBu^n$ (12)	$N_4P_4Cl_8$ (1)	Reflux 30 h	Colourless oil. Mass spectrometry indicates $(Bu^nS)_3P$ and $(Bu^nS)_3P{=}O$
Tetrahydrofuran	NaSPh (12)	$N_4P_4Cl_8$ (1)	Reflux 30 h	Triphenyl trithiophosphate isolated. T.l.c. evidence for $P(SPh)_3$
Dioxan	NaS·C_6H_4·Me-*p* (10)	$N_4P_4Cl_8$ (1)	Reflux 3 h	45
Dimethylformamide	$NaSPr^n$ (10)	$N_4P_4Cl_8$ (1)	100 °C 4 h	Viscous oil

TABLE 4

Physical constants and analyses

		Found (%)							Required (%)					
Compound	M.p. or b.p./°C	C	H	Cl	N	P	S	Formulae	C	H	Cl	N	P	S
$N_4P_4Cl_4(SEt)_4$	106	17·1	3·6	—	—	21·75	22·2	$C_8H_{20}Cl_4N_4P_4S_4$	17·0	3·5	—	—	21·9	22·6
$N_4P_4Cl_4(SPr^n)_4$	75	24·1	5·0	23·6	9·1	19·6	—	$C_{12}H_{28}Cl_4N_4P_4S_4$	23·1	4·5	22·8	9·0	19·9	—
$N_4P_4Cl_4(SBu^n)_4$	148—150 (0·2 mm)	—	—	20·6	—	18·5	18·8	$C_{16}H_{36}Cl_4N_4P_4S_4$	—	—	20·9	—	18·3	18·9
$N_4P_4Cl_4(SPh)_4$	156	38·2	2·8	19·1	—	—	17·0	$C_{24}H_{20}Cl_4N_4P_4S_4$	38·0	2·7	18·7	—	—	16·9
$N_4P_4Cl_4(S{\cdot}C_6H_4{\cdot}Me\text{-}p)_4$	192	40·9	3·2	—	6·6	—	—	$C_{28}H_{28}Cl_4N_4P_4S_4$	41·3	3·4	—	6·9	—	—
$N_4P_4Cl_4(S{\cdot}C_6H_4{\cdot}Cl\text{-}p)_4$	180	32·1	1·8	—	—	—	14·0	$C_{24}H_{16}Cl_8N_4P_4S_4$	32·3	1·8	—	—	—	14·3
$N_4P_4(NMe_2)_4(SEt)_4$	39	32·1	7·4	—	18·6	—	—	$C_{16}H_{44}N_8P_4S_4$	32·0	7·3	—	18·7	—	—
$N_4P_4(NMe_2)_4(SPh)_4$	192	48·5	5·6	—	14·3	—	—	$C_{32}H_{44}N_8P_4S_4$	48·5	5·9	—	14·1	—	—
$N_4P_4(NMe_2)_4(S{\cdot}C_6H_4{\cdot}Me\text{-}p)_4$	145	51·5	5·0	—	13·7	—	—	$C_{36}H_{52}N_8P_4S_4$	51·6	5·0	—	13·4	—	—
$N_4P_4(NMe_2)_4(S{\cdot}C_6H_4{\cdot}Cl\text{-}p)_4$	154	40·9	4·5	—	—	—	—	$C_{32}H_{40}Cl_4N_8P_4S_4$	41·3	4·3	—	—	—	—

*2,2,6,6-Tetrachloro-4,4,8,8-tetrakis-*p*-tolylthiocyclotetraphosphazatetraene.*—Toluene-*p*-thiol (12·4 g, 0·1 mol) dissolved in dry ether (25 ml) was added dropwise to a stirred suspension of sodium hydride (2·4 g, 0·1 mol) in ether (75 ml). The evolution of hydrogen was very swift and the formation of sodium toluene-*p*-thiolate was complete in 1 h. Octachlorocyclotetraphosphazatetraene (4·6 g, 0·01 mol) dissolved in ether (200 ml) was added to the thiolate and the mixture heated under reflux (10 h). The sodium chloride formed together with the excess of thiolate were filtered off by means of a glass sinter. After the solid material had been washed thoroughly with hot benzene, the combined filtrate and washings were evaporated to dryness. A sticky oil was obtained which was crystallised only with considerable difficulty after frequent triturations with diethyl ether and light petroleum. The solid obtained was recrystallised from light petroleum (b.p. 80—100 °C) to give 2,2,6,6-*tetrachloro*-4,4,8,8-*tetrakis*-p-*tolylthiocyclotetraphosphazatetraene* (2·35 g, 29%), m.p. 192 °C. A t.l.c. examination of the mother liquors indicated only the presence of di-*p*-tolyl disulphide. This reaction was repeated with boiling dioxan as the solvent. The mixture was heated (3 h) and the products extracted as before. The tetrakis-derivative, m.p. 192 °C, described above was obtained in 37% yield. Starting material, $N_4P_4Cl_8$, could not be detected in the reaction mixture.

2,2,6,6-Tetrachloro-4,4,8,8-tetrakis-n-butylthiocyclotetraphosphazatetraene.—Octachlorocyclotetraphosphazatetraene (4·7 g, 0·01 mol) dissolved in diethyl ether (50 ml) was added to a stirred suspension of sodium n-butanethiolate (10·2 g, 0·09 mol) in ether (150 ml). The mixture was allowed to

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[21] A. P. Carroll and R. A. Shaw, *Inorg. Synth.*, 1966, **8**, 84.

stand (48 h) at room temperature. Filtration of the mixture was difficult but eventually a crude oil was obtained on evaporation of the solvent. This crude product was thermally unstable and therefore was distilled in small batches under vacuum. Even so, considerable decomposition was observed. The first fractions were discarded and the bulk of the distillate (140—160 °C/0·2 mmHg) collected. When the major portion of the distillate was redistilled, most of the material boiled at a constant temperature and little decomposition occurred. A final distillation gave 2,2,6,6-tetrachloro-4,4,8,8-tetrakis-n-butylthiocyclotetraphosphazatetraene (2·8 g, 41%), b.p. 148—150 °C/0·2 mmHg.

Attempted Preparation of Octakis-n-butylthiocyclotetraphosphazatetraene.—Octachlorocyclotetraphosphazatetraene (4·6 g, 0·01 mol) and sodium n-butanethiolate (13·6 g, 0·12 mol) in tetrahydrofuran (300 ml) were heated under reflux (30 h). Filtration of the mixture, followed by evaporation of the solvent, yielded a viscous yellow oil. A small quantity of this oil was distilled under vacuum. Two major fractions were collected. The first consisted of di-n-butyl disulphide. The second fraction (148—155 °C/0·08 mmHg) yielded a colourless oil which contained phosphorus and sulphur, but no nitrogen or chlorine. The mass spectrum of this oil indicated that it was predominantly tri-n-butyl trithiophosphite $P(SBu^n)_3$; a little of the trithiophosphate $P(O)(SBu^n)_3$ was also present.

Preparation of Dimethylamino-derivatives.—2,2,6,6-*Tetrakisdimethylamino*-4,4,8,8-*tetrakis*-p-*tolylthiocyclotetraphosphazatetraene.* A large excess of dimethylamine (2 g) was added to an ice-cold solution of 2,2,6,6-tetrachloro-4,4,8,8-tetrakis-*p*-tolylthiocyclotetraphosphazatetraene (0·81 g, 0·01 mol) in chloroform (50 ml). The mixture was allowed to reach room temperature and was then heated under reflux (2 h). The chloroform was removed under reduced pressure and benzene (30 ml) was added to the crude product. The insoluble portion of the product, dimethylamine hydrochloride, was filtered off and the filtrate was evaporated to dryness to give a colourless solid. This solid was recrystallised from light petroleum to give 2,2,6,6-*tetrakisdimethylamino*-4,4,8,8-*tetrakis*-p-*tolylthiocyclotetraene* (0·77 g, 91%), m.p. 145 °C.

The other dimethylamino-derivatives were prepared in an analogous manner.

I.r. and Raman Data (*Major Bands* 1200—200 cm^{-1}).—$N_4P_4Cl_4(SPh)_4$. I.r., 1067w, 1023m, 1003w, 739vs, 702m, 684s, 623w, 593s, 587s, 562s, 510m, 485s, 472s, 426w, 419w, 382w, 355w, and 316w; Raman, 1180w, 1158m, 1127w, 1084s, 1024s, 1003vs, 701m, 616m, 573m, 518m, 503m, 483m, 477m, 423m, 378vs, 341s, 300w, 289w, 263m, and 229m.

$N_4P_4Cl_4(SEt)_4$. I.r., 1171w, 1052m, 976m, 875m, 779m, 722m, 660m, 607s, 548m, 508vs, 399m, 382w; Raman, 1182w, 1059m, 1041w, 978m, 879w, 779w, 711m, 664s, 596m, 584s 567m, 516w, 494w, 419s, 384s, 331m, 277s, 251w, and 231w.

The ^1H n.m.r. spectra were obtained from a Varian A60 D spectrometer for *ca.* 0·5M solutions in CCl_4 with tetramethylsilane as internal standard. I.r. spectra (KBr disc or Nujol mull) were recorded with Perkin-Elmer spectrometers (models 137 and 457) and Raman spectra with a Cary 81 model (4880 Å Ar/Kr laser excitation). Mass spectra were obtained from an A.E.I. mass spectrometer, model MS9, operating at 70 eV.

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