Studies of Phosphazenes. Part 4.[1] Reactions of Octachlorocyclotetraphosphazatetraene with t-Butylamine.

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The reaction of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, with t-butylamine yields the derivatives, $N_4P_4Cl_{8-n}(NHBu^t)_n$ [n = 1,2 (two isomers), 3, and 8] [(2)—(6)] and $N_4P_4(NHBu^t)_8 \cdot HCl$ (7). Resin formation is a prominent feature of many reactions and attempts to prepare the derivatives $N_4P_4Cl_{8-n}(NHBu^t)_n$ (n = 4—7) have been unsuccessful. Phosphorus-31 n.m.r. spectroscopy establishes 2,4- and 2,6-structures for the bis-isomers [(4) and (3)]. The tris-compound (5) also has a non-geminal structure. ^1H and ^{31}P n.m.r. data for the hydrochloride (7) show that the exchange of the proton is slow on the n.m.r. time scale at ambient temperature. The t-butylamino(ethylamino)-derivatives, 2,6- and 2,4-$N_4P_4Cl_6(NHBu^t)(NHEt)$ [(12) and (13)], have been prepared. The relative yields of these isomers and also of the isomers (3) and (4) vary markedly with the reaction solvent. The dominant role of the nucleophile in determining the course of halogen-atom replacement in the aminolysis reactions of $N_4P_4Cl_8$ is inferred.

THE reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with ethylamine [2] and t-butylamine [3] differ markedly and some of the features observed in the two systems have been rationalised in terms of a proton-abstraction mechanism, possibly aided by cyclic hydrogen-bonded complexes as intermediates.[2-5] We have extended these studies to octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (1), in order to investigate the effect of ring size on the mode of replacement of chlorine atoms. We have recently shown that the reaction of the tetramer (1) with ethylamine proceeds *via* a non-geminal path up to the replacement of four chlorine atoms.[6] Although the fully aminolysed pro-

[1] Part 3, S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw, M. Woods, and R. Keat, *J. Chem. Res.*, 1977, (*S*) 70; (*M*) 0860.
[2] R. N. Das, R. A. Shaw, B. C. Smith, and M. Woods, *J.C.S. Dalton*, 1973, 709.
[3] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 5032.
[4] R. A. Shaw, *Z. Naturforsch.*, 1976, **31b**, 641.
[5] S. S. Krishnamurthy, R. A. Shaw, and M. Woods, *Current Sci.*, 1976, **45**, 433.
[6] S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. Keat, R. A. Shaw, and M. Woods, *J.C.S. Dalton*, 1976, 1405.

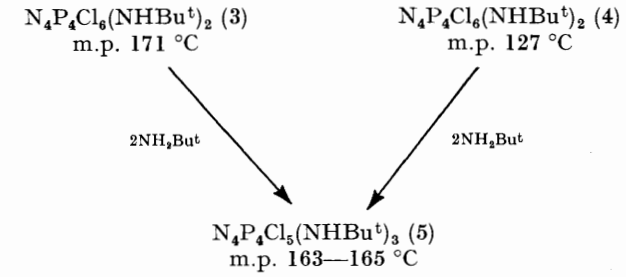
duct, $N_4P_4(NHEt)_8$, could be obtained in good yield under mild conditions (excess of amine, 0 °C) attempts to prepare penta- or hexa-ethylamino-derivatives were unsuccessful. Following this comprehensive study of the octachloride (1) with ethylamine, we report here a detailed investigation of the reactions of tetramer (1) with another primary amine, t-butylamine. Mixed ethylamino-t-butylamino-derivatives have been prepared to assess the role of the substituent and the nucleophile in determining the structures of products in the tetrameric system.

RESULTS

The reaction of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (1), with t-butylamine in organic solvents (benzene, chloroform, and methyl cyanide) gives the derivatives: $N_4P_4Cl_7(NHBu^t)$ (2), $N_4P_4Cl_6(NHBu^t)_2$ isomers (3) and (4), $N_4P_4Cl_5(NHBu^t)_3$ (5), and $N_4P_4(NHBu^t)_8$ (6). A hydrochloride adduct, $N_4P_4(NHBu^t)_8 \cdot HCl$ (7) has also been isolated.

The mono-t-butylamino-compound (2) is obtained from a 1 : 2 tetramer : amine stoicheiometric reaction in benzene or chloroform after column chromatography. Small quantities of the bis-isomers [(3) and (4)] are detected and unchanged starting material (1) is recovered. The bis-t-butylamino-compounds [(3) and (4)] are isolated from 1 : 4 reactions in boiling benzene, methyl cyanide, or chloroform. The relative yields of these isomers vary markedly with the reaction solvent and the rate of addition of the amine. Compound (3) is the major product in methyl cyanide; the use of benzene or chloroform as the reaction medium and slow addition of the amine greatly enhance the relative proportion of the other bis-isomer (4). In diethyl ether, both bis-isomers [(3) and (4)] are formed in very poor yields (<5%). The isolation of two distinct bis-isomers in this study reconciles earlier observations.[7,8]

The tris-t-butylamino-compound (5) is obtained from a 1 : 6 reaction in methyl cyanide. It is also the only crystalline compound isolated from the reaction of the bis-compounds [(3) and (4)] with two equivalents of t-butylamine in methyl cyanide. The purification of the bis- and tris-t-butylamino-compounds is hindered by the presence of non-crystalline resins in the reaction mixtures.



Reaction of $N_4P_4Cl_8$ (1) with eight equivalents of t-butylamine in boiling methyl cyanide gives the tris-derivative (5) and a considerable amount of resinous material. Attempts to obtain a tetrakis-derivative by the reaction of the tris-compound (5) with two equivalents of t-butylamine in boiling methyl cyanide have been unsuccessful: an amorphous material (*ca.* 50%) and unchanged starting material (5) (*ca.* 30%) are isolated. Reactions involving ten or twelve equivalents of t-butylamine in boiling methyl cyanide result in the predominant formation of a resinous substance: only small quantities of tris- and octakis-t-butylamino-derivatives [(5) and (6)] and the hydrochloride adduct (7) could be isolated. Compound (7) was also obtained by using an excess of amine in boiling benzene. A $^{31}P-\{^1H\}$ spectrum of the resinous substance showed complex multiplets at $\delta = -5$ and 3.5 p.p.m. The i.r. spectrum consists of many bands characteristic of the t-butylamino-group and also a broad band at 1 275 cm^{-1} [ν(P=N)]. Hence, it is likely that the resin contains tetrameric units linked by $>NBu^t$ group(s).

The octakis-compound (6) can be prepared in *ca.* 50% yield by the rapid addition of an excess of amine to a solution of the octachloride (1) in boiling methyl cyanide. This method of preparation is more convenient than the one reported previously [8] and does not require sealed tubes or lengthy reaction times.

The reactions of the bis-t-butylamino-compounds [(3) and (4)] with an excess of dimethylamine in methyl cyanide give the hydrochlorides, $N_4P_4(NHBu^t)_2(NMe_2)_6 \cdot HCl$ [(9) and (11)] and also the free bases [(8) and (10)]. The hydrochlorides [(7), (9), and (11)] are converted into the free bases, $N_4P_4(NHBu^t)_8$ (6) and $N_4P_4(NHBu^t)_2(NMe_2)_6$ [(8) and (10)] respectively, by treatment with one mole equivalent of triethylamine in boiling benzene. This is the first time that hydrochloride adducts have been isolated from the aminolysis reactions of the octachloride (1).

The reaction of the mono-t-butylamino-compound $N_4P_4Cl_7(NHBu^t)$ (2) with two equivalents of ethylamine yields the mixed amino-derivative, $N_4P_4Cl_6(NHEt)(NHBu^t)$ (12), whereas the monoethylamino-compound, $N_4P_4Cl_7(NHEt)$, reacts with two equivalents of t-butylamine to give compound (12) and an isomeric product (13).

DISCUSSION

The A_2B_2 $^{31}P-\{^1H\}$ n.m.r. spectrum [Figure, (*b*)] obtained for the bis-isomer (3) is consistent with a 2,6-disposition of t-butylamino-groups. We have suggested previously a geminal structure for isomer (4) on the basis of its asymmetric $^{31}P-\{^1H\}$ spectrum (at 24.3 MHz).[9] We have now found that this asymmetric appearance was due to slight contamination of the sample with isomer (3). The pure isomer (4) has an AA'BB' ^{31}P spectrum [Figure, (*a*)] and a 2,4-structure is indicated accordingly.

The tris-compound (5) is assigned a 2,4,6-non-geminal structure because it can be obtained from both the bis-isomers [(3) and (4)]. As anticipated for an A_2BC spin system, the ^{31}P n.m.r. spectrum of this compound is a complex multiplet. The assignment of non-geminal structures to both the bis-isomers [(3) and (4)] and to the tris-compound (5) is also consistent with the observed chemical shifts (δ 3.0—3.2 p.p.m.) of the N–*H* proton(s) [6,11] (Table 1).

The ^1H and ^{31}P n.m.r. data are summarised in Table 1. A striking feature of the proton spectrum of the hydrochloride adduct (7) is the appearance of two C–C*H*$_3$ and

[7] K. John, T. Moeller, and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1960, **82**, 5616.

[8] S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1963, 3236.

[9] R. Keat, S. S. Krishnamurthy, A. C. Sau, R. A. Shaw, M. N. Sudheendra Rao, A. R. Vasudeva Murthy, and M. Woods, *Z. Naturforsch.*, 1974, **29b**, 701.

TABLE 1

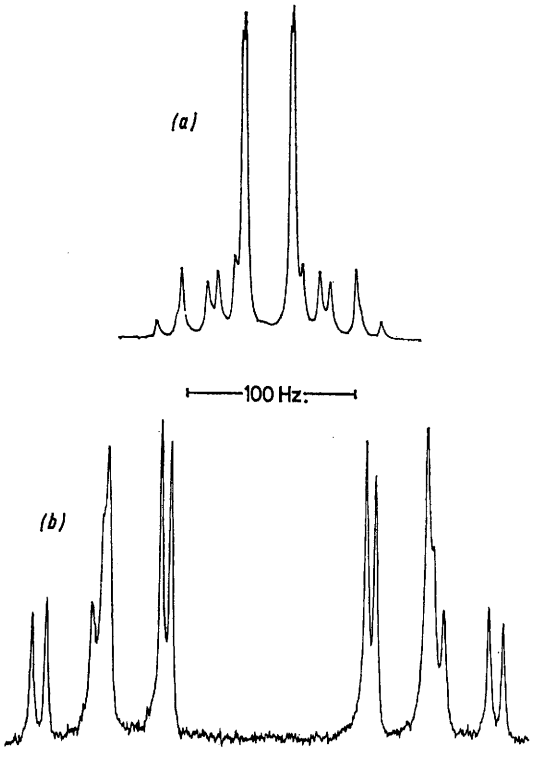
N.m.r. data [a]

Compound	M.p. (θ/°C)	NHBu^t δ(N–*H*)	NHBu^t δ(C–*Me*)	NMe$_2$ δ(N–*Me*)	NMe$_2$ ^3J*(*P*–*H*)/Hz	Proposed structure
$N_4P_4Cl_7NHBu^t$ (2)	51—52	3.2	1.40			
$N_4P_4Cl_6(NHBu^t)_2$ (3)	171	3.1	1.38			2,4,4,6,8,8 : 2,6
$N_4P_4Cl_6(NHBu^t)_2$ (4)	127	3.1	1.36			2,4,6,6,8,8 : 2,4
$N_4P_4Cl_5(NHBu^t)_3$ (5)	163—165	3.0	1.38			2,4,6,8,8 : 2,4,6
$N_4P_4(NHBu^t)_8$ (6)	180—200 (decomp.)	2.1	1.28			
$N_4P_4(NHBu^t)_8$·HCl (7)	190—195 (decomp.)	3.8 (1) 2.4 (1)	1.44 (1) 1.42 (1)			
$N_4P_4(NMe_2)_6(NHBu^t)_2$ (8)	Liquid [b]	2.2	1.22	2.64 (2) 2.68 (1)	10.4 10.4	2,4,4,6,8,8 : 2,6
$N_4P_4(NMe_2)_6(NHBu^t)_2$·HCl (9)	164—165 (decomp.)	*c*	1.34 (1) 1.30 (1)	2.74	11.0	2,4,4,6,8,8 : 2,6
$N_4P_4(NMe_2)_6(NHBu^t)_2$ (10)	Liquid [b]	2.3	1.24	2.68 (1) 2.66 (1) 2.65 (1)	10.4 11.2 10.8	2,4,6,6,8,8 : 2,4
$N_4P_4(NMe_2)_6(NHBu^t)_2$·HCl (11)	155—156 (decomp.)	*c*	1.32	2.74 (2) 2.70 (1)	10.8 11.4	2,4,6,6,8,8 : 2,4
$N_4P_4Cl_6(NHBu^t)(NHEt)$ (12)	145—148	*e*	1.20 [f] 1.41		14.5 [g]	2,4,4,6,8,8 : 2 : 6
$N_4P_4Cl_6(NHBu^t)(NHEt)$ (13)	Liquid	*e*	1.26 [f] 1.40		14.5 [g]	2,4,6,6,8,8 : 2 : 4

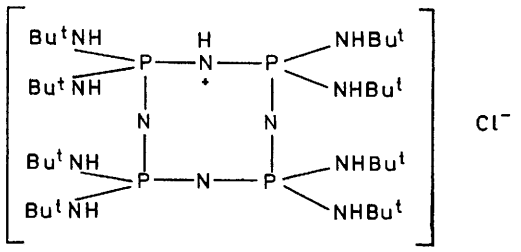
Phosphorus-31 data (CH_2Cl_2 solution; 85% H_3PO_4 external reference): (3) δ(PCl_2) = −5.8, δ[PCl(NHBu^t)] = −10.6 p.p.m.; ^2J(*P*–N–*P*) = 38.1 Hz; (4) centre of AA′BB′ signal at δ *ca.* −8.0 p.p.m. (not fully analysed); (5) complex multiplet at δ *ca.* −6.0 p.p.m.; (6) δ[P(NHBu^t)$_2$] = −3.1 p.p.m.; (7) centre of AA′BB′ spectrum at δ *ca.* −5.0 p.p.m. (not fully analysed).

[a] $CDCl_3$ solution; p.p.m., $SiMe_4$ internal reference. [b] Obtained as solids, m.p. 120—140 °C, after several months. [c] N–*H* resonance not observed. [d] Pronounced ' virtual coupling '. [e] N–*H* resonance hidden by NCH_2 multiplets centred at *ca.* 3.1 p.p.m. [f] CH_2CH_3 protons. [g] ^3J*(*P*–N–CH_2).

two N–*H* signals showing that the exchange of the proton among the four equivalent ring-nitrogen atoms is slow on the n.m.r. time scale at ambient temperatures. The ^{31}P n.m.r. spectrum is an AA′BB′ type and confirms the above conclusion. The high-field ^{31}P signals are broader than the low-field ones in the absence of proton decoupling and are therefore assigned to the phosphorus nuclei adjacent to the site of protonation. The ^1H resonance at δ 3.78 p.p.m. is assigned to N–*H* protons adjacent to the site of protonation. We have not been able to observe the signal due to the lone acidic proton, presumably for reasons discussed elsewhere.[1,10]



^1H-decoupled ^{31}P spectra at 40.5 MHz of (*a*) 2,4-$N_4P_4Cl_6(NHBu^t)_2$ (4) and (*b*) 2,6-$N_4P_4Cl_6(NHBu^t)_2$ (3)



(7)

(7) (multiple bonding not shown)

Basicity measurements and i.r. and n.m.r. spectroscopic data suggest that protonation of aminocyclophosphazenes takes place at a ring nitrogen atom.[4,10,11] The *X*-ray crystal structures of protonated cyclophosphazene species substantiate this idea.[4,11,12] In the present study, evidence for ring protonation has been obtained from both ^{31}P and ^1H n.m.r. data.

The reaction of $N_4P_4Cl_8$ (1) with t-butylamine or

[10] T. Moeller and S. G. Kokalis, *J. Inorg. Nuclear Chem.*, 1963, **25**, 875.

[11] S. S. Krishnamurthy, A. C. Sau, and M. Woods, 'Advances in Inorganic Chemistry and Radiochemistry,' eds. H. J. Emeléus and A. G. Sharpe, in the press.

[12] H. P. Calhoun, R. T. Oakley, N. L. Paddock, and J. Todd, *Canad. J. Chem.*, 1975, **53**, 2413.

ethylamine [6] gives chloroamino-derivatives which have non-geminal structures. In contrast, geminal products are formed exclusively in the reaction of $N_3P_3Cl_6$ with t-butylamine; [3] the tetrakis-ethylamino-derivative, $N_3P_3Cl_2(NHEt)_4$, also has a geminal structure. It seems likely that this difference in behaviour between $N_3P_3Cl_6$ and $N_4P_4Cl_8$ is related to the greater reactivity of the latter. Reaction of $N_4P_4Cl_8$ with an excess of t-butylamine in boiling benzene or methyl cyanide results in the reactions of $N_4P_4Cl_8$ with ethylamine [6] and t-butylamine is much greater than that observed in the analogous reactions of $N_3P_3Cl_6$.[2,3]

The mixed t-butylamino(ethylamino)derivatives, $N_4P_4Cl_6(NHEt)(NHBu^t)$ [(12) and (13)], are assigned non-geminal structures on the basis of $^3J^*(P\text{–}N\text{–}CH_2)$ values of 14.5 Hz (Table 1) which is characteristic of the ≡PCl(NHEt) group.[2,6] These isomers have distinct t.l.c. R_f values (0.72 and 0.55 respectively, see Table 2).

TABLE 2

Analytical [a] and t.l.c. data

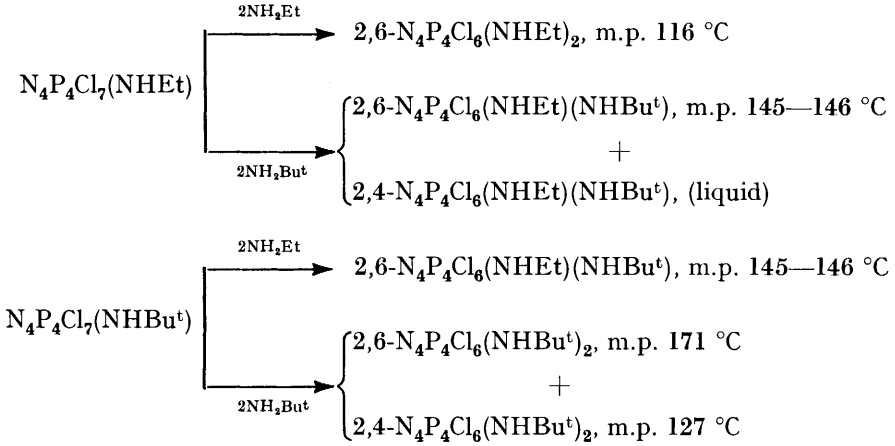
Compound	Found (Calculated) % C	H	N	Cl	Formula	R_f values [b]
(2)	9.8 (9.6)	2.6 (2.1)			$C_4H_{10}N_5Cl_7P_4$	0.87
(3)	18.0 (17.9)	3.6 (3.7)	15.8 (15.7)		$C_8H_{20}N_6Cl_6P_4$	0.74
(4)	17.8	3.6	15.9	39.8 (39.6)		0.65
(5)	26.4 (25.1)	5.5 (5.3)	17.5 (17.1)		$C_{12}H_{30}N_7Cl_5P_4$	0.40
(6)	50.5 (50.8)	10.7 (10.7)	22.6 (22.2)		$C_{32}H_{80}N_{12}P_4$	
(7)	49.7 (48.4)	10.3 (10.3)	20.1 (21.2)	4.8 (4.5)	$C_{32}H_{81}N_{12}ClP_4$	
(9)	37.5 (38.5)	9.1 (9.1)	27.0 (26.9)		$C_{20}H_{57}N_{12}ClP_4$	
(11)	38.2	9.2	27.2			
(12)	14.3 (14.2)	3.1 (3.2)	16.5 (16.5)		$C_6H_{16}N_6Cl_6P_4$	0.72
(13)	14.4	3.3				0.55

[a] Analytical data were not obtained for compounds (8) and (10); however, their preparation from the respective hydrochlorides (9) and (11) and the relative intensities of N–*Me* and C–*Me* protons in their ^1H n.m.r. spectra establish the molecular formulae. [b] Eluant: benzene–light petroleum (b.p. 60—80 °C) (1 : 1).

the complete replacement of chlorine atoms. The analogous reaction of the hexachloride, $N_3P_3Cl_6$, gives the tetrakis-t-butylamino-derivative, $N_3P_3Cl_2(NHBu^t)_4$, as the major product and there is no evidence for the formation of the hexakis-compound, $N_3P_3(NHBu^t)_6$.

After the tris-stage of replacement in the $N_4P_4Cl_8$–NH_2Bu^t system (and after the tetrakis-stage in the analogous ethylamine system), resinous materials are the major reaction product and the chloro-t-butylamino-derivatives, $N_4P_4Cl_{8-n}(NHBu^t)_n$ ($n \geqslant 4$, $\neq 8$), were not detected. A possible mechanism for the formation of the octakis-derivative, $N_4P_4(NHEt)_8$, with an excess of amine, and that of resins when limited amounts of amine are used, has been proposed recently.[6] Also, it is interesting to note that the amount of resin formed in

The two non-geminal bis-t-butylamino-derivatives [(3) and (4)] also exhibit different R_f values: the 2,6-isomer (3) has a higher R_f than the 2,4-isomer (4). The similar trend observed in these R_f values provides tentative evidence for the 2,6- and 2,4-disposition of amino-groups in compounds (12) and (13) respectively. Additional support for these assignments can be deduced from a comparison of the reactions depicted below.



When ethylamine is the attacking nucleophile, only one compound (2,6-isomer) is obtained * whereas two isomeric products (2,6- and 2,4-) are formed with t-butylamine as the reagent. The relative proportions of the bis-t-butylamino-isomers, $N_4P_4Cl_6(NHBu^t)_2$ [(3) and (4)], can be altered by varying the reaction solvent (see Experimental section). A similar pattern is observed in the formation of the two mixed-amino-isomers [(12) and (13)] although the absolute yields are somewhat

* A small quantity (<1%) of another isomer, $N_4P_4Cl_6(NHEt)_2$, has been isolated in the ethylamine system.[6]

different in the two systems. These results suggest that the nucleophile plays an important part in determining the course of chlorine-atom replacement of the octachloride (1). The dominant role of the nucleophile in determining the chlorine-atom replacement pattern in the aminolysis reactions of the trimeric chloride, $N_3P_3Cl_6$, has already been established.[4,13,14] The precise role of solvents in influencing the stereochemistry of products formed in the aminolysis reactions of halogenocyclophosphazenes is little understood.

EXPERIMENTAL

Standard procedures have been described previously.[6] Some typical reactions are given below and others are summarised in Table 3. Analytical data and t.l.c. R_f values are given in Table 2. N.m.r. spectra were recorded with a JEOL MH 100 spectrometer and ^{31}P n.m.r. spectra with JEOL C60HL and Varian XL 100 spectrometers.

Reactions of Octachlorocyclotetraphosphazatetraene (1).—(a) *With 2 equivalents of t-butylamine in chloroform.* t-Butylamine (2.92 g, 0.04 mol) was added dropwise to a boiling solution of (1) (9.28 g, 0.02 mol) in chloroform (200 cm³) with constant stirring. The reaction mixture was heated under reflux for 4 h. t-Butylamine hydrochloride was filtered off and evaporation of the filtrate gave an oil which was then extracted with hot light petroleum (b.p. 40—60 °C). The extract was cooled and crystals of 2,4-bis-(t-butylamino)hexachlorocyclotetraphosphazatetraene (4) (2.68 g, 25%), m.p. 127 °C (literature,[7] m.p. 124 °C), were obtained. The mother-liquor was chromatographed on silica gel (200 g) and elution with light petroleum (b.p. 40—60 °C)–benzene (4 : 1) gave the octachloride (1) (0.65 g, 7.0%). Elution with light petroleum (b.p. 40—60 °C)–benzene (3 : 2) gave *mono(t-butylamino)heptachlorocyclotetraphosphazatetraene* (2) as an oil which crystallised at 0 °C after several months (3.5 g, 35%), m.p. 51—52 °C.

(b) *With 6 equivalents of t-butylamine in methyl cyanide.* t-Butylamine (8.76 g, 0.12 mol) was allowed to react with the octachloride (1) (9.28 g, 0.02 mol) in boiling methyl cyanide (225 cm³). Evaporation of the solvent left an oil as in (a) which on cooling to room temperature gave a crystalline residue. Recrystallisation from light petroleum (b.p. 60—80 °C) gave 2,4,6-*tris(t-butylamino)pentachlorocyclotetraphosphazatetraene* (5) (3.44 g, 30%), m.p. 163—165 °C. A small quantity (0.64 g, 6%) of compound (3) was isolated from later crops. Evaporation of the mother-liquor gave a resin (*ca.* 50%).

Preparation of $N_4P_4Cl_6(NHBu^t)(NHEt)$ [(12) *and* (13)].—Compound (2) (1.0 g, 0.002 mol) reacts with aqueous ethylamine (0.2 g, 0.004 mol) in the presence of anhydrous

TABLE 3
Experimental details

	Phosphazene		t-Butylamine		Solvent	Time of addition of the amine	Total reaction time	Products and yields		
	g	mmol	g	mmol	(V/cm³)	h	h	Compound	g	%
(1)	4.64	10	1.46	20	PhH (100)	1.0	5.0	(1)	2.10	45.2
								(2)	1.20	24.0
								(4)	Trace	*a*
								(3)	Trace	*a*
(1)	4.64	10	3.00	40	PhH (100)	0.5	6.0	(2)	0.65	17.0
								(4)	1.20	22.0
								(3)	0.60	11.0
(1)	9.28	20	5.84	80	$CHCl_3$ (150)	0.5	4.0	(2) [b]	0.20	2.0
								(4)	5.30	49.3
								(3)	0.40	3.7
(1)	4.64	10	5.84	80	MeCN (110)	1.0	6.0	(3) [b]	0.06	1.0
								(5)	1.43	25.0
(1)	9.28	20	14.60	200	MeCN (230)	1.0	6.0	(5) [c]	2.25	20.0
								(7)	0.16	1.0
(1)	9.28	20	17.52	240	MeCN (230)	1.5	6.0	(5) [c]	0.42	3.6
								(6)	1.04	14.0
								(7)	0.16	1.0
(1)	9.28	20	31.40	360	PhH (215)	0.25	8.5	(3) [c]	3.01	28.0
								(5)	0.20	1.7
								(7)	0.50	3.1
(1)	4.64	10	17.00	200	MeCN (175)	0.25	7.0	(6) [b]	3.93	52.0
(1)	9.28	20	5.84	80	MeCN (150)	0.5	4.0	(3) [b]	3.76	35.0
								(4)	1.61	15.0
(4)	2.0	3.7	0.55	7.4	MeCN (100)	0.5	2.0	(5) [b]	0.73	37.0
(3)	1.0	1.8	0.28	3.7	MeCN (85)	0.5	4.5	(3) [b]	0.15	15.0
								(5)	0.69	65.0
(4)	2.0	3.7	1.09	14.8	PhH (100)	0.5	5.5	(4) [c]	Trace	*a*
								(5)	Trace	*a*
(3)	2.0	3.7	1.09	14.8	PhH (100)	0.5	5.5	(3)	1.83	92.4
				$HNMe_2$						
(3)	1.0	1.8	9.20	200	MeCN (100)	Rapid	6.0	(8)	0.50	45.8 [d]
								(9)	0.30	26.7
(4)	1.0	1.8	9.20	200	MeCN (100)	Rapid	6.0	(10)	0.30	27.5 [d]
								(11)	0.42	36.0

[a] Not isolated; t.l.c. evidence. [b] Resinous material as minor product. [c] Resinous material as major product (*ca.* 65%). [d] Recovered from the mother-liquor after treatment with triethylamine.

[13] R. Keat and R. A. Shaw, *Angew. Chem. Internat. Edn.*, 1968, **7**, 212.
[14] J. M. E. Goldschmidt and E. Licht, *J.C.S. Dalton*, 1972, 732.

sodium sulphate [6] (15 g) in diethyl ether (80 cm^3) (0 °C, 1.5 h) to give *hexachloro-2-t-butylamino-6-ethylaminocyclotetraphosphazatetraene* (12) (0.35 g, 34.4%), m.p. 145—148 °C. t-Butylamine (0.95 g, 0.013 mol) reacts with $N_4P_4Cl_7(NHEt)$ [6] (3.0 g, 0.006 mol) in boiling chloroform (120 cm^3) to give a mixture of *hexachloro-2-t-butylamino-4-ethylaminocyclotetraphosphazatetraene* (13) and the 2,6-isomer (12). T.l.c. indicates that the relative proportions of these isomers is *ca.* 2 : 1. A similar reaction in benzene gives (12) and (13) (ratio *ca.* 1 : 3); in methyl cyanide, the ratio is 2 : 1. Compound (13) could only be isolated (0.03 g) by preparative-scale t.l.c. [silica gel: eluant, light petroleum (b.p. 60—80 °C)–benzene (1 : 1)].

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