Studies of Phosphazenes. Part I. Reactions of Octachlorocyclotetraphosphazatetraene with Ethylamine *

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The reaction of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, with ethylamine has been investigated. Seven derivatives, $N_4P_4Cl_{8-n}(NHEt)_n$ [n = 1, 2 (two isomers), 3, 4 (two isomers), and 8] have been isolated and their structures established by ^1H and ^{31}P n.m.r. spectroscopy. A non-geminal chlorine atom replacement scheme is observed. Attempts to prepare penta- or hexa-ethylamino derivatives were unsuccessful: only sticky, non-crystalline resins were obtained from 1 : 10 or 1 : 12 reactions. The preparation and n.m.r. spectroscopic data of mixed ethylamino(methoxy)-derivatives, $N_4P_4(NHEt)_{8-n}(OMe)_n$ [n = 6, 4 (two isomers)], and an ethylamino-(dimethylamino)-derivative, $N_4P_4(NHEt)_2(NMe_2)_6$, are generally consistent with the proposed structures. The reaction pattern is discussed.

THE reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with primary and secondary amines have been studied extensively.[1,2] Geminal and non-geminal replacement patterns are observed in most systems, although one or the other usually predominates. Similar systematic studies on the aminolysis reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (I), have not been reported and so far only the chlorodimethylamino-derivatives, $N_4P_4Cl_{8-n}(NMe_2)_n$, have been investigated in some detail.[3,4] The absence of reliable data can be attributed to the practical problems of separating complex mixtures of reaction products and to the subsequent difficulties in making reliable structure assignments. The number of isomers that can arise in the tetrameric system is much larger than that in the corresponding trimeric system (33 possible derivatives in the former system compared to 12 in the latter). With the advent of better separation techniques and the availability of sensitive spectroscopic aids, it is now possible to study the reactions of the octachloride, $N_4P_4Cl_8$ (I), with more confidence. In particular, it is of interest to ascertain whether the hypotheses advanced to rationalise the aminolysis reactions of the hexachloride, $N_3P_3Cl_6$, will be applicable to the analogous reactions of the octachloride, (I). We report here the first comprehensive study of the reaction of the tetramer (I) with a primary amine.

RESULTS

Octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (I), reacted with ethylamine in organic solvents (diethyl ether, benzene, methyl cyanide) to give the ethylamino-derivatives, $N_4P_4Cl_{8-n}(NHEt)_n$ and ethylamine hydrochloride. The compounds obtained from these reactions were $N_4P_4Cl_7(NHEt)$ (II), $N_4P_4Cl_6(NHEt)_2$ isomers (III) and (IV), $N_4P_4Cl_5(NHEt)_3$ (V), $N_4P_4Cl_4(NHEt)_4$ isomers (VI) and (VII), and $N_4P_4(NHEt)_8$ (VIII). These products were isolated and purified by fractional crystallisation and/or column chromatography. Products with different degrees of replacement are often formed in a reaction and the use of a particular stoicheiometry gives no guarantee that the desired number of chlorine atoms will be replaced. The temperature and solvent used in a reaction, together with the rate of addition of NH_2Et, appear to be the most critical factors involved. Aqueous solutions of NH_2Et or anhydrous NH_2Et can be used in the preparations but yields of products were only modest in most cases.

The monoethylamino-, (II), and bis(ethylamino)-derivatives, (III), are conveniently obtained from 1 : 2 and 1 : 4 reaction stoicheiometries in diethyl ether. The bis compound (III), m.p. 116 °C, is easier to obtain in high yield than any of the other derivatives reported. It was isolated previously by two groups of workers, although a definite structural assignment could not be made at that time.[5] The other bis(ethylamino)-isomer, (IV), m.p. 124 °C, was obtained only in milligram quantities. The tris(ethylamino)-compound, (V), is conveniently obtained from a 1 : 6 reaction in diethyl ether. Formation of the tetrakis(ethylamino)-isomers appears to depend on the reaction solvent: the isomer $N_4P_4Cl_4(NHEt)_4$ (VI), m.p. 96 °C, predominated in benzene whereas (VII), m.p. 158 °C, was the only crystalline product obtained in methyl cyanide. Both isomers (VI) and (VII) could be isolated from a 1 : 8 reaction in diethyl ether and the relative yield of compound (VI) was enhanced by slow addition of NH_2Et.

Higher reaction stoicheiometries (1 : 10 and 1 : 12 in diethyl ether) gave trace amounts of the isomer (VI), but the bulk of the octachloride (I) was converted into sticky resinous materials. Pentakis- or hexakis-(ethylamino)-derivatives could not be isolated from these reactions and t.l.c. gave no indication of their presence. The 1 : 14 stoicheiometric reaction in diethyl ether (using aqueous NH_2Et) gave a crystalline substance, m.p. 144—145 °C, in addition to trace amounts of the isomer (VII) and a large quantity of resin. T.l.c. and spectroscopic data reveal that this substance is essentially a 1 : 1 adduct of compounds (VII) and (VIII).

The octakis compound, $N_4P_4(NHEt)_8$, (VIII), was prepared by rapid addition of an excess of NH_2Et (aqueous or anhydrous) to a solution of the octachloride (I) in diethyl ether. The presence of an excess of amine facilitates the rapid replacement of chlorine atoms and thus minimises the formation of resins. The hydrochloride adduct, $N_4P_4(NHEt)_8 \cdot HCl$, was not obtained and this observation can be

* Reprints are available from Professor R. A. Shaw.

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contrasted with the ready isolation [6] of the hydrochloride adduct of $N_3P_3(NHEt)_6$.

The methoxy-derivatives, $N_4P_4(NHEt)_2(OMe)_6$ (XII), $N_4P_4(NHEt)_4(OMe)_4$, (XIII) and (XIV), and the dimethylamino-derivative, $N_4P_4(NHEt)_2(NMe_2)_6$ (XV), were prepared from the chloro-precursors (III), (VI), (VII), and (III), respectively. These compounds and the ethylamino-derivatives obtained are listed in Table 1.

N.m.r. spectroscopy has been widely used for assigning structures to aminochloro-derivatives of the hexachloride,[1] $N_3P_3Cl_6$, and also to the chlorodimethylamino-derivatives of the octachloride,[3,7] $N_4P_4Cl_8$ (I). Evidence obtained from i.r. and n.q.r. spectroscopy [8] and measurement of dipole moment and/or basicity can also give structural information on cyclophosphazene derivatives.[1,2] However, these techniques are rarely definitive unless all the isomers for a given degree of chlorine replacement are available. The structures of the chloroethylamino-compounds, $N_4P_4Cl_{8-n}(NHEt)_n$ (n = 2, 2, 3, 4, or 4) discussed below have been assigned largely on the basis of ^1H and ^{31}P n.m.r. spectroscopy. It should be stressed though that these assignments are more tentative than those made previously for the chloroethylamino-compounds,[6] $N_3P_3Cl_{6-n}(NHEt)_n$. N.m.r. data are summarised in Table 1; three derivatives of the hexachloride are included for comparative purposes.

The methylene proton spectrum of the monoethylamino-compound (II) appeared as a broad absorption band which simplified to a six-line signal after the sample had undergone exchange with deuterium oxide. Coupling of the methylene protons to the adjacent phosphorus atoms and methyl protons gives rise to two overlapping quartets but the numerical relation between the respective coupling constants [$^3J^*$(P–H) ≈ 2 ^3J(H–H)] reduces these eight lines to six. The value of the apparent phosphorus–hydrogen coupling constant (measured always after D_2O exchange) does not vary significantly for any of the chloroethylamino-compounds (II)—(VII) obtained [$^3J^*$(P–H) ≈ 14—15 Hz] and suggests that these compounds contain PCl(NHEt) but not $P(NHEt)_2$ groups. A similar value of the apparent coupling constant, $^3J^*$(P–H), was observed for the bis(ethylamino)-derivative of the hexachloride, $N_3P_3Cl_4(NHEt)_2$ (IX), which has a non-geminal disposition of ethylamino-groups.[6] In contrast, the fully substituted compounds, $N_4P_4(NHEt)_8$ (VIII) and $N_3P_3(NHEt)_6$ (XI) and *gem*-$N_3P_3Cl_2(NHEt)_4$ (X) have $^3J^*$(P–H) values in the range 10.5—11.0 Hz. A similar trend is observed for the dimethylamino-derivatives, $N_3P_3Cl_{6-n}(NMe_2)_n$ [9] and $N_4P_4Cl_{8-n}(NMe_2)_n$ [3,7] [PCl(NMe_2): $^3J^*$(P–H) 15—17; $P(NMe_2)_2$: $^3J^*$(P–H) 10—12 Hz], and helps to distinguish non-geminal and geminal isomers. These structural assignments for compounds (III)—(VIII) are consistent with data reported previously [6] on the chemical shift of the N*H* protons in PCl(NHEt) and $P(NHEt)_2$ groups, which generally occur in the ranges τ 6.1—6.4 and 7.1—7.6 respectively (Table 1).

The ^{31}P n.m.r. spectrum of the bis compound, $N_4P_4Cl_6(NHEt)_2$ (III), supports the assignment of a non-geminal structure to this derivative and also indicates that the ethylamino-groups are situated on distant 2,6-phosphorus atoms. The ^{31}P spectrum is of the A_2B_2 rather than the AA′BB′ type (Figure 1). The general appearance of this spectrum is comparable to that of the published spectrum of hexachloro-2,6-bis(t-butylamino)cyclotetraphosphazatetraene,[10] $N_4P_4Cl_6(NHBu^t)_2$, except that the larger value of J/δ observed for the bis(ethylamino)-derivative causes the inner lines to become more intense. Treatment of the bis(ethylamino)-derivative, 2,4,4,6,8,8:2,6-$N_4P_4Cl_6(NHEt)_2$ (III), with an excess of dimethylamine in diethyl ether or treatment of the hexakis(dimethylamino)-compound, 2,*trans*-6:2,4,4,6,8,8-$N_4P_4Cl_2(NMe_2)_6$ (*X*-ray structure reported [11]),

TABLE 1

Hydrogen-1 and ^{31}P n.m.r. data for ethylamino-derivatives of $N_4P_4Cl_8$ (I)

Compound	M.p. or b.p., θc/°C [p/mmHg]	^1H N.m.r. [a] NHCH$_2$CH$_3$ τ(NH)	τ(CH_2)	τ(CH_3)	$^3J^*$(P–H) Hz	NMe$_2$ or OMe τ(Me)	$^3J^*$(P–H) Hz	^{31}P N.m.r. [b]	Proposed structure
$N_4P_4Cl_8$ (I)	124							$\delta(PCl_2)$ −7.4	
$N_4P_4Cl_7(NHEt)$ (II)	133—135 [0.3]	c	6.77	8.70	15.0			Complex asymmetric multiplet at *ca.* −6.0	
$N_4P_4Cl_6(NHEt)_2$ (III)	116	c	6.88	8.74	15.0			$\delta(PCl_2)$ −3.4; δ[PCl(NHEt)] −4.9; J(P–N–P) 46.0 Hz	2,4,4,6,8,8 : 2, *trans*-6
$N_4P_4Cl_4(NHEt)_2$ (IV)	124	c	6.82	8.76	15.0				Non-geminal
$N_4P_4Cl_5(NHEt)_3$ (V)	68—70	c	6.82 [d]	8.72	15.0			Complex multiplet at −1.5	2,4,6,8,8 : 2, *cis*-4, *trans*-6
$N_4P_4Cl_4(NHEt)_4$ (VI)	96	c	6.88 [d]	8.79	14.0			δ[PCl(NHEt)] 2.3	2,4,6,8 : 2, *cis*-4, *trans*-6, *trans*-8
$N_4P_4Cl_4(NHEt)_4$ (VII)	158	c	7.00 [d]	8.80	14.0			δ[PCl(NHEt)] 0.9	2,4,6,8 : 2, *cis*-4, *cis*-6, *trans*-8
$N_4P_4(NHEt)_8$ (VIII)	116	7.6	7.14 [d]	8.87	11.0			δ[$P(NHEt)_2$] 4.3	
$N_3P_3Cl_4(NHEt)_2$ (IX)	85	6.2	6.84	8.72	15.0				2,4,6,6 : 2, *trans*-4
$N_3P_3Cl_2(NHEt)_4$ (X)	126	7.3	7.10	8.83	11.0				2,2 : 4,4,6,6
$N_3P_3(NHEt)_6$ (XI)	121	7.4	7.17	8.89	10.5				
$N_4P_4(NHEt)_2(OMe)_6$ (XII)	Liq.	7.6	7.06	8.90	e	6.38 [d] (2)	11.2		2,4,4,6,8,8 : 2, *trans*-6
						6.43 [d] (1)	11.2		
$N_4P_4(NHEt)_4(OMe)_4$ (XIII)	99	7.6	7.00	8.84	e	6.36 [d]	13.0		2,4,6,8 : 2, *cis*-4, *trans*-6, *trans*-8
$N_4P_4(NHEt)_4(OMe)_4$ (XIV)	102	7.7	7.08	8.89	e	6.40 [d,f]	12.0		2,4,6,8 : 2,4,6,8
$N_4P_4(NHEt)_2(NMe_2)_6$ (XV)	136—138	7.9	7.13	8.93	11.0	7.37 [d] (1)	11.0	δ[$P(NMe_2)_2$] 9.2; δ[P(NHEt)(NMe_2)] 6.8; J(P–N–P) 41.2 Hz	2,4,4,6,8,8 : 2, *trans*-6
						7.40 [d] (2)	11.4		

[a] In $CDCl_3$ (100 MHz) with $SiMe_4$ as internal reference. [b] In CH_2Cl_2 [24.3 MHz (^1H)]. Upfield shifts are negative and the external reference (δ 0) was 85% H_3PO_4. [c] Hidden by CH_2 signal. [d] Pronounced virtual coupling. [e] Insufficient resolution for accurate measurement. [f] Appears as a doublet with split peaks (separation 0.01 p.p.m.).

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with an excess of NH_2Et gave the same fully aminolysed base, $N_4P_4(NHEt)_2(NMe_2)_6$ (XV). Provided that no nett inversion occurs, a *trans* arrangement of ethylamino-groups in compound (III) seems most probable. This is also consistent with the ^1H and ^{31}P n.m.r. data for compound (XV) and the ^1H n.m.r. data for the methoxy-derivative (XII) (Table 1).

A ^{31}P n.m.r. spectrum of the other bis compound, $N_4P_4Cl_6(NHEt)_2$ (IV), could not be obtained due to the small quantity of material available; the proton spectrum confirms that it is non-geminal. Compound (IV) is readily distinguished from isomer (III) by its more complex i.r. spectrum and lower R_F value on t.l.c. (Table 3). An attempt to isomerise the major bis isomer (III) (ethylamine hydrochloride–boiling chloroform) was unsuccessful: the starting material was recovered unchanged and t.l.c. indicated the absence of isomer (IV). Hence, the available evidence is insufficient to determine the exact structure of compound (IV).

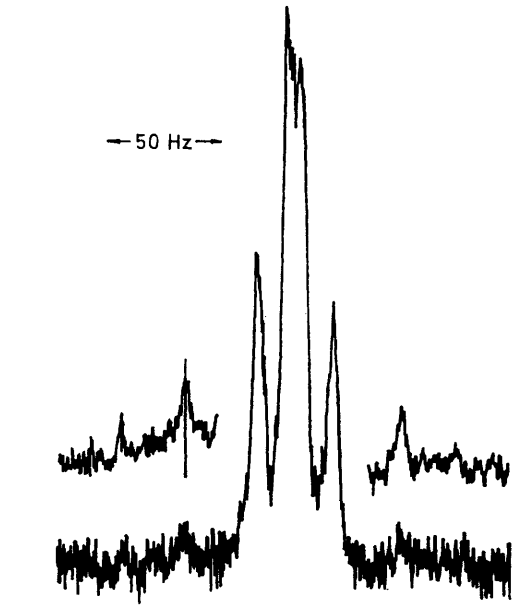

FIGURE 1 ^{31}P N.m.r. spectrum of $N_4P_4Cl_6(NHEt)_2$ (III)

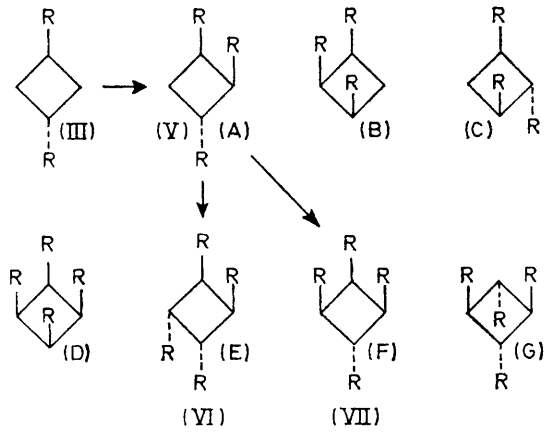

FIGURE 2 Proposed structures for $N_4P_4Cl_{8-n}(NHEt)_n$ derivatives

The 100-MHz ^1H n.m.r. spectrum of the tris(ethylamine) derivative (V) is complex (even after D_2O exchange) due to the overlap of signals from very similar methylene environments. However, a 220-MHz spectrum showed clearly that there are three distinct methylene environments [average $^3J^*$(P–H) *ca.* 15.0 Hz]. There are three possible structures for a tris compound containing only PCl(NHEt) groups (Figure 2) but only one of these structures, (A), can give rise to three ethylamino-environments. On this basis, it seems probable that compound (V) has a 2,*cis*-4,*trans*-6 arrangement of ethylamino-substituents. Chemical evidence provides strong support for this assertion: treatment of the bis isomer (III) with 2 equivalents of NH_2Et in diethyl ether gave the tris compound (V) in 69% yield. As the precursor (III) has a 2,*trans*-6 structure (see earlier) and provided that isomerisation does not take place during the replacement step, the alternative structures for compound (V) [Figure 2, (B) and (C)] can be rejected. The above assumption is not unreasonable as aminochlorocyclophosphazenes are not known to undergo ready isomerisation in diethyl ether in the presence of amine hydrochlorides.[12]

The 100-MHz ^1H n.m.r. spectra of the isomers of $N_4P_4Cl_4(NHEt)_4$, (VI) and (VII), are not very helpful for a precise assignment of their structures; 220-MHz spectra give little clarification. The methylene regions of the spectra of compounds (VI) and (VII) were multiplets and broad absorption bands beneath the peaks (' long-range virtual coupling ') obscured much of the detail. The methyl triplets are uninformative: the low sensitivity of β-protons of ethylamino-groups to subtle changes in chemical environment has been discussed elsewhere.[6] The ^{31}P n.m.r. spectra of both compounds (VI) and (VII) showed a single line after proton decoupling: only one phosphorus environment is indicated [*i.e.* PCl(NHEt) groups only (four possible isomers)] as would be anticipated from the approximate $^3J^*$(P–H) values obtained from the proton spectra (Table 1). The ^{31}P decoupled proton n.m.r. spectrum of compound (VII) indicates the presence of more than one methylene environment and consequently we assign a 2,*cis*-4,*cis*-6,*trans*-8 structure (for nomenclature see ref. 13) to this derivative [Figure 2(F)]. We suggest that compound (VI) has a 2,*cis*-4,*trans*-6,*trans*-8 structure [Figure 2(E)] but this assignment is more tentative. It is clear that both these isomers can be formed from the tris precursor (A) whereas structures (D) and (G) would arise only if isomerisation takes place during the replacement step. The chemical shift of the methylene protons of isomers (VI) and (VII) would be consistent with the presence of two and three *cis*-ethylamino-environments respectively (see also R_F values in Table 3). The ^1H n.m.r. data for the methoxy-derivative (XIII) of the tetrakis isomer (VI) are consistent with the above assignment; the three methoxy-proton environments predicted for compound (XIV) are not resolved in the spectrum.

The reaction of the octachloride (I) with NH_2Et yields copious quantities of sticky resinous materials, particularly when polar reaction media are employed. Purification of these materials was not possible, but ^{31}P n.m.r. spectra (δ 0.4–4.0 p.p.m.) of crude samples suggest that they contain tetrameric units $\{N_3P_3(NHEt)_6$ and acyclic $[NP(NHEt)_2]_n$ have ^{31}P shifts of δ 19.3 [14] and −26.6 p.p.m.[15] respectively$\}$.

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TABLE 2
Experimental details

Cyclophosphaza-tetraene	Amount g	Amount mmol	Amount of ethylamine g	Amount of ethylamine mmol	Volume of solvent cm³	Time of addition of NH_2Et h	Total reaction time h	Products and yields No.	g	%
(I)	9.28	20	3.60	80	OEt_2 200	1.5	2.5	(II)	0.80	8.4
								(III)	5.77	60.0
								(IV)	0.06	0.6
(I)	4.64	10	1.80 [a]	40	OEt_2 100	1.5	3.0	(II)	0.30	6.3
								(III)	2.90	60.2
								(IV)	0.02	0.4
(I)	4.64	10	2.70 [a]	60	OEt_2 100	1.5	3.0	(III)	0.10	2.0
								(V)	0.80	16.0 [b]
								(VI)	Trace	c
(III)	2.00	4.14	0.38	8.28	OEt_2 60	1.5	3.0	(III)	0.10	5.0
								(V)	1.40	68.7
(I)	9.28	20	7.20	160	OEt_2 200	0.25	1.5	(VI)	2.00	20.0
								(VII)	0.26	2.6 [b]
(I)	9.28	20	7.20 [a]	160	PhH [d] 200	1.0	1.5	(VI)	0.99	9.9 [e]
(I)	4.64	10	3.60 [a]	80	MeCN 200	2.0	4.0	(VII)	0.70	14.0 [e]
(VI)	2.00	4	0.72 [a]	16	PhH 150	1.25	3.25	(VI)	0.10	5.0 [e]
(I)	4.64	10	4.50 [a]	100	OEt_2 200	1.0	3.0	(VI)	0.50	10.0
								(VII)	0.10	2.0 [e]
(I)	4.64	10	5.40 [a]	120	MeCN 200	0.25	6.0		e	
(I)	9.28	20	12.60	280	OEt_2 200	2.0	5.0		1.2 [f]	11.6 [e]
(I)	4.64	10	20.0	440	OEt_2 150	0.10	6.0	(VIII)	2.50	46.5
$N_4P_4Cl_2(NMe_2)_6$	2.00	3.86	2.00 [d] $NHMe_2$	44	OEt_2 100	0.10	3.0	(XV)	1.55	75.0
(III)	2.00	4.14	5.00 Na(OMe)	110	OEt_2 100	0.10	3.0	(XV)	1.77	80.0
(III)	1.00	2.08	2.35	43.5	PhH [d] 50	0.25	48.0	(XII)	0.20	21.1 [g]
(VI)	1.00	2.00	2.35	43.5	PhH [d] 50	0.25	48.0	(XIII)	0.12	12.5 [g]
(VII)	1.00	2.00	2.35	43.5	PhH [d] 50	0.25	48.0	(XIV)	0.10	10.4 [g]

[a] Anhydrous NH_2Et; in other cases 50% (w/v) aqueous NH_2Et was used. [b] Additional resinous material (<10%). [c] Not isolated; t.l.c. evidence. [d] Reaction carried out in boiling solvent. [e] Additional resinous material (>50%). [f] Adduct $N_4P_4Cl_4(NHEt)_4$–$N_4P_4(NHEt)_8$ (see text). [g] Water-soluble products.

TABLE 3
Analytical (%) and t.l.c. data

Compound	Found C	Found H	Found N	Found Cl	Formula	Calc. C	Calc. H	Calc. N	Calc. Cl
(II)	5.2	1.4	14.9	52.2	$C_2H_6Cl_7N_5P_4$	5.1	1.3	14.8	52.6
(III)	10.1	2.6	17.3	44.0	$C_4H_{12}Cl_6N_6P_4$	10.0	2.5	17.5	44.3
(IV)	10.2	2.7				10.0	2.5		
(V)	14.5	3.8	19.3		$C_6H_{18}Cl_5N_7P_4$	14.7	3.7	20.0	
(VI)	19.7	4.8	22.2		$C_8H_{24}Cl_4N_8P_4$	19.3	4.9	22.5	
(VII)	19.3	4.7	22.7			19.3	4.9	22.5	
(VIII)	35.5	9.0	31.8		$C_{16}H_{48}N_{12}P_4$	36.1	9.1	31.6	
(XII)	33.9	8.6	23.1		$C_{10}H_{30}N_6O_6P_4$	33.6	8.4	23.5	
(XIII)	29.8	7.5	23.2		$C_{12}H_{36}N_8O_4P_4$	30.0	7.5	23.3	
(XIV)	30.2	7.5	23.8			30.0	7.5	23.3	
(XV)	36.0	9.1	31.3		$C_{16}H_{48}N_{12}P_4$	36.1	9.1	31.6	

R_F Values for the chloroethylamino-derivatives were: 0.71 (II); 0.58 (III); 0.53 (IV); 0.18 [eluant; light petroleum (b.p. 40—60 °C)–benzene (1 : 1)]; 0.74 (V); 0.65 (VI); 0.58 (VII) [eluant: ethyl acetate–benzene (1 : 9)].

Resin formation is also a prominent feature of the reactions of the hexachloride, $N_3P_3Cl_6$, with primary amines.[6]

DISCUSSION

Reactions of ethylamine with the hexachloride proceed *via* a non-geminal route to the bis stage of replacement and then largely by the geminal route, although trace amounts of a non-geminal tris derivative have been isolated.[6] The reactions of the octachloride, $N_4P_4Cl_8$ (I), with NH_2Et proceed *via* a non-geminal path to the tetrakis stage of replacement, *i.e.* until reaction has taken place at every PCl_2 group. The higher reactivity of the octachloride (I) would explain this difference. In neither system have compounds containing both PCl(NHEt) and $P(NHEt)_2$ groups been obtained. Furthermore, in both trimeric and tetrameric systems it is only at the point where the geminal mechanism (possibly related to hydrogen bonding [6]) dominates that the major reaction product becomes a sticky resinous material. The failure to isolate pentakis- or hexakis-(ethylamino)-derivatives of the octachloride (I) is therefore in keeping with earlier observations.[6] A possible explanation for the formation of resinous material when limited amounts of amine are added on the one hand, and the ability to isolate $N_3P_3(NHEt)_6$ (XI) and $N_4P_4(NHEt)_8$ (VIII) with excess of amine on the other, would be that both arise from common reactive intermediate species. Such species could be related to those based on three-co-ordinate phosphorus formed by the elimination of hydrogen chloride from PCl(NHEt) groups (metaphosphorimi-

dates). This type of mechanism has been invoked earlier [16] and more recently such species have been isolated.[17]

The isolation of an adduct between isomer (VII) and the derivative (VIII) is paralleled by the formation of the adduct non-*gem*-$N_3P_3Cl_4(NHPr^i)_2$–*gem*-$N_3P_3Cl_2(NHPr^i)_4$ in the $N_3P_3Cl_6$–NH_2Pr^i system.[18] The common structural feature appears to be the presence of primary alkylamino-groups.

EXPERIMENTAL

Octachlorocyclotetraphosphazatetraene, (I), was purified by recrystallisation from light petroleum (b.p. 60—80 °C) to constant m.p. 124 °C. Light petroleum (b.p. 60—80 °C unless stated otherwise), benzene, chloroform, methyl cyanide, and diethyl ether were purified by conventional methods.

Reactions were carried out using either aqueous (50% w/v) or anhydrous ethylamine (Riedel, Germany). Typical reactions are described below with full experimental details. Details of other reactions are summarised in Table 2. Chromatographic procedures were as previously described.[19] ^1H N.m.r. spectra were recorded with Jeol MH 100 and Varian HR 220 spectrometers. ^{31}P N.m.r. spectra were obtained on a Jeol C 60 HL spectrometer.[14] Analytical data and t.l.c. R_F values are given in Table 3.

Reactions of Octachlorocyclotetraphosphazatetraene, (I).—(*a*) *With 2 equivalents of ethylamine in diethyl ether.* Anhydrous sodium sulphate (50 g) was suspended in a solution of (I) (4.64 g, 0.01 mol) in diethyl ether (100 cm^3) cooled to 0 °C. Aqueous ethylamine (0.02 mol) was added dropwise to the vigorously stirred solution for 0.5 h. Stirring was continued at 0 °C for 1.5 h before the reaction mixture was allowed to attain room temperature. Ethylamine hydrochloride and sodium sulphate were filtered off and evaporation of the filtrate gave a pale yellow oil. The oil was chromatographed on silica gel (100 g) and elution with light petroleum (b.p. 40—60 °C)–benzene (3 : 1) gave unchanged octachlorocyclotetraphosphazatetraene (I) (0.16 g, 3.6%), and heptachloro(ethylamino)cyclotetraphosphazatetraene, (II), b.p. 133—135 °C (0.3 mmHg) (3.1 g, 65.5%).* Hexachloro-2,*trans*-6-bis(ethylamino)cyclotetraphosphazatetraene (III), m.p. 116 °C (lit.,[5] 114.5 °C) (0.4 g, 8.3%) was eluted with light petroleum (b.p. 40—60 °C)–benzene (1 : 1).

(*b*) *With 4 equivalents of ethylamine in diethyl ether.* Aqueous NH_2Et (0.08 mol) was added to a solution of (I) (9.28 g, 0.02 mol) in diethyl ether (200 cm^3) as in (*a*). After filtration and evaporation of the solvent, the residual oil was extracted with hot light petroleum (b.p. 40—60 °C). Several crude crops of crystals were obtained from the petroleum extracts which on recrystallisation from light petroleum gave hexachloro-2,*trans*-6-bis(ethylamino)cyclotetraphosphazatetraene (III), m.p. 116 °C (5.3 g, 55%). From the mother liquor a second crop of crystals was isolated which on recrystallisation from light petroleum gave *hexachlorobis(ethylamino)cyclotetraphosphazatetraene* (IV), m.p. 124 °C (0.06 g, 0.6%). The residual mixture contained trace amounts of the mono compound (II), the two bis isomers (III) and (IV), and the tris derivative (V).

(*c*) *With 6 equivalents of ethylamine in diethyl ether.* Aqueous NH_2Et (0.12 mol) was allowed to react with (I) (9.28 g, 0.02 mol) in diethyl ether (200 cm^3) as described in (*a*). Removal of the solvent gave a pale brown oil. The oil was extracted with hot light petroleum (40—60° C) and filtered to remove trace amounts of ethylamine hydrochloride. Several crops of crystals, m.p. 63—68 °C (2.2 g), were obtained from the filtrate after 6—7 d at 0 °C. The crude crop was dissolved in hot light petroleum (b.p. 40—60 °C), boiled with activated charcoal, and filtered. On cooling in a refrigerator for 3—4 d the filtrate gave colourless crystals of *pentachloro*-2,cis-4,trans-6-*tris(ethylamino)cyclotetraphosphazatetraene* (V), m.p. 68—70 °C (1.95 g, 20%). The mother liquor was chromatographed on silica gel (50 g) using light petroleum (b.p. 40—60 °C)–benzene (3 : 1) as eluant to give the bis derivative (III) (*ca.* 10 mg). The tris derivative (V) was obtained (*ca.* 5—10 mg) by using benzene–ethyl acetate (7 : 3) as eluant.

(*d*) *With 8 equivalents of ethylamine in benzene.* A solution of (I) (9.28 g, 0.02 mol) in benzene (200 cm^3) was allowed to react with aqueous NH_2Et (0.16 mol) as in (*a*). Removal of the solvent gave a colourless viscous oil which on shaking with hot light petroleum (b.p. 40—60 °C) (30 cm^3) became a crystalline mass. Benzene was added slowly until the solution was almost clear and filtration removed the remaining trace amounts of ethylamine hydrochloride. The solution was allowed to crystallise at room temperature and the crude product, m.p. 90—93 °C (5.00 g), was recrystallised from light petroleum (b.p. 40—60 °C)–benzene (4 : 1) to give *tetrachloro*-2,cis-4,trans-6,cis-8-*tetrakis(ethylamino)cyclotetraphosphazatetraene* (VI), m.p. 96 °C (4.92 g, 49.2%). Thin-layer chromatography of the mother liquor [silica gel; benzene–ethyl acetate (4 : 1) eluant] indicated trace amounts of the tris (V) and of the other tetrakis derivative (VII).

(*e*) *With 8 equivalents of ethylamine in methyl cyanide.* Aqueous NH_2Et (0.08 mol) was allowed to react with (I) (4.64 g, 0.01 mol) in methyl cyanide (200 cm^3) as in (*a*) [(I) was only partially soluble in MeCN at 0 °C but dissolved as the reaction progressed]. After removing the solvent, a viscous oil was obtained which was extracted with hot benzene. The extract was filtered to remove ethylamine hydrochloride and the filtrate concentrated (5 cm^3) under reduced pressure. The concentrated solution was mixed with light petroleum (b.p. 40—60 °C)–benzene (4 : 1; 20 cm^3) and allowed to crystallise at room temperature. After 5—6 d a crystalline solid and a resinous material co-precipitated. Repeated recrystallisation of the crude material from the same solvent mixture gave *tetrachloro*-2-cis-4,cis-6,trans-8-*tetrakis(ethylamino)cyclotetraphosphazatetraene*, (VII), m.p. 158 °C (0.90 g, 18%). Considerable amounts of resinous material (2.5 g) were formed in this reaction but no other products were detected by t.l.c.

(*f*) *With 12 equivalents of anhydrous ethylamine in diethyl ether.* Anhydrous NH_2Et (0.12 mol) was added dropwise to a stirred solution of (I) (4.65 g, 0.01 mol) in diethyl ether (200 cm^3) for 2 h. Ethylamine hydrochloride was filtered off and evaporation of the solvent *in vacuo* yielded an oil which was then extracted with hot benzene–hexane (1 : 4). The insoluble portion was a sticky resinous material. The benzene–hexane extract became turbid on standing and a crystalline product could not be obtained. T.l.c. of this extract on silica gel [eluant benzene–ethyl acetate (4 : 1)]

* 1 mmHg ≈ 13.6 × 9.8 Pa.

[16] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 5032, and refs. therein.

[17] E. Niecke and W. Flick, *Angew. Chem. Internat. Edn.*, 1974, **13**, 134; O. J. Scherer and N. Kuhn, *Chem. Ber.*, 1974, **107**, 2123.

[18] S. K. Das, D. Feakins, W. A. Last, S. N. Nabi, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1970, 616.

[19] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.

revealed trace amounts of the tetrakis derivatives (VI) and (VII) and a base-line component which probably corresponds to the resinous material.

(*h*) *With an excess of ethylamine in diethyl ether.* An excess of anhydrous NH_2Et (0.30 mol) was allowed to react with (I) (4.65 g, 0.01 mol) in diethyl ether (200 cm^3) at 0 °C with constant stirring for 3 h. Amine hydrochloride was filtered off and removal of the solvent under reduced pressure gave a solid residue which was extracted with hot light petroleum (b.p. 60—80 °C). The insoluble resinous material remaining was filtered off and the filtrate was allowed to crystallise at room temperature to yield octakis(ethylamino)cyclotetraphosphazatetraene (VIII), m.p. 118 °C (lit.,[20] 116 °C) (4.2 g, 80%).

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

Compound (VIII) could also be prepared in *ca.* 45—50% yields by rapidly adding an excess of aqueous NH_2Et to a solution of (I) in diethyl ether, as described in (*a*).

Methoxy-derivatives.—Compounds $N_4P_4(NHEt)_2(OMe)_6$ (XII) and $N_4P_4(NHEt)_4(OMe)_4$, (XIII) and (XIV), were prepared by heating the chloro-precursors (III), (VI), and (VII) with sodium methoxide in boiling benzene for 48 h.

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