Studies of Phosphazenes. Part 15.[1] Chloro(phenoxy)cyclotetraphosphazenes, $N_4P_4Cl_{8-n}(OPh)_n$

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The reaction of $N_4P_4Cl_8$ (1) with sodium phenoxide (or phenol in the presence of triethylamine) has been studied under a variety of experimental conditions. The chloro(phenoxy)-derivatives, $N_4P_4Cl_{8-n}(OPh)_n$ [n = 1 or 2 (mixture of four non-geminal isomers), 3(mixture of non-geminal isomers), 4(mixture of isomers), 5(mixture of isomers), 6(mixture of four non-geminal isomers), or 8], have been isolated by column chromatography over silica gel. Attempts to separate geometric isomers were unsuccessful. Structural elucidation of the products is based on the ^{31}P n.m.r. data for the chloro-precursors and ^1H and ^{31}P n.m.r. spectra of the dimethylamino- and/or methoxy-derivatives. The chlorine-replacement pattern is discussed.

Cyclophosphazenes and poly(phosphazenes) containing alkoxy- and aryloxy-substituents have engendered a great deal of interest in view of their high thermal stability and potential use as flame-retardant additives.[2] Although many fully substituted compounds $[NP(OR)_2]_n$ (n = 3 or 4) have been prepared,[3,4] only a limited number of partially substituted alkoxychloro- and aryloxychloro-cyclophosphazenes have been characterised satisfactorily. The reactions of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) with trifluoroethoxide [5] and phenoxide [6,7] have been investigated in some detail and a predominantly non-geminal mode of chlorine replacement has been established. Our previous studies of the aminolysis reactions [8–11] of octachlorocyclotetraphosphazene (1) have revealed significant differences in its reactivity [12] and in the chlorine-replacement pattern compared to the analogous reactions of hexachlorocyclotriphosphazene. In view of these results, it is of interest to explore the behaviour of the eight-membered ring system towards an oxygen-containing nucleophile. Furthermore, the reactions of homologue (1) can serve as a better model for the reactions of polymeric systems than those of the more rigid $N_3P_3Cl_6$.[13]

Experimental

Octachlorocyclotetraphosphazene (1) was recrystallised from light petroleum (b.p. 40—60 °C) to constant m.p. 124 °C. Organic solvents were purified by conventional methods. 'AnalaR' grade phenol was used as supplied. Hydrogen-1 n.m.r. spectra ($CDCl_3$ solution, $SiMe_4$ internal standard) were recorded with a Bruker WH-270 spectrometer. Phosphorus-31 n.m.r. spectra were obtained with Bruker HFX-90 and WH-400 spectrometers using $CDCl_3$ solutions and 85% phosphoric acid as external standard. Chemical shifts are expressed on the δ scale with upfield shifts negative. Computer analyses of the n.m.r. spectra were carried out using a modified version of the LAOCOON program.[14] Mass spectrometric data were obtained from the P.C.M.U. service, Harwell.

Reactions were carried out in diethyl ether, tetrahydrofuran, acetone, and benzene using either sodium phenoxide or phenol in the presence of triethylamine. They were monitored by thin-layer chromatography (t.l.c.). Complex mixtures of products were obtained in most experiments and these were partially separated by column chromatography over silica gel. Considerable loss of material occurred during these separations and yields of products were modest. Two typical experiments are described below; other details are summarised in Table 1.

Reaction of $N_4P_4Cl_8$ (1) *with 3 mol equivalents of Phenol in Benzene.*—A solution of phenol (2.85 g, 30 mmol) and triethylamine (3.76 g, 40 mmol) in dry benzene (100 cm^3) was added dropwise to a stirred solution of octachlorocyclotetraphosphazene (1) (4.64 g, 10 mmol) in benzene (200 cm^3) at 30 °C. After 24 h the precipitate of triethylamine hydrochloride was filtered off and the benzene was evaporated. The residual oil (5.2 g) was chromatographed over silica gel (75 g) and the following fractions were collected: A, 0.9 g [eluant: light petroleum (b.p. 40—60 °C)–benzene (49 : 1) (800 cm^3); B, 0.75 g [eluant: light petroleum–benzene (20 : 1) (800 cm^3)]; C, *ca.* 0.01 g of *2,4,6,8-tetrachloro-2,4,6,8-tetraphenoxycyclotetraphosphazene*, $N_4P_4Cl_4(OPh)_4$ (5), m.p. 116 °C [eluant: light petroleum–benzene (10 : 1) (400 cm^3)]. Fraction A was an oil which was dissolved in light petroleum and kept at 0 °C for 12 h. Some crystals were deposited and characterised as *hexachlorodiphenoxycyclotetraphosphazene*, $N_4P_4Cl_6(OPh)_2$ (3), m.p. 97—99 °C (Found: C, 24.7; H, 1.9; N, 9.5. Calc. for $C_{12}H_{10}Cl_6N_4O_2P_4$: C, 24.9; H, 1.7; N, 9.7%). Fraction B was an oil that did not solidify even at −75 °C. Its mass spectrum (Table 2) and ^{31}P n.m.r. spectrum indicated that it was *pentachlorotriphenoxycyclotetraphosphazene*, $N_4P_4Cl_5(OPh)_3$ (4) (see Results and Discussion section).

Reaction of $N_4P_4Cl_8$ (1) *with 8 mol equivalents of Sodium Phenoxide in Diethyl Ether.*—A solution of $N_4P_4Cl_8$ (1) (4.64 g, 10 mmol) in dry diethyl ether (100 cm^3) was added dropwise (0.8 h) to a stirred solution of sodium phenoxide (9.28 g, 80 mmol) in diethyl ether (200 cm^3) at 0 °C. The reaction mixture was allowed to attain room temperature (*ca.* 2 h) and the precipitate of sodium chloride was filtered off. During filtration, a salt-like material (3.0 g), m.p. 165—180 °C, was precipitated from the filtrate which eluded attempts at characterisation. The diethyl ether was evaporated and the residual oil (3.1 g) chromatographed over silica gel (60 g). The following fractions were collected: A, 0.005 g of compound (5) [eluant: light petroleum (b.p. 40—60 °C)–benzene (5 : 1) (500 cm^3)]; B, 0.3 g [eluant: light petroleum–benzene (10 : 3) (700 cm^3)]; C, 0.25 g [eluant: light petroleum–benzene (5 : 2) (500 cm^3)]. Fraction B remained an oil at 0 °C even after several months. Its mass spectrum (Table 2) indicated that it was *trichloropentaphenoxycyclotetraphosphazene*, $N_4P_4Cl_3(OPh)_5$ (7), which was a mixture of isomers (see text). Fraction C was an oil even at −75 °C. Its mass spectrum (Table 2) showed that it was *dichlorohexaphenoxycyclotetraphosphazene*, $N_4P_4Cl_2(OPh)_6$ (8). The ^{31}P n.m.r. spectrum indicated that it was a mixture of the 2,4- and 2,6-dichloro-isomers.

Table 1. Preparative details

$N_4P_4Cl_8$ (1)		Phenol		NEt_3		Solvent	Reaction temperature	Products and yields		
g	mmol	g	mmol	g	mmol	(V/cm^3)	(°C)	No.	g	%
4.64	10.0	0.95	10.0	1.88	20.0	Et_2O (300)	−78	(1)	0.80	17.3
								a	1.20	
								(2)	0.25	4.8
								(3)	Trace	
5.3	11.5	2.14	22.8	2.33	29.7	Et_2O (300)	−78	*a*	2.10	
								(2)	0.80	13.4
								(3)	0.60	9.1
								(4) [b]	Trace	
4.64	10.0	2.85	30.0	3.76	40.0	C_6H_6 (300)	75	(3)	0.50	8.6
								(4)	0.10	1.6
								(5)	Trace	
4.64	10.0	3.80	40.0	4.69	50.0	C_6H_6 (300)	30	(3)	0.10	1.7
								(4)	0.50	7.9
								(5)	0.12	1.7
4.64	10.0	3.80	40.0	5.64	60.0	Et_2O (300)	−78	*a*	1.30	
								(3)	0.10	1.7
								(4)	0.50	7.9
								(5)	0.10	1.4
4.64	10.0	4.75	50.0	5.64	60.0	C_6H_6 (300)	30	(3) [b]		
								(4)	0.10	1.6
								(5)	2.50	36.6
								(7)	0.05	0.7
4.64	10.0	5.70	60.0	7.52	80.0	Et_2O (300)	−78	*a*	1.80	
								(5)	Trace	
								(7)	0.30	4.2
								(8)	0.25	3.1
4.64	10.0	5.70	60.0	7.52	80.0	C_6H_6 (300)	30	(6)	0.30	4.3
								(7)	1.57	20.9
								(8)	0.05	0.6
4.64	10.0	7.60	80.0	9.40	100.0	C_6H_6 (300)	30	(5)	0.05	0.7
								(7)	0.52	6.9
								(8)	0.41	5.1
		NaOPh								
4.64	10.0	1.16	10.0			Et_2O (300)	−78	*a*	2.75	
								(2)	0.50	9.8
								(3)	0.45	7.8
								(4) [b]	Trace	
4.64	10.0	1.16	10.0			thf [c] (300)	−78	*a*	2.80	
								(2)	0.32	6.3
								(3)	0.60	10.4
								(4) [b]	Trace	
								(5) [b]	Trace	
4.64	10.0	1.16	10.0			Me_2CO (300)	0	*a*	3.10	
								(5) [b]	Trace	
								(7)	0.32	4.1
								(8)	0.52	6.2
4.64	10.0	2.32	20.0			thf (300)	−78	*a*	2.40	
								(3)	0.21	3.6
								(4)	0.72	11.3
								(5)	0.11	1.6
4.64	10.0	9.28	80.0			Et_2O (150) C_6H_6 (100)	0	(2)	2.20	
								(5) [b]	Trace	
								(7)	0.28	3.7
								(8)	0.45	5.7

[a] A solid, m.p. >270 °C, insoluble in organic solvents (Found: C, 9.45; H, 2.75; N, 10.85%), δ_p +0.5 to −5.0 (in $HCONMe_2$–CD_2Cl_2) for which no definite structure could be assigned. [b] T.l.c. evidence. [c] Tetrahydrofuran.

The dimethylamino-derivatives $N_4P_4(NMe_2)_6(OPh)_2$ (10), $N_4P_4(NMe_2)_5(OPh)_3$ (11), $N_4P_4(NMe_2)_3(OPh)_5$ (12), and $N_4P_4(NMe_2)_2(OPh)_6$ (13) and the methoxy-derivatives $N_4P_4(OMe)_6(OPh)_2$ (14) and $N_4P_4(OMe)_3(OPh)_5$ (15) were prepared as described previously [7,10] using diethyl ether (dimethylamino-derivatives) or benzene (methoxy-derivatives) as the solvent. All these compounds were liquids at *ca.* 25 °C and were characterised by mass spectrometry [$N_4P_4(OMe)_6(OPh)_2$ (14), *m/e* (obs.) 552; $N_4P_4(OMe)_3(OPh)_5$ (15), *m/e* (obs.) 738] and/or by ^1H and ^{31}P n.m.r. spectroscopy.

Results and Discussion

Reactions of octachlorocyclotetraphosphazene (1) with phenol in the presence of triethylamine or sodium phenoxide in benzene, diethyl ether, tetrahydrofuran, or acetone give the

Table 2. M.p., t.l.c., and mass spectrometric data for chlorophenoxycyclotetraphosphazenes, $N_4P_4Cl_{8-n}(OPh)_n$

Compound [a]	M.p. (°C)	t.l.c.[b] R_f	m/e obs.	m/e calc.
(2) $N_4P_4Cl_7(OPh)$	57	0.94	517.7237	517.7237
(3) $N_4P_4Cl_6(OPh)_2$	97—99	0.86	575.7865	575.7885
(4) $N_4P_4Cl_5(OPh)_3$	*c*	0.75	633.8545	633.8539
(5) $N_4P_4Cl_4(OPh)_4$	116	0.61	691.9182	691.9188
(6) $N_4P_4Cl_4(OPh)_4$	*c*	0.61	692	692
(7) $N_4P_4Cl_3(OPh)_5$	*c*	0.49	749.9820	749.9838
(8) $N_4P_4Cl_2(OPh)_6$	*c*	0.38	808.0437	808.0488
(9) $N_4P_4(OPh)_8$ [d]	85—86	0.28		

[a] Phosphorus and proton n.m.r. of the chlorophenoxy-' compounds ' (3), (4), and (6)—(8) and their dimethylamino-derivatives indicate that they are mixtures of isomers of the stated formulae. [b] On silica gel with benzene–light petroleum (2 : 3) as eluant. [c] Liquid. [d] Prepared as described previously.[3]

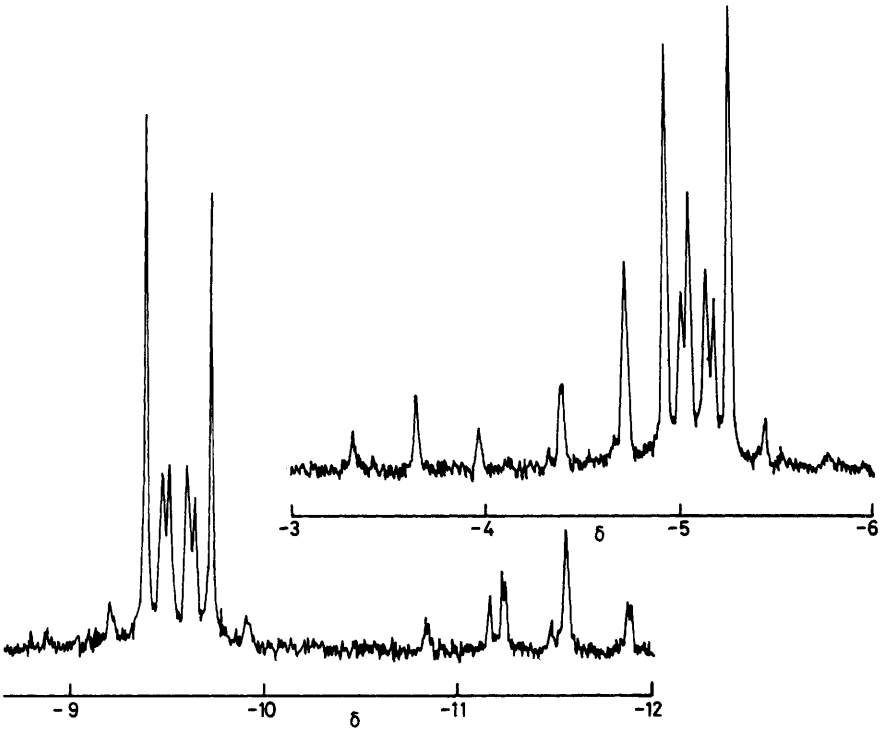

Figure 1. $^{31}P-\{^1H\}$ n.m.r. spectrum (162 MHz, $CDCl_3$) of $N_4P_4Cl_6(OPh)_2$ (3)

phenoxy-derivatives, $N_4P_4Cl_{8-n}(OPh)_n$ (n = 1—6 or 8) (2)—(9). The most reactive reagent is sodium phenoxide in polar solvents. The use of a specific ratio of reagents does not guarantee that a derivative containing the desired number of phenoxy-substituents will be obtained: products with different degrees of replacement are formed in all reactions. This observation, together with the additional problem of distinguishing positional isomers by t.l.c., poses major difficulties in isolating individual compounds in a pure state. Similar separation problems were also encountered in the reaction of the hexachloride $N_3P_3Cl_6$ with sodium phenoxide.[6]

The chloro(phenoxy)-derivatives (2)—(8) obtained by column chromatography were studied initially by phosphorus-31 n.m.r. spectroscopy and mass spectrometry (Table 2). Additional information was obtained from the ^{31}P and ^1H n.m.r. spectra of their dimethylamino- (10)—(13) or methoxy-derivatives (14) and (15).

The 36.43-MHz $^{31}P-\{^1H\}$ n.m.r. spectrum of the bis-(phenoxy)-derivative (3) is very complex. A spectrum recorded at 162 MHz is illustrated in Figure 1. Three sets of symmetrical line patterns are clearly seen. The two sets of lines centred at δ −7.40 and −8.13 are of an A_2X_2 type. Such a pattern could arise only from a 2,6 disposition of phenoxy-groups (*cis* and *trans* isomers). The remaining set of lines centred at δ −7.32 constitutes an AA'XX' pattern (chemical shifts and coupling constants in Figure 2) and arises from the 2,4-substituted products. The symmetrical nature of the three sets of lines excludes the presence of the geminal bis isomer.[15] The relative intensities of the A_2X_2 and AA'XX' portions of the spectrum (Figure 1) suggest that 2,4-substitution of chlorine atoms by phenoxy-groups is favoured over 2,6-substitution at the bis stage.

The 270-MHz proton n.m.r. spectrum of either the fully substituted dimethylamino- (10) or methoxy-derivative (14) of substance (3) shows the presence of more than nine dimethylamino- (δ 2.15—2.74) or methoxy-doublets (δ 3.37—3.79). The number of proton environments anticipated for the non-geminal isomers of $N_4P_4(NMe_2)_6(OPh)_2$ (10) or N_4P_4-

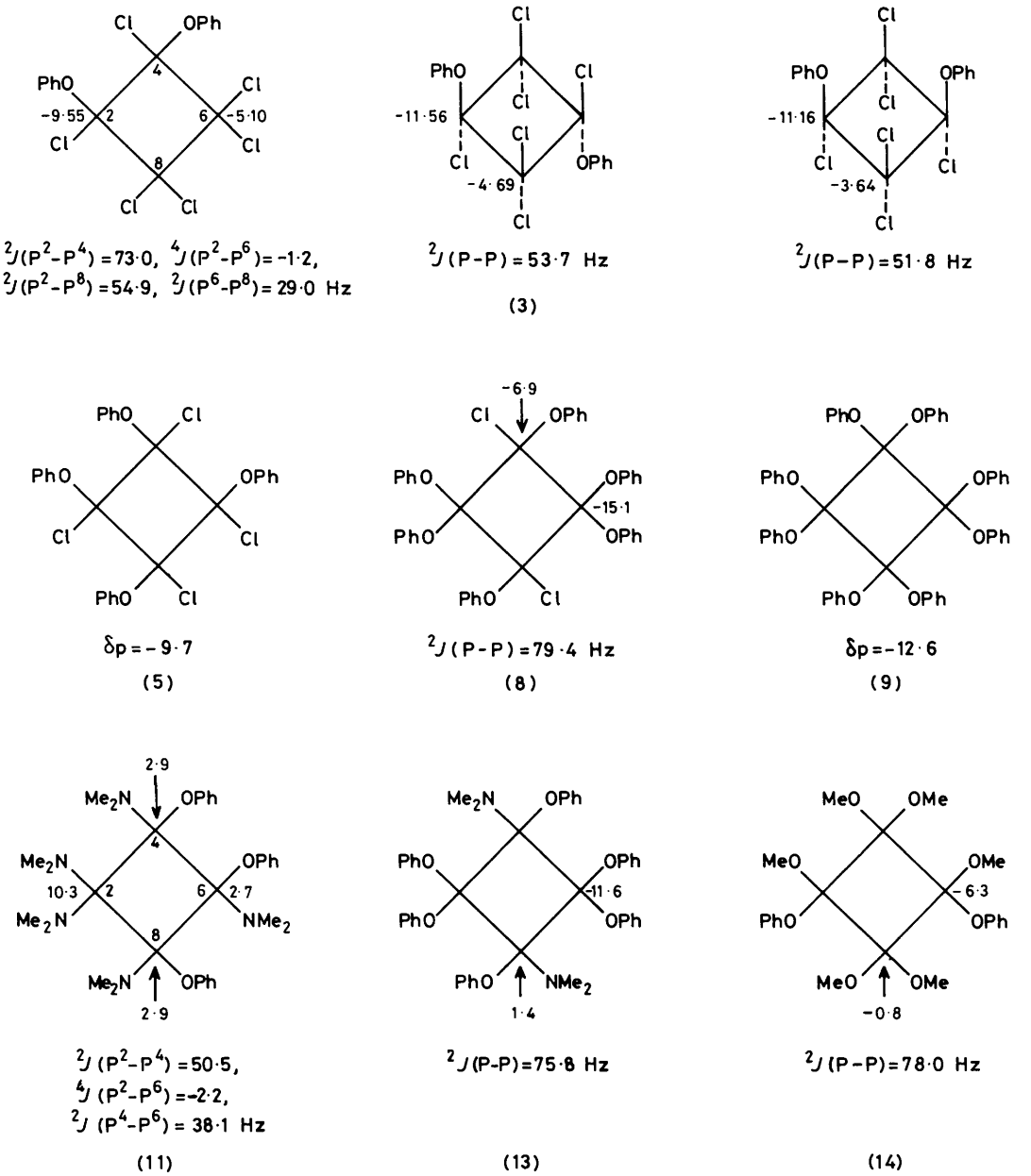

Figure 2. δ_P and J(P–P) values for chloro(phenoxy)cyclotetraphosphazenes and their dimethylamino- or methoxy-derivatives [isomeric configuration not differentiated except for 2,6-$N_4P_4Cl_6(OPh)_2$]. The corners of the squares represent the phosphorus atoms; ring nitrogen atoms are not shown

$(OMe)_6(OPh)_2$ (14), *viz.* 2-*cis*-4, 2-*cis*-6, 2-*trans*-4, and 2-*trans*-6, are 3(relative intensity 1 : 1 : 1), 3(1 : 1 : 1), 3(1 : 1 : 1), and 2(2 : 1) respectively. We conclude that the hexachloro-bis(phenoxy)-precursor (3) is also a mixture of all the four non-geminal bis isomers as net inversion of structure is unlikely to be significant for chlorine-replacement reactions using dimethylamine in diethyl ether or sodium methoxide.[15]

The ^{31}P n.m.r. spectrum of substance (3) discussed earlier is also consistent with the above conclusion; whilst the geometrical isomers of 2,6-$N_4P_4Cl_6(OPh)_2$ are distinguished by their slightly different ^{31}P chemical shifts, the geometrical isomers of 2,4-$N_4P_4Cl_6(OPh)_2$ are not differentiated even at the high field deployed for recording the spectrum. The assignments shown for 2-*cis*-6- and 2-*trans*-6-$N_4P_4Cl_6(OPh)_2$ (Figure 2) are only tentative and a reversal is possible.

There are five possible isomers of $N_4P_4Cl_5(OPh)_3$, three of which have the non-geminal structure.[15] The ^{31}P-{^1H} n.m.r. spectrum of the tris derivative (4) consists of two groups of signals in the ratio 1 : 3. The group of signals of lower intensity (centre δ *ca.* −6) are downfield from the major group and can be unambiguously assigned to a $\equiv PCl_2$ unit by comparing the phosphorus spectra obtained with and without proton decoupling. The remaining group of signals at higher field (δ −10) are assigned to $\equiv PCl(OPh)$ groups. The presence of either of the geminal isomers of $N_4P_4Cl_5(OPh)_3$ seems very unlikely: the phosphorus chemical shifts of the $\equiv P(OPh)_2$ group should be further upfield and also well separated from the shift of $\equiv PCl(OPh)$ or $\equiv PCl_2$ groups [see data in Figure 2, particularly $\equiv P(OPh)_2$ values for derivatives (8) and (9)]. The absence of a geminal tris isomer is also supported by the ^{31}P n.m.r. spectrum of the dimethylamino-derivative, $N_4P_4(NMe_2)_5(OPh)_3$ (11). Two groups of signals are seen with

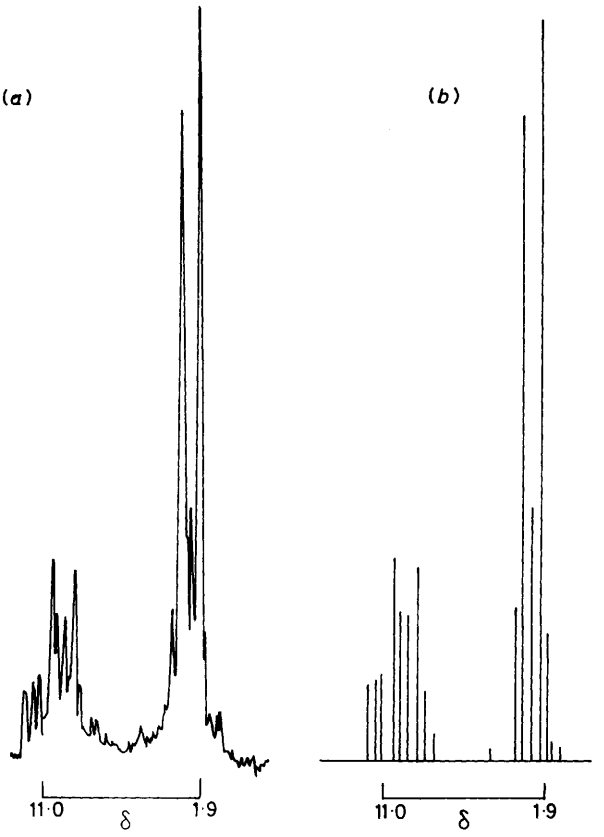

Figure 3. ^{31}P-{^{1}H} n.m.r. spectrum (36.43 MHz, $CDCl_3$) of $N_4P_4(NMe_2)_5(OPh)_3$ (11): (*a*) experimental, (*b*) simulated

centres at δ ≈ 10 and ≈ 3 with an intensity ratio 1 : 3. The appearance of signals around δ 10 clearly indicates the presence of a $\equiv P(NMe_2)_2$ group [*cf.* $N_4P_4(NMe_2)_8$: δ_p 9.6 [16]]. The ^{31}P n.m.r. spectrum of derivative (11) has been simulated (Figure 3) using the parameters shown in Figure 2. The 270-MHz proton n.m.r. spectrum of the dimethylamino-derivative (11) contains seven dimethylamino-doublets and reveals the presence of more than one tris isomer.

The tetraphenoxy-derivative, $N_4P_4Cl_4(OPh)_4$ (5), m.p. 116 °C, is obtained in very small yield. Its ^{31}P n.m.r. spectrum is a single line at δ −9.7 and indicates a 2,4,6,8 non-geminal structure (each phosphorus atom bears one phenoxy-substituent). Product (6) is a mixture of tetrakis isomers: its ^{31}P n.m.r. spectrum contains *ca.* 25 lines in the range δ −5.0 to −22.0. It seems probable that the wide range observed for these signals is only compatible with the presence of $\equiv PCl_2$, $\equiv PCl(OPh)$, and $\equiv P(OPh)_2$ groups (Figure 2). As there are ten possible tetrasubstituted isomers [15] of $N_4P_4Cl_4(OPh)_4$, no definite conclusion can be reached on the isomeric composition of substance (6).

The ^{31}P n.m.r. spectrum of the penta(phenoxy)-compound (7) shows multiplets centred at δ −12.0 and −22.0 in an intensity ratio 3 : 1. This observation clearly suggests the presence of only one $\equiv P(OPh)_2$ group and three $\equiv P(OPh)Cl$ groups. The 270-MHz ^{1}H n.m.r. spectrum of the derivatives $N_4P_4R_3(OPh)_5$ [R = NMe_2 (12) or OMe (15)] are exceedingly complex and even a partial analysis cannot be made with certainty.

It is possible to make some deductions on the isomeric composition of substance (7) after considering the clear-cut evidence available for the hexakis derivative, $N_4P_4Cl_2(OPh)_6$ (8). The ^{31}P n.m.r. spectrum of compound (8) is symmetrical and hence a geminal structure need not be considered.[15] Fourteen lines of high intensity are easily discerned. They constitute an A_2B_2 spin pattern (data given in Figure 2). The remaining lines (symmetrical around δ −9.1) constitute an AA′BB′ spin pattern; attempts to reproduce this part of the spectrum by computer simulation have not proved successful. The 270-MHz proton n.m.r. spectrum of the dimethylamino-derivative $N_4P_4(NMe_2)_2(OPh)_6$ (13) obtained from the chloro-precursor (8) shows four distinct dimethylamino-doublets at δ 2.56, 2.48, 2.38, and 2.35 with relative intensities 6, 5, 24, and 2 respectively (Figure 4). The two doublets at high field which do not show ' virtual coupling ' [15] are assigned to the geometric isomers with the 2,6 disposition of NMe_2 groups.[15,17] The high-intensity doublet at δ 2.38 is assigned to the *trans* isomer and the low-intensity doublet at higher field to the *cis* isomer (Figure 4): the shielding effects of aryl substituents are well documented in cyclophosphazene chemistry.[7,10] The remaining doublets which show intense ' virtual coupling ' clearly arise from the 2,4-isomers.[17] Thus we conclude that the hexakis(phenoxy)-precursor (8) also contains all four non-geminal isomers. As anticipated, the ^{31}P n.m.r. spectrum of $N_4P_4(NMe_2)_2(OPh)_6$ (13) is complex consisting of two sets of symmetrical lines. The A_2B_2 portion of the spectrum is of high intensity and is easily analysed [18] (data in Figure 2). The relative intensity of the two groups of signals (A_2B_2 and AA′-BB′) clearly shows that 2,6 isomers are predominant at the hexakis stage of chlorine replacement.

As the major isomer of $N_4P_4Cl_2(OPh)_6$ (8) has a 2-*trans*-6 structure, it is possible to make some deductions on the composition of the pentaphenoxy-precursor (7) by scrutinising the reaction scheme illustrated in Figure 5. The 2-*trans*-6 hexakis derivative [(G) in Figure 5] can only be formed from two pentakis isomers (B) and (E) (assuming that net inversion is negligible). The pentakis isomer (B) can also give rise to two of the other hexakis isomers, *viz.* 2-*cis*-4 (F) and 2-*trans*-4 (H). Hence, it is logical to suggest that the major pentakis derivative formed in this reaction is 2,4,6-*trichloro*-2-cis-4-trans-6,8,8-*pentaphenoxycyclotetraphosphazene* (B).

Phosphorus-31 n.m.r. data for chloro(phenoxy)cyclotetraphosphazenes (Figure 2) show that δ[P(OPh)Cl] lies upfield of δ(PCl_2) but downfield of δ[$P(OPh)_2$]. The two-bond phosphorus–phosphorus couplings are in the range 25—79 Hz and reflect the dependence of the coupling constant on the electronegativity of the substituent attached to phosphorus.[19] The coupling constants involving $\equiv P(OPh)_2$ and $\equiv P(OPh)Cl$ are slightly less than that observed for chloropentaphenoxycyclotriphosphazene, $N_3P_3Cl(OPh)_5$ [$^{2}J(P-P)$ = 83.3 Hz].[20] A similar trend is noticed for the two-bond P · · · P couplings of amino-substituted cyclotri- and cyclotetra-phosphazenes.[21] The four-bond phosphorus–phosphorus couplings (Figure 2) are small and negative as found for the amino-substituted cyclotetraphosphazenes.[15,21]

The reaction of octachlorocyclotetraphosphazene (1) with phenol appears to be one of the most complex systems investigated in cyclophosphazene chemistry and a much larger number of isomeric products is formed than in comparable reactions with primary and secondary amines.[8–11,22] A non-geminal mode of substitution predominates in contrast to the exclusive geminal mode of replacement observed in the reaction of compound (1) with ethanethiol.[23] The mode of replacement in the latter system has been explained on the basis of Pearson's concept of ' hard ' and ' soft ' acids and bases.[24] The increased polarisability of the $\equiv PCl(SR)$ group compared with $\equiv PCl_2$ causes further thiolysis at the former to give a geminal derivative.

The phenoxide ion resembles t-butylamine,[8] benzylamine,[25] and *N*-methylaniline [10] in that both 2,4- and 2,6-substituted cyclotetraphosphazenes, $N_4P_4R_2Cl_6$, are formed in com-

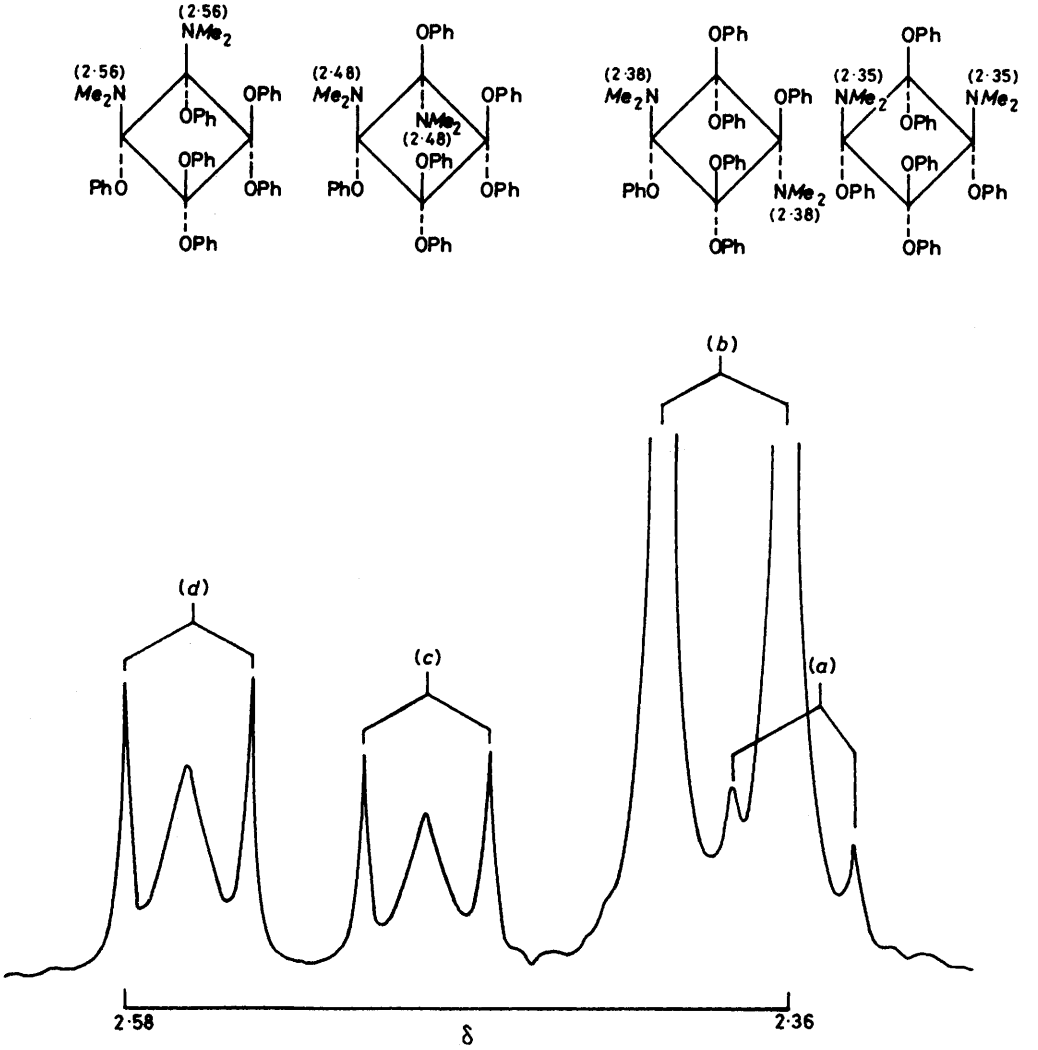

Figure 4. Proton n.m.r. (270 MHz, $CDCl_3$) spectrum (NMe region) of $N_4P_4(NMe_2)_2(OPh)_6$ (13), a mixture of (*a*) 2-*cis*-6, (*b*) 2-*trans*-6, (*c*) 2-*trans*-4, and (*d*) 2-*cis*-4 isomers

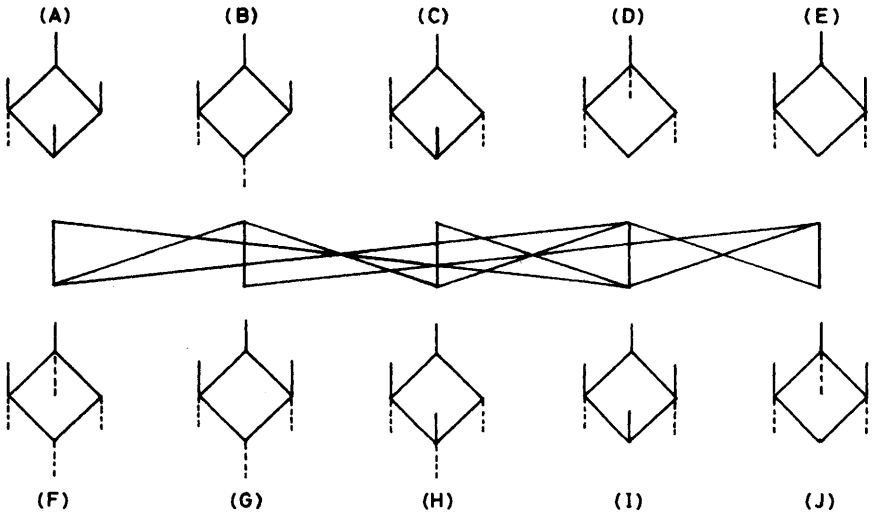

Figure 5. Possible substitution products from $N_4P_4Cl_8$ (1) at the pentakis and hexakis stages of chlorine replacement and their interrelationship (chlorine atoms not shown)

parable quantities at the bis stage of chlorine replacement. This observation may be contrasted with the almost exclusive formation of the 2-*trans*-6 (amino) derivative $N_4P_4Cl_6(NRR')_2$ when highly reactive amines, *e.g.* dimethylamine,[22] methylamine,[25] and ethylamine,[9] are used. The observed difference (2,4 *versus* 2,6 substitution) in the reactions of the amines has been explained on the basis of the relative ease of mesomeric electron release from the amino substituents.[10] The same explanation may be valid for the behaviour of phenoxide towards $N_4P_4Cl_8$; the electron-releasing power of the phenoxy-group is less than that of NMe_2, NHMe, or NHEt as shown by the substituent constants evaluated from basicity measurements.[26] At the hexakis stage, all four non-geminal isomers of $N_4P_4Cl_2(OPh)_6$ are formed with the 2-*trans*-6 isomer predominating (*ca.* 65%). In contrast, only one isomer of $N_4P_4Cl_2(NMe_2)_6$ has been isolated [22] from the reaction of $N_4P_4Cl_8$ (1) with dimethylamine; it also has the 2-*trans*-6 disposition of chlorine atoms.[27] An analogous compound was obtained in tiny yield from the reaction of compound (1) with *N*-methylaniline.[10] No hexa-aminodichlorocyclotetraphosphazenes are known with primary amino-substituents. Cross-linking reactions predominate in the attempted syntheses.[8,9]

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