Phosphorus–Nitrogen Compounds. Part XXVIII.[1] Some Reactions of 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene with Amines

By V. B. Desai, R. A. Shaw,* and B. C. Smith, Department of Chemistry, Birkbeck College (University of London), Malet Street, London, W.C.1

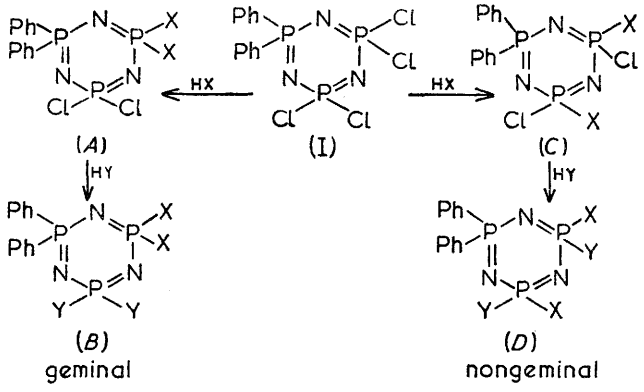
The replacement of chlorine in 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene by amino-, anilino-, and dimethylamino-groups has been investigated. A range of chloroamino- and mixed amino-derivatives has been prepared. Structures are assigned from their dimethylamino-^{1}H n.m.r. spectra, and are confirmed in some cases from their basicities. The replacement of chlorine by amino- and anilino-groups follows a geminal reaction pattern whereas replacement by dimethylamino-groups follows a nongeminal pattern. An erroneous structural assignment is corrected, and hence an apparent contradiction in the literature is resolved. The preparations of 2,2-bisanilino- and 2,2-bisdimethylamino-4,4,6,6-tetraphenylcyclotriphosphazatrienes are reported.

2,2,4,4-TETRACHLORO-6,6-DIPHENYLCYCLOTRIPHOSPHAZATRIENE (I) is prepared from the Friedel–Crafts reaction of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with benzene. The geminal arrangement of the phenyl groups has been established.[2,3]

Reactions of the geminal diphenyl-derivative, $N_3P_3Ph_2Cl_4$ (I), with ammonia and aniline were investigated by Bode, Bütow, and Lienau.[4] A bisamino-derivative, $N_3P_3Ph_2Cl_2(NH_2)_2$, m.p. 162—163°, and a bisanilino-derivative, $N_3P_3Ph_2Cl_2(NHPh)_2$, m.p. 193°, were isolated. Further reactions with aniline and ammonia respectively gave the same product, a bisaminobisanilino-derivative, $N_3P_3Ph_2(NH_2)_2(NHPh)_2$, m.p. 118°. It was assumed[4] that all three products contained like groups in geminal positions, as in the Scheme: (*A*), X = NH_2 or NHPh; (*B*), X = NH_2, Y = NHPh; although the evidence was compatible with a nongeminal pattern, (*C*) and (*D*), provided all compounds had either *cis*- or *trans*-arrangements of amino-groups. The bisamino-derivative, $N_3P_3Ph_2Cl_2(NH_2)_2$, m.p. 163°, was prepared subsequently by Becke-Goehring and John,[5] who stated that the amino-groups were in nongeminal positions, as in the Scheme: (*C*), X = NH_2. It was also stated[5,6] that the replacement of chlorine by arylamino-groups follows a geminal pattern. It is clear that not all of the foregoing assertions can be correct.

Reactions of the diphenyl derivative (I) with dimethylamine to give dimethylamino-derivatives, $N_3P_3Ph_2Cl_{4-n}(NMe_2)_n$ (n = 1, 2, and 4), were reported by Hills and Shaw,[7] but the structure of the bisdimethylamino-derivative was not established at that time. A re-investigation of the reactions of the diphenyl derivative (I) with ammonia, aniline, and dimethylamine is reported here. The compounds prepared during this work are listed in Table 1. The ^{1}H n.m.r. spectra of the dimethylamino-derivatives in carbon tetrachloride or deuteriochloroform, were measured and the chemical shifts (τ) and apparent phosphorus–hydrogen spin–spin coupling constants (J^*_{P-H}) for the dimethylamino-groups are recorded in Table 2.

The diphenyl derivative, $N_3P_3Ph_2Cl_4$ (I), reacts with an excess of ammonia to give the bisamino-derivative, $N_3P_3Ph_2Cl_2(NH_2)_2$ (II), and the hydrochloride, $N_3P_3Ph_2(NH_2)_4$,HCl (III), of the tetrakisamino-derivative. The



SCHEME. Replacement Patterns

bisamino-derivative (II) reacts with an excess of aniline to give the bisaminobisanilino-derivative, $N_3P_3Ph_2(NH_2)_2(NHPh)_2$ (X), and with an excess of dimethylamine to give the bisaminobisdimethylamino-derivative, $N_3P_3Ph_2(NH_2)_2(NMe_2)_2$ (XI), whose dimethylamino- ^{1}H n.m.r. spectrum [Figure (a)] exhibits one doublet without the 'hump' characteristic of long-range virtual coupling. This indicates a geminal structure, (*B*; X = NH_2, Y = NMe_2).[8] It is clear that the bisamino- (II) and bisaminobisanilino- (X) derivatives are identical to the compounds prepared previously,[4,5] and that these can be assigned geminal structures provided that a nongeminal to geminal rearrangement (so far unknown) has not taken place during aminolysis.

The diphenyl derivative (I) reacts with aniline to give mono- (IV), bis- (V), and tetrakis- (VI) anilino-derivatives. The monoanilino-derivative, $N_3P_3Ph_2Cl_3(NHPh)$ (IV), reacts with an excess of dimethylamine to give the anilinotrisdimethylamino-derivative,

[1] Part XXVII, M. Biddlestone and R. A. Shaw, *J. Chem. Soc.* (*A*), 1969, 178.
[2] H. Bode and H. Bach, *Ber.*, 1942, **75***B*, 215.
[3] R. A. Shaw and F. B. G. Wells, *Chem. and Ind.*, 1960, 1189; K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 1964, 121.
[4] H. Bode, G. Bütow, and G. Lienau, *Chem. Ber.*, 1948, **81**, 547.
[5] M. Becke-Goehring and K. John, *Angew. Chem.*, 1958, **70**, 657; *Z. anorg. Chem.*, 1960, **304**, 126.
[6] M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. Chem.*, 1959, **302** 103.
[7] K. Hills and R. A. Shaw, *J. Chem. Soc.*, 1964, 130.
[8] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1966, 1677.

$N_3P_3Ph_2(NHPh)(NMe_2)_3$ (XIV), whose dimethylamino-^{1}H n.m.r. spectrum shows three overlapping doublets of equal intensity characteristic of three different proton environments.

The bisanilino-derivative (V) reacts with an excess of ammonia to give the geminal bisaminobisanilino-derivative, $N_3P_3Ph_2(NH_2)_2(NHPh)_2$ (X), and with an excess of dimethylamine to give the bisanilinobisdimethylamino-derivative, $N_3P_3Ph_2(NHPh)_2(NMe_2)_2$ (XVII), whose dimethylamino- ^{1}H n.m.r. spectrum shows one doublet without any indication of long-range virtual coupling, which indicates a geminal structure,[8] (*B*; X = NHPh, Y = NMe_2) [*cf.* Figure (a)].

The diphenyl derivative (I) reacts with dimethylamine to give mono- (VII), bis- (VIII), and tetrakis- (IX) dimethylamino-derivatives. The dimethylamino-^{1}H n.m.r. spectra of the three products each consist of one doublet. The bisdimethylamino-derivative (VIII) exhibits virtual coupling characteristic of a nongeminal structure[8] (*C*; X = NMe_2) [*cf.* Figure (b)]. The chemical shift is only slightly greater than that of the monodimethylamino-derivative (VII), which indicates that the dimethylamino-groups in the bisdimethylamino-derivative (VIII) have a *trans*-nongeminal relationship. Attempts to isomerise this compound (VIII) to the *cis*-nongeminal isomer, by treatment with aluminium chloride in boiling 1,2-dichloroethane and with dimethylamine hydrochloride in boiling chloroform, were unsuccessful. The tetrakisdimethylamino-derivative (IX), which exhibits virtual coupling, has a significantly higher τ-value and a significantly lower J^*_{P-H} value.

TABLE 1

Diphenyl- and tetraphenyl-cyclotriphosphazatrienes

No.	Compound	M.p. (°c)	Structure
(I)	$N_3P_3Ph_2Cl_4$	95—97° [a]	2,2:4,4,6,6
(II)	$N_3P_3Ph_2Cl_2(NH_2)_2$	165 [b]	2,2:4,4:6,6
(III)	$N_3P_3Ph_2(NH_2)_4$,HCl	120 (decomp.)	2,2:4,4,6,6
(IV)	$N_3P_3Ph_2Cl_3(NHPh)$	118	2,2:4,4,6:6
(V)	$N_3P_3Ph_2Cl_2(NHPh)_2$	198 [c]	2,2:4,4:6,6
(VI)	$N_3P_3Ph_2(NHPh)_4$	204—205 [d]	2,2:4,4,6,6
(VII)	$N_3P_3Ph_2Cl_3(NMe_2)$	110 [e]	2,2:4,4,6:6
(VIII)	$N_3P_3Ph_2Cl_2(NMe_2)_2$	144 [f]	2,2:4,6:4,6(*trans*)
(IX)	$N_3P_3Ph_2(NMe_2)_4$	122 [g]	2,2:4,4,6,6
(X)	$N_3P_3Ph_2(NH_2)_2(NHPh)_2$	115 [h]	2,2:4,4:6,6
(XI)	$N_3P_3Ph_2(NH_2)_2(NMe_2)_2$	137 [i]	2,2:4,4:6,6
(XII)	$N_3P_3Ph_2(NH_2)_2(NMe_2)_2$	171	2,2:4,6:4,6
(XIII)	$N_3P_3Ph_2Cl_2(NHPh)(NMe_2)$	143	2,2:4,4:6:6
(XIV)	$N_3P_3Ph_2(NHPh)(NMe_2)_3$	122—123	2,2:4:4,6,6
(XV)	$N_3P_3Ph_2(NHPh)_2(NMe_2)_2$		2,2:4,6:4,6(*cis*)
(XVI)	$N_3P_3Ph_2(NHPh)_2(NMe_2)_2$		2,2:4,6:4,6(*trans*)
(XVII)	$N_3P_3Ph_2(NHPh)_2(NMe_2)_2$	153	2,2:4,4:6,6
(XVIII)	$N_3P_3Ph_2(NHPh)_3(NMe_2)$		2,2:4,4,6:6
(XIX)	$N_3P_3Ph_4Cl_2$	145 [j]	2,2,4,4:6,6
(XX)	$N_3P_3Ph_4(NHPh)_2$	242	2,2,4,4:6,6
(XXI)	$N_3P_3Ph_4(NMe_2)_2$	145 [k]	2,2,4,4:6,6

[a] Lit.,[2,3,5] 95°. [b] Lit.,[4,5] 163°. [c] Lit.,[4] 193°. [d] Lit.,[4] 198—199°. [e] Lit.,[7] 110°. [f] Lit.,[7] 143—144°. [g] Lit.,[5,7] 120°. [h] Lit.,[4] 118°. [i] Lit.,[5] 137°. [j] Lit.,[3] 142—143°. [k] Lit.,[7] 145°.

TABLE 2

Dimethylamino- ^{1}H n.m.r. data

No.	Compound	τ			J^*_{P-H}		Solvent
(VII)	$N_3P_3Ph_2Cl_3(NMe_2)$	7·29			16·2		*a*
(VIII)	$N_3P_3Ph_2Cl_2(NMe_2)_2$	7·30			17·2		*a*
(IX)	$N_3P_3Ph_2(NMe_2)_4$	7·48			11·6 †		*a*
(XI)	$N_3P_3Ph_2(NH_2)_2(NMe_2)_2$	7·42			11·4		*b*
(XII)	$N_3P_3Ph_2(NH_2)_2(NMe_2)_2$	7·41			13·4 †		*b*
(XIII)	$N_3P_3Ph_2Cl_2(NHPh)(NMe_2)$	7·37			12·8		*a*
(XIV)	$N_3P_3Ph_2(NHPh)(NMe_2)_3$	7·36	7·43	7·56	11·5 †	11·9 11·6 †	*a*
(XV)	$N_3P_3Ph_2(NHPh)_2(NMe_2)_2$	7·37			12·2		*a*
(XVI)	$N_3P_3Ph_2(NHPh)_2(NMe_2)_2$	7·47			12·4		*a*
(XVII)	$N_3P_3Ph_2(NHPh)_2(NMe_2)_2$	7·52			11·9		*a*
(XVIII)	$N_3P_3Ph_2(NHPh)_3(NMe_2)$	7·39			11·6		*a*
(XXI)	$N_3P_3Ph_4(NMe_2)_2$	7·53			11·1		*a*

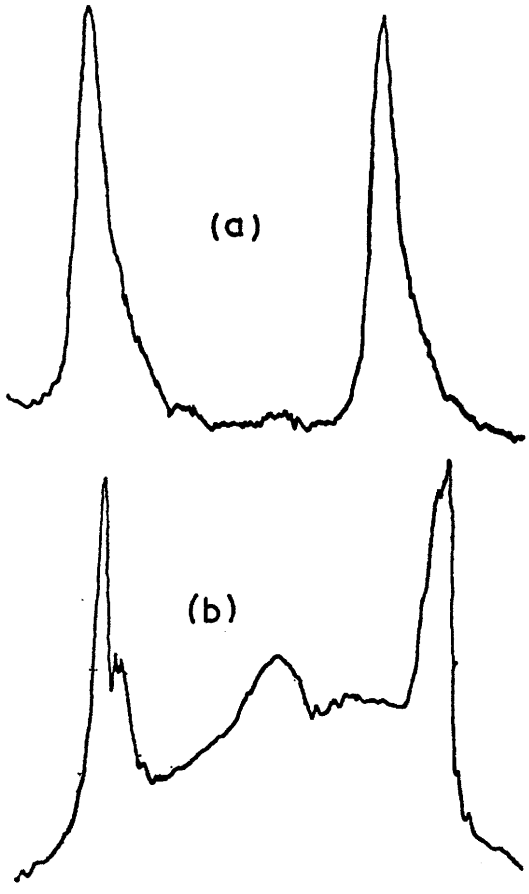
† Long-range virtual coupling observed.
[a] Carbon tetrachloride. [b] Deuteriochloroform.

The bisdimethylamino-derivative (VIII) reacts with an excess of ammonia to give the bisaminobisdimethylamino-derivative, $N_3P_3Ph_2(NH_2)_2(NMe_2)_2$ (XII), whose dimethylamino-^{1}H n.m.r. spectrum [Figure (b)], consists of one doublet with long-range virtual coupling characteristic of a non-geminal structure, (*D*; X = NMe_2, Y = NH_2). The J^*_{P-H} value is significantly higher than that of its geminal isomer (XI).

The monodimethylamino-derivative (VII), reacts with an excess of aniline under comparatively vigorous conditions to give the anilinodimethylamino-derivative, $N_3P_3Ph_2Cl_2(NHPh)(NMe_2)$ (XIII), whose dimethyl-

amino-^{1}H n.m.r. spectrum shows one doublet, without virtual coupling. The low J^*_{P-H} value confirms that the two dimethylamino-groups have a geminal relationship.

The *trans*-nongeminal bisdimethylamino-derivative (VIII) reacts with an excess of aniline to give a mixture



The dimethylamino- ^{1}H n.m.r. spectra of isomeric bisaminobis-dimethylamino-derivatives:
(a) 2,2:4,4:6,6-$N_3P_3Ph_2(NH_2)_2(NMe_2)_2$ (XI) and
(b) 2,2:4,6:4,6-$N_3P_3Ph_2(NH_2)_2(NMe_2)_2$ (XII)

the analysis of which suggests that it contains bisanilino-bisdimethylamino-derivatives. The dimethylamino-^{1}H n.m.r. spectrum shows two overlapping doublets with virtual coupling, the chemical shifts of which are consistent with the presence of *cis*- (XV) and *trans*- (XVI) nongeminal isomers of composition $N_3P_3Ph_2(NHPh)_2(NMe_2)_2$. Prolonged reaction with aniline causes the replacement of a dimethylamino- by an anilino-group. The dimethylamino- ^{1}H n.m.r. spectrum of the crude reaction product shows a third doublet the chemical shift of which is that expected from the trisanilinomonodimethylamino-derivative (XVIII).

[9] D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *J. Chem. Soc.*, 1965, 2804; D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1831; D. Feakins, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1968, 10; *J. Chem. Soc.* (*A*), in the press.

The geminal arrangement of the phenyl groups in 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene (XIX) has been established.[3] Reactions with aniline and dimethylamine give the tetraphenylbisanilino- and tetraphenylbisdimethylamino-derivatives, $N_3P_3Ph_4(NHPh)_2$ (XX) and $N_3P_3Ph_4(NMe_2)_2$ (XXI) respectively. The dimethylamino-^{1}H n.m.r. spectrum of the latter (XXI) shows a doublet without virtual coupling [*cf.* Figure (a)], with low J^*_{P-H} and high τ-values, characteristic of a geminal arrangement of dimethylamino-groups.

The basic strengths in nitrobenzene of a number of cyclotriphosphazatrienes [9] are recorded in Table 3.

TABLE 3

Basic strengths of some cyclotriphosphazatrienes

	Compound	$pK'_{a,1}$
(I)	$N_3P_3Ph_2Cl_4$	< -6.0
(II)	$N_3P_3Ph_2Cl_2(NH_2)_2$	0.0
(IV)	$N_3P_3Ph_2Cl_3(NHPh)$	< -6.0
(V)	$N_3P_3Ph_2Cl_2(NHPh)_2$	-2.7
(VI)	$N_3P_3Ph_2(NHPh)_4$	$+1.7$
(VII)	$N_3P_3Ph_2Cl_3(NMe_2)$	-5.8
(VIII)	$N_3P_3Ph_2Cl_2(NMe_2)_2$	-4.0
(IX)	$N_3P_3Ph_2(NMe_2)_4$	$+6.2$
(XIII)	$N_3P_3Ph_2Cl_2(NHPh)(NMe_2)$	-2.0
(XX)	$N_3P_3Ph_4(NHPh)_2$	$+1.6$
(XXI)	$N_3P_3Ph_4(NMe_2)_2$	$+3.8$
(XXII)	$N_3P_3Ph_6$	$+1.2$
(XXIII)	$N_3P_3(NHPh)_6$	$\sim+1.6$

The monodimethylamino-derivative (VII) is a stronger base than the monoanilino-derivative (IV); whose $pK'_{a,1}$ value is too low to be measured by this method. The tetrakisdimethylamino-derivative (IX) is a stronger base than the tetrakisanilino-derivative (VI) the $pK'_{a,1}$ value of which is close to that of hexaphenylcyclotriphosphazatriene (XXII) and hexakisanilinocyclotriphosphazatriene (XXIII). However, the basicity of the bisdimethylamino-derivative (VIII) is lower than that of the bisamino- (II), bisanilino- (V), or anilinodimethylamino- (XIII) derivatives. This provides supporting evidence that the bisdimethylamino-derivative has a nongeminal structure and that the other three compounds (II), (V), and (XIII) have geminal arrangements of amino-groups. As expected, the geminal tetraphenylbisdimethylamino-derivative (XXI) is more basic than the geminal tetraphenylbisanilino-derivative (XX).

The three amines investigated here react with the diphenyl derivative (I) and with hexachlorocyclotriphosphazatriene to give bisamino-derivatives, $N_3P_3Ph_2Cl_4X_2$ and $N_3P_3Cl_4X_2$, respectively, in which the amino-groups have similar dispositions: geminal ($X = NH_2$ [10] or NHPh [11]) or nongeminal ($X = NMe_2$).[12] This is not always the case. For example, the compounds isolated

[10] E. T. McBee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, 1966, **5**, 450; W. Lehr, *Z. anorg. Chem.*, 1967, **350**, 18; R. Keat and R. A. Shaw, unpublished results.
[11] V. B. Desai, R. A. Shaw, and B. C. Smith, unpublished results.
[12] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215; R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.

TABLE 4

Preparation of aminocyclotriphosphazatrienes

	Phosphazene		Amine					Products							
No.	(g.)	(mmole)		(g.)	(mmole)	Solvent	Temp.	Time (days)	No.	(%)	No.	(%)	No.	(%)	No. (%)
(I)	8·59	19·9	NH_3	Excess		$CHCl_3$	−78°	3	(II)	36	(III)	5			
(I)	8·59	19·9	NH_3	Excess		$CHCl_3$	−78	0·1	(II)	85					
(I)	2·10	4·9	NH_2Ph	0·90	9·7	C_6H_6	160	7	(I)	16	(IV)	18	(V)	25	(VI) 14
(I)	5·00	11·6	NH_2Ph	4·30	46·2	C_6H_6	160	7	(I)	27	(IV)	7	(V)	25	(VI) 2
(I)	5·00	11·6	NH_2Ph	6·50	69·9	C_6H_6	160	7	(I)	17	(IV)	4	(V)	30	(VI) 6
(I)	3·00	7·0	$NHMe_2$	0·63	14·0	C_6H_6	110	1	(VII)	92					
(I)	3·35	7·8	$NHMe_2$	1·40	31·1	C_6H_6	110	1	(VII)	11	(VIII)	67			
(I)	2·50	5·8	$NHMe_2$	1·60	35·6	C_6H_6	110	1	(VII)	2	(VIII)	5	(IX)	50	
(I)	2·57	6·0	$NHMe_2$	Excess		C_6H_6	110	1	(IX)	83					
(II)	0·50	1·3	NH_2Ph	Excess		$C_6H_5{\cdot}CH_3$	140	7	(X)	22					
(II)	0·26	0·7	$NHMe_2$	Excess		C_6H_6	110	1	(XI)	67					
(IV)	0·56	1·1	$NHMe_2$	Excess		C_6H_6	110	1	(XIV)	85					
(V)	1·02	1·9	NH_3	Excess		$CHCl_3$	140	1	(X)	62					
(V)	0·98	1·8	$NHMe_2$	Excess		C_6H_6	110	1	(XVII)	84					
(VII)	0·86	1·9	NH_2Ph	Excess		C_6H_6	140	7	(XIII)	31					
(VIII)	0·13	0·3	NH_3	Excess		$CHCl_3$	110	1	(XII)	50					
(VIII)	0·43	1·0	NH_2Ph	Excess		$C_6H_5{\cdot}CH_3$	140	7	(XV)		(XVI)				
(VIII)	2·00	4·5	NH_2Ph	Excess		$C_6H_5{\cdot}CH_3$	140—180	7	(XV)		(XVI)		(XVIII)		
(XIX)	1·90	3·7	NH_2Ph	Excess		$C_6H_5{\cdot}CH_3$	170	1	(XX)	15					
(XIX)	1·00	1·9	$NHMe_2$	Excess		C_6H_6	120	1	(XXI)	77					

TABLE 5

Analysis of aminocyclotriphosphazatrienes

	Found (%)					Required (%)			
No.	C	H	Cl	N	Formula	C	H	Cl	N
(II)	37·1	3·5	18·2	17·7	$C_{12}H_{14}Cl_2N_5P_3$	36·8	3·6	18·1	17·9
(III)	37·6	5·4	8·7	24·6	$C_{12}H_{19}ClN_7P_3$	37·0	4·9	9·1	25·2
(IV)	44·5	3·6	21·8	11·6	$C_{18}H_{16}Cl_3N_4P_3$	44·3	3·3	21·8	11·5
(V)	52·7	4·2	13·4	13·2	$C_{24}H_{22}Cl_2N_5P_3$	53·0	4·1	13·0	12·9
(VI)	65·7	5·3		14·8	$C_{36}H_{34}N_7P_3$	65·7	5·2	0·0	14·9
(VII)	38·4	3·9	23·9	12·9	$C_{14}H_{16}Cl_3N_4P_3$	38·2	3·7	24·25	12·75
(VIII)	42·5	5·1	16·0	15·5	$C_{16}H_{22}Cl_2N_5P_3$	42·9	4·9	15·8	15·6
(IX)	51·7	7·6		21·35	$C_{20}H_{34}N_7P_3$	51·6	7·3	0·0	21·1
(X)	56·65	5·3		19·7	$C_{24}H_{26}N_7P_3$	57·0	5·2	0·0	19·4
(XI)	46·75	6·7		23·7	$C_{16}H_{26}N_7P_3$	46·9	6·4	0·0	23·95
(XII)	47·1	6·4		23·4	$C_{16}H_{26}N_7P_3$	46·9	6·4	0·0	23·95
(XIII)	49·4	4·8		14·2	$C_{20}H_{22}Cl_2N_5P_3$	48·8	4·5	14·3	14·1
(XIV)	55·9	6·6		18·6	$C_{24}H_{34}N_7P_3$	56·1	6·6	0·0	19·1
(XV) and (XVI)	57·7	6·5		16·8	$C_{28}H_{34}N_7P_3$	59·9	6·1	0·0	17·5
(XVII)	59·4	6·0		17·8	$C_{28}H_{34}N_7P_3$	59·9	6·1	0·0	17·5
(XX)	68·2	5·1		10·6	$C_{36}H_{32}N_5P_3$	69·1	5·1	0·0	11·2
(XXI)	63·1	5·9		13·1	$C_{28}H_{32}N_5P_3$	63·3	6·0	0·0	13·1

from similar reactions with ethylamine have geminal-$N_3P_3Ph_2Cl_2(NHEt)_2$ [9] and nongeminal-$N_3P_3Cl_4(NHEt)_2$ [13] structures respectively. We have shown elsewhere [14] that, in at least some systems, it is the nature of the nucleophiles rather than that of the substituents, which determines the structure of the products. The results in this paper are in keeping with this. The dimethylamino-derivative, $N_3P_3Ph_2Cl_3NMe_2$ (VII), reacts with aniline to give the anilinodimethylamino-derivative (XV) the two amino-groups of which have a geminal relationship.

EXPERIMENTAL

A solution of hexachlorocyclotriphosphazatriene (104·4 g., 0·3 mole) in benzene (500 ml.) was added to a mixture of triethylamine (91·2 g., 0·9 mole) and aluminium chloride (306 g., 2·3 mole) in benzene (450 ml.). The stirred mixture was boiled under reflux (48 hr.), cooled, and hydrolysed with cold dilute hydrochloric acid. The benzene layer was dried ($CaSO_4$), and the solvent was removed by means of a rotary film evaporator. Recrystallisation of the product from light petroleum (b.p. 40—60°) gave 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene (I) (106·8 g., 83%). Recrystallisation of the residue from methylene chloride–light petroleum (b.p. 60—80°) (2 : 3) gave 2,2,4,4-tetraphenyl-6,6-dichlorocyclotriphosphazatriene (XIX) (6·6 g., 4%).

The methods of preparation of the amino-derivatives are summarised in Table 4. The general procedures are as before.[12] The analytical data are recorded in Table 5.

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[13] R. N. Das, R. A. Shaw, and B. C. Smith, unpublished results.

[14] R. Keat and R. A. Shaw, *Angew. Chem. Internat. Edn.*, 1968, **7**, 212; R. A. Shaw, *Chem. and Ind.*, 1967, 1737.