Phosphorus–Nitrogen Compounds. Part XLI.[1] Reactions of Hexachlorocyclotriphosphazatriene with Dibenzylamine and Benzylamine: the Importance of Steric Effects. Isolation of a Stable Chlorodibenzylaminotetrakisdimethylamino-derivative

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Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, reacts with dibenzylamine to give two dibenzylamino-derivatives, $N_3P_3Cl_{6-n}[N(CH_2Ph)_2]_n$ (n = 1 or 2), and with benzylamine to give benzylamino-derivatives, $N_3P_3Cl_{6-n}(NHCH_2Ph)_n$ [n = 1, 2 (two isomers), 4, or 6]. Dimethylamino-derivatives, $N_3P_3Cl_{6-n-m}[N(CH_2Ph)_2]_n(NMe_2)_m$ [n = 1, m = 1 (two isomers), 4, or 5; n = 2, m = 1 or 2)] and $N_3P_3Cl_{6-n-m}(NHCH_2Ph)_n(NMe_2)_m$ [n = 1; m = 1 (two isomers); n = 2, m = 4, (two isomers)] have been prepared. The structures of these derivatives are deduced from n.m.r. spectroscopy. The role of steric effects in the reactions of $N_3P_3Cl_6$ with bulky nucleophiles, particularly in the isolation of the stable penta-aminomonochloro-derivative, $N_3P_3Cl[N(CH_2Ph)_2](NMe_2)_4$, is discussed.

We have recently described some reactions of phenylphosphonic dichloride and phenylphosphonothioic dichloride with dibenzylamine.[2] The reactions are complex because the bulkiness of dibenzylamine permits competitive solvolysis reactions. Compounds containing two dibenzylamino-groups attached to phosphorus were not obtained. Also, dealkylation reactions occur in the case of phenylphosphonothioic dichloride. We have now extended this study to the chlorocyclotriphosphazatriene system in order to observe the effect of a bulky secondary amine on the replacement pattern. The stereochemistry of some mixed amino-derivatives containing dibenzylamino- and dimethylamino-groups is also discussed.

RESULTS AND DISCUSSION

The reaction of dibenzylamine with hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (I), gave only two derivatives. The monodibenzylamino-compound, $N_3P_3Cl_5[N(CH_2Ph)_2]$ (II), was obtained in diethyl ether and the bisdibenzylamino-compound, $N_3P_3Cl_4[N(CH_2Ph)_2]_2$ (III), in chloroform. The preparation of higher substituted derivatives was attempted using various solvents (boiling toluene, xylene, methyl cyanide, or dioxan) and also sealed tubes at elevated temperatures. In every case substitution of the cyclotriphosphazatriene ring did not exceed the bis stage. It is clear that steric factors influence the reaction as the polar deactivation of the cyclotriphosphazatriene ring by two dibenzylamino-groups is undoubtedly small. The reaction of $N_3P_3Cl_6$ (I) with another bulky secondary amine, dicyclohexylamine,[3] or with triphenylmonophosphazene,[4] $Ph_3P{=}NH$, also terminates at the bis stage of replacement, $N_3P_3Cl_4R_2$ [R = $N(C_6H_{11})_2$ and $NPPh_3$].

The importance of steric factors in this system can be demonstrated by preparing derivatives of the dibenzylamino-compounds (II) and (III). Treatment of the mono-compound (II) with dimethylamine in toluene at 75—80 °C gave the monochloromonodibenzylaminotetrakisdimethylamino-derivative, $N_3P_3Cl[N(CH_2Ph)_2](NMe_2)_4$ (IV), and under more forcing conditions (sealed tube, 110 °C), the monodibenzylaminopentakisdimethylamino-derivative, $N_3P_3[N(CH_2Ph)_2](NMe_2)_5$, (V). Similar experiments with the bis-compound (III) yielded a monodimethylamino-compound, $N_3P_3Cl_3[N(CH_2Ph)_2]_2(NMe_2)$ (VI), and a bisdimethylamino-compound, $N_3P_3Cl_2[N(CH_2Ph)_2]_2(NMe_2)_2$ (VII). Even when sealed tubes were used, the relative yield of compound (VII) was very small compared to that of compound (VI). In contrast, complete replacement of the four remaining chlorine atoms of the bis-compound (III) by the smaller methoxide anion proceeded easily in boiling benzene to give the bisdibenzylaminotetramethoxy-derivative, $N_3P_3[N(CH_2Ph)_2]_2(OMe)_4$ (VIII). The compounds are listed in Table 1.

^{1}H N.m.r. data for compounds (II)—(VIII) are included in Table 2. The methylene protons of the dibenzylamino-groups and the methyl protons of the dimethylamino (or methoxy) groups appeared as doublets because of coupling to the nearby phosphorus nucleus. Humps of considerable intensity were often observed between the sharp outer lines of the doublets. This phenomenon (long-range virtual coupling) is a prominent feature of the n.m.r. spectra of many cyclophosphazene derivatives.

In cyclophosphazene chemistry secondary amines (*e.g.* dimethylamine,[5] diethylamine,[6] piperidine,[7] or pyrrolidine[8]) show an overall preference for non-geminal replacement (*i.e.*, further reaction takes place preferentially at a $\geqslant PCl_2$ rather than at a $\geqslant PCl{\cdot}NR_2$ group), although substantial quantities of the geminal tris compounds, $N_3P_3Cl_3R_3$ (R = NMe_2, NEt_2, or pip), can be obtained. Hence, it seems probable that compound (III) has a non-geminal structure. Support for

[1] Part XL, S. N. Nabi, R. A. Shaw, and C. Stratton, *J.C.S. Dalton*, 1975, 588.
[2] J. D. Healy, R. A. Shaw, B. C. Smith, C. P. Thakur, and M. Woods, *J.C.S. Dalton*, 1974, 1286.
[3] S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 1961, 872.
[4] M. Biddlestone and R. A. Shaw, *J.C.S. Dalton*, 1973, 2740.
[5] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215; R. Keat, S. K. Ray, and R. A. Shaw, *ibid.*, p. 7913.
[6] W. Lehr and N. Rosswag, *Z. anorg. Chem.*, 1974, **406**, 221; D. Lingley, R. A. Shaw, M. Woods, and Hon Sum Yu, unpublished work.
[7] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.
[8] A. A. Kropacheva and N. M. Kashnikova, *J. Gen. Chem.* (*U.S.S.R.*), 1965, **35**, 1978.

this assignment comes from: (*a*) the close similarity of the values of $^3J^*$(P–H) for compounds (II) and (III); (*b*) the complexity of the ^{31}P n.m.r. spectrum {the chemical shifts of the phosphorus nuclei were very similar, which suggests the presence of $\geqslant$PCl[N(CH$_2$Ph)$_2$] groups [9]}; and (*c*) the absence of mononuclear phosphorus compounds containing two dibenzylamino-groups.[2] Other bisamino-derivatives formed in substantial amounts from the reaction of (I) with secondary amines have *trans*-non-geminal structures.[5-7] At present we do not have any physical data which permits a definitive assignment of structure to derivative (III).

TABLE 1

Dibenzylamino- and benzylamino-cyclotriphosphazatrienes

Compound	M.p. (θ_c/°C)	Proposed structure
$N_3P_3Cl_5[N(CH_2Ph)_2]$ (II)	112°	
$N_3P_3Cl_4[N(CH_2Ph)_2]_2$ (III)	108	2,4,6,6:2,4
$N_3P_3Cl[N(CH_2Ph)_2](NMe_2)_4$ (IV)	102	2:2:4,4,6,6
$N_3P_3[N(CH_2Ph)_2](NMe_2)_5$ (V)	107	2:2,4,4,6,6
$N_3P_3Cl_3[N(CH_2Ph)_2]_2(NMe_2)$ (VI)	99	2-*cis*-4-*trans*-6:2,4:6
$N_3P_3Cl_2[N(CH_2Ph)_2]_2(NMe_2)_2$ (VII)	131	2-*cis*-4:2,4:6,6
$N_3P_3[N(CH_2Ph)_2]_2(OMe)_4$ (VIII)	100—105 (0.05 mmHg)	2,4:2,4,6,6
$N_3P_3Cl_4[N(CH_2Ph)_2](NMe_2)$ (IXa)	75	2-*trans*-4,6,6:2:4
(IXb)	77	2-*cis*-4,6,6:2:4
$N_3P_3Cl_5(NHCH_2Ph)$ (X)	61	
$N_3P_3Cl_4(NHCH_2Ph)_2$ (XIa)	70	2-*trans*-4,6,6:2,4
(XIb)	110	2,2,4,4:6,6
$N_3P_3Cl_2(NHCH_2Ph)_4$ (XII)	86	2,2:4,4,6,6
$N_3P_3(NHCH_2Ph)_6$ (XIII)	93	
$N_3P_3Cl_4(NHCH_2Ph)(NMe_2)$ (XIVa)	40	2-*trans*-4,6,6:2:4
(XIVb)	52	2-*cis*-4,6,6:2:4
$N_3P_3(NHCH_2Ph)_2(NMe_2)_4$ (XVa)	76	2-*trans*-4:2,4,6,6
(XVb)	83	2,2:4,4,6,6

TABLE 2

^{1}H N.m.r. data (60 MHz, CCl_4 solution)

Compound	τ(CH$_2$)	$^3J^*$(P–H) Hz	τ(N–H) [a]	τ(NMe$_2$)	$^3J^*$(P–H) Hz
(II)	5.78	15.0			
(III)	5.70	14.4			
(IV)	5.77 [b]	13.5		7.37, 7.47	11.4, 11.2
(V)	6.02	10.4		7.39, 7.42, 7.50	10.6, 11.0, 11.0
(VI)	5.68	13.4		7.27 [b]	16.6
(VII)	5.75	13.0		7.28,[b] 7.49 [b]	11.6, 11.6
(VIII)	5.82	10.8		6.38,[c] 6.49 [c]	11.6, 12.5
(IXa)	5.78	13.4		7.24 [b]	16.0
(IXb)	5.81	13.4		7.33 [b]	17.0
(X)	5.79	12.0	6.2		
(XIa)	5.85	12.0	6.1		
(XIb)	5.92 [b]	12.0	7.1		
(XII)	6.04	11.4	7.3		
(XIII)	6.08	10.2	7.1		
(XIVa)	5.81	11.6	6.4	7.29 [b]	17.0
(XIVb)	5.80	11.0	6.5	7.35 [b]	16.0
(XVa)	6.01	8.0	*d*	7.42, 7.48	11.6, 10.8
(XVb)	5.97 [b]	9.0	*d*	7.48	10.8

[a] Centre of broad band. [b] No virtual coupling. [c] O*Me*. [d] *ca.* 7.5, largely hidden by NMe$_2$ proton signal.

The ^{1}H n.m.r. spectrum of the methoxy-derivative (VIII) showed two doublets with split peaks in the ratio 1 : 1 in the methoxy-region of the spectrum (τ 6.38 and 6.49). Although the two observed methoxy-proton environments suggest a *trans* structure for compound (VIII), our experience of substituents with modest steric requirements (*e.g.* ethylamino [10]) is that different chemical environments are not necessarily resolved: a *cis* structure cannot entirely be discounted. The coupling constant, $^3J^*$(P–N–CH$_2$) for compound (VIII) is 10.8 Hz {$\geqslant$P-[N(CH$_2$Ph)$_2$](OMe) group} as compared with 14.4 Hz {$\geqslant$PCl[N(CH$_2$Ph)$_2$] group} for its precursor (III).

The dangers of inferring the structure of a precursor from data obtained for a derivative are well known. Inversion of configuration (either partial or total) often occurs during the synthesis of derivatives. A consideration of the structures of the two dimethylamino-derivatives of compound (III) clearly indicates the above dilemma. The ^{1}H n.m.r. spectrum of compound (VI) indicates that dimethylamine reacts at the $\geqslant$PCl$_2$ centre of the precursor (III): the dimethylamino-proton resonance appeared as a doublet without virtual coupling, $^3J^*$(P–H) 16.6 Hz (typical [5] for a $\geqslant$PCl·NMe$_2$ group). However, the chemical shift of this group (τ 7.27) suggests that the dimethylamino-group is *cis* to two chlorine atoms and hence, by implication, *trans* to *both* dibenzylamino-groups {*cf.* dimethylamino-chemical shifts of the isomers of $N_3P_3Cl_4[N(CH_2Ph)_2](NMe_2)$ [(IXa) and (IXb)] (Table 2) and of chlorodimethylamino-derivatives,[9] $N_3P_3Cl_{6-n}(NMe_2)_n$}.

The ^{1}H n.m.r. spectrum of compound (VII) indicates that both dimethylamino-groups are attached to the same phosphorus atom: *i.e.* $\geqslant$PCl[N(CH$_2$Ph)$_2$] groups are much less susceptible to nucleophilic attack by dimethylamine than either $\geqslant$PCl$_2$ or PCl·NMe$_2$. The values of $^3J^*$(P–N–CH$_3$) and $^3J^*$(P–N–CH$_2$) (11.6 and 13.0 Hz respectively) support the structural assignment. The dimethylamino-proton signals of compound (IXb) appeared as two overlapping doublets without virtual coupling in the ratio 1 : 1, *i.e.* two distinct environments. The most probable structure based solely on this data is one with a dimethylamino-group flanked by two chlorine atoms (τ 7.28) and the other group shielded by two benzylamino-groups (τ 7.49).

The *cis*-disposition of three bulky substituents (two dibenzylamino- and a dimethylamino-group) in (VII) is somewhat surprising if steric effects are very important. *cis* Structures have been assigned to the non-geminal tetra-amino-compounds $N_3P_3Cl_2R_4$ (R = NMe$_2$ or NC$_5$H$_{10}$), although *trans*-$N_3P_3Cl_2(NMe_2)_4$ can also be isolated in small quantities. However, in the case of the non-geminal diethylamino-isomers,[6] $N_3P_3Cl_2(NEt_2)_4$, the *trans*-isomer always predominates, presumably because diethylamine is more sterically demanding than

[9] R. Keat, personal communication.
[10] R. Das, R. A. Shaw, B. C. Smith, and M. Woods, *J.C.S. Dalton*, 1973, 709.

dimethylamine. Our assignment of structures for compounds (VI) and (VII) are based on dimethylamino-proton chemical shifts, the number of dimethylamino-environments, and the coupling constants. These criteria have previously been considered valid n.m.r. evidence for indicating the structures of many cyclophosphazene derivatives. However, we cannot entirely discount the possibility of significant distortion of the planar cyclotriphosphazatriene ring in derivatives containing several bulky substituents. In that case, the above arguments could be invalidated. Clearly, more derivatives of this type have to be studied in order to clarify the subtle balance between steric and other important factors.

Other evidence for classifying dibenzylamine as an exclusively non-geminal nucleophile in replacement reactions of chlorocyclophosphazenes is provided by the reaction of the mono-dimethylamino-compound $N_3P_3Cl_5(NMe_2)$ with two equivalents of the amine in boiling acetonitrile. Two products were obtained (in the ratio 1 : 1), (IXa) and (IXb). The dimethylamino-proton resonance appeared as a doublet with virtual coupling in the ^1H n.m.r. spectra of both compounds. The J^*(P–H) values of 16.0 (IXa) and 17.0 Hz (IXb) (Table 2) indicate that the dibenzylamino-group substitutes exclusively at a $\geqslant PCl_2$ centre. The increased shielding of the dibenzylamino-methylene protons and of the dimethylamino-protons in compound (IXb) [compared with compound (IXa)] is good evidence for assigning a *cis*-non-geminal structure to the former and a *trans*-non-geminal structure to the latter. The ready formation of the *cis* isomer (VII) indicates that steric crowding in mixed dimethylamino–dibenzylamino-compounds is less important than might have been expected.

The elemental analysis of compound (IV) indicates that it is a genuine penta-aminomonochloro-derivative. Its mass spectrum showed a molecular ion at *m/e* 542.2093 (calc. for $C_{22}H_{38}{}^{35}ClN_8P_3$: *m/e* 542.2121). The chlorine isotope pattern clearly indicates the presence of a single chlorine atom. The peak at *m/e* 507 $(M - 35)^+$ corresponds to $\{N_3P_3[N(CH_2Ph)_2](NMe_2)_3\}^+$. The ^1H n.m.r. spectrum of compound (IV) suggests that the four dimethylamino-groups are in geminal positions (4,4,6,6), *i.e.* the chlorine atom of the $\geqslant PCl[N(CH_2Ph)_2]$ group is the last to be displaced by further nucleophilic attack of dimethylamine. The dimethylamino-proton resonance appeared as two overlapping doublets in the ratio 1 : 1 with $^3J^*$(P–H) 11.4 and 11.2 Hz. If a $\geqslant P[N(CH_2Ph)_2](NMe_2)$ group is present in the molecule, four doublets in the ratio 1 : 1 : 1 : 1 are predicted and one of these doublets should have a $^3J^*$(P–H) value of *ca.* 15—16 Hz, typical of the $\geqslant PCl{\cdot}NMe_2$ group. The methylene proton resonance appeared as a doublet *without* virtual coupling [$^3J^*$(P–H) 13.5 Hz; *cf.* derivative (VIII), 13.4 Hz]. The n.m.r. evidence is internally consistent and compound (IV), is assigned the 2:2:4,4,6,6 structure.

Compound (IV) possesses unusual stability: *e.g.* it can be isolated by column chromatography, recrystallised, and stored for some time without appreciable decomposition. A recent paper [11] by Shvetsov-Shilovskii and Pitina described the preparation of penta-amino-derivatives, $N_3P_3Cl(NHR)(NMe_2)_4$ (R = Pr, Bu^n, and n-C_5H_{11}), from the reaction of $N_3P_3Cl_5(NHR)$ with Me_2NH in diethyl ether. It is suggested [11] that the chlorine atom is on the same phosphorus as a Me_2N group, *i.e.* a 2:4:2,4,6,6 structure. Analysis and preparation of the ethoxy-derivatives, $N_3P_3(NHR)(NMe_2)_4(OEt)$, indicates that the compounds are authentic penta-amino-derivatives, although it would be interesting to have supporting spectroscopic data. The general absence of penta-amino-compounds in direct aminolysis reactions of $N_3P_3Cl_6$ (I) has been noted by many authors: only the pentakisdimethylamino-compound,[12] $N_3P_3Cl(NMe_2)_5$, and the penta-aziridino-derivative [13] were satisfactorily characterised. It appears that compounds of this type can be isolated in some circumstances, particularly if one of the substituents is sufficiently bulky to protect the sole P–Cl bond from further nucleophilic attack. The relative inertness of the chlorine atom in a $\geqslant PCl[N(CH_2Ph)_2]$ group to attack by dimethylamine (or by water) presumably contributes to the unusual stability of compound (IV).

The dimethylamino-proton signal of the fully substituted derivative (V) [obtained only in a sealed tube reaction from compounds (II) or (IV)] occurred as three overlapping doublets in the ratio of 1 : 2 : 2. The value of $^3J^*$(P–N–CH_2) (10.4 Hz) decreased significantly [13.5 Hz for its precursor (IV)] with replacement of the chlorine atom in the $\geqslant PCl[N(CH_2Ph)_2]$ group by dimethylamine.

Mononuclear phosphorus compounds containing two benzylamino-groups are well known [*e.g.* $PhP(S)(NHCH_2Ph)_2$].[2] In contrast to dibenzylamine, benzylamine is not a nucleophile that is likely to give rise to steric problems. However, it is a primary amine with a reactivity that is attenuated considerably by the presence of the phenyl group. Hence, it was of interest to study the reaction of $N_3P_3Cl_6$ (I) with benzylamine and to compare the replacement pattern with that observed for other primary amines (both aliphatic and aromatic). For example, t-butylamine [14] and aniline [15] react with $N_3P_3Cl_6$ (I) to give products with geminal structures, although a minute amount of non-geminal $N_3P_3Cl_4(NHPh)_2$ can be isolated. Ethylamine [10] and isopropylamine [16] give rise to a more complex replacement pattern: non-geminal replacement is observed in the initial and geminal replacement in the latter stages.

[11] N. I. Shvetsov-Shilovskii and M. R. Pitina, *J. Gen. Chem.* (*U.S.S.R.*), 1971, **41**, 1028.
[12] P. Clare and D. B. Sowerby, *J. Inorg. Nuclear Chem.*, 1974, **36**, 729.
[13] J. Kobayashi, L. A. Chasin, and L. B. Clapp, *Inorg. Chem.*, 1963, **2**, 213.
[14] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 5032.
[15] V. B. Desai, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1970, 2023.
[16] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1966, 1677.

Methylamine [17] behaves similarly to ethylamine and isopropylamine in forming non-geminal bis isomers, $N_3P_3Cl_4(NHMe)_2$ (the geminal isomer is obtained only as a minor product).

The preparation of the derivatives $N_3P_3Cl_{6-n}(NHCH_2Ph)_n$ depends mainly on the reaction stoicheiometry and on the organic solvent employed. Five derivatives were characterised [$n = 1$, 2 (two isomers), 4, and 6; compounds (X)—(XIII), Table 1]. The mono compound (X) was obtained in reasonable yield (70%) in boiling diethyl ether. The bis isomer (XIa) was prepared in boiling chloroform. The reaction of six equivalents of benzylamine with $N_3P_3Cl_6$ (I) for 8 h in boiling toluene gave a second bis isomer (XIb) together with compounds (X) and (XIa) in the approximate ratio 2 : 4 : 5. Attempts to obtain a tris derivative from the above reaction were unsuccessful. A characteristic feature of the six-equivalent reaction is that the quantities of (X) and (XIa) diminished after prolonged heating under reflux and a sticky resinous material (m.p. >300 °C) was formed. The occurrence of resins and the absence of tris derivatives in the reaction of $N_3P_3Cl_6$ (I) with most primary aliphatic amines has been noted previously.[10] In this respect, benzylamine behaves as a typical primary amine.

The tetrabenzylamino-compound (XII) was obtained in poor yield from the reaction of $N_3P_3Cl_6$ (I) with eight equivalents of benzylamine in toluene: resinous materials were formed in copious quantities. The hexabenzylamino-compound (XIII) could only be obtained from a reaction with an excess of benzylamine in a sealed tube at 150 °C (yield 50%). This observation reflects the much poorer nucleophilic properties of benzylamine compared to primary amines such as methylamine and ethylamine, which give fully aminolysed derivatives under much less drastic reaction conditions.

Table 1 indicates the probable structures of the benzylamino-compounds, $N_3P_3Cl_{6-n}(NHCH_2Ph)_n$, and also of some benzylaminodimethylamino-derivatives, $N_3P_3(NHCH_2Ph)_n(NMe_2)_{6-n}$. The proposed structures are based mainly on ^1H n.m.r. spectroscopy (Table 2). The resonance of the methylene protons and also of the NH proton move upfield with increasing substitution of the cyclotriphosphazatriene ring (*cf.* ethylamino-derivatives [10]). An interesting feature of the n.m.r. data is that J^*(P–H) values for $N_3P_3Cl_{6-n}(NHCH_2Ph)_n$ derivatives ($n = 1$, 2, or 4) are almost identical: the degree of replacement and stereochemistry of the substituents is apparently less important than in most other aminocyclophosphazene systems.

A comparison of the ^1H n.m.r. data for the bis isomers (XIa) and (XIb) is particularly interesting. The methylene protons of compound (XIb) are much more shielded than those of compound (XIa); a similar trend can be noted for the N–H resonances. Indeed, the N–H resonance of compound (XIb) is at the same τ value as that of the hexakis compound (XIII). These trends and the absence of virtual coupling in the spectrum of compound (XIb) suggest that the bis isomers possess different structural features, *i.e.* compound (XIa) is non-geminal and compound (XIb) is geminal. Support for these assignments comes from ^{31}P n.m.r. spectra.[9] The spectrum of the geminal isomer (XIb) consists of two signals in the ratio 2 : 1, a doublet (in the $\geqslant PCl_2$ region of the spectrum) and a triplet. The spectrum of the non-geminal isomer (XIa) shows a complex overlap of lines because of the close similarity of the resonance positions of the ^{31}P nuclei of the $\geqslant PCl_2$ and $\geqslant PCl(NHCH_2Ph)$ groups.

The non-geminal structure of compound (XIa) can also be inferred from the ^1H n.m.r. spectrum of its dimethylamino-derivative (XVa). Two doublets with virtual coupling were observed (ratio 1 : 1) for the dimethylamino-protons, indicating a *trans*-non-geminal structure for derivative (XVa). A *trans*-non-geminal structure can also be assigned to compound (XIa), provided net inversion has not occurred during dimethylaminolysis. The main bis products formed in the reaction of $N_3P_3Cl_6$ (I) with methylamine, ethylamine, and isopropylamine are also believed to have *trans* structures. Similarly, the geminal structure of compound (XIb) is confirmed by the ^1H n.m.r. spectrum of its dimethylamino-derivative (XVb). One doublet was observed for the dimethylamino-protons and indicates the presence of only one environment [*cf.* *gem*-$N_3P_3(NHBu^t)_2(NMe_2)_4$].[14] The ^1H n.m.r. spectrum of the tetrakis derivative (XII) showed one doublet with virtual coupling, suggesting that only one methylene environment is present. This observation, taken in conjunction with the values of the chemical shifts of the methylene and N–H protons [almost identical to those of the hexakis compound (XIII)], indicates a geminal structure for compound (XII). This conclusion is not unexpected as all known tetrakis compounds, $N_3P_3Cl_2(NHR)_4$, with primary amino-substituents are also geminal in structure (*e.g.* refs. 10 and 14—16).

Reaction of pentachloromonodimethylaminocyclotriphosphazatriene, $N_3P_3Cl_5(NMe_2)$, with two equivalents of benzylamine in boiling diethyl ether gave two compounds of formula, $N_3P_3Cl_4(NHCH_2Ph)(NMe_2)$ [(XIVa) and (XIVb) in the ratio 5 : 2]. The ^1H n.m.r. spectrum of compound (XIVa) shows that benzylamine has reacted at a $\geqslant PCl_2$ group: the Me_2N doublet had $^3J^*$(P–H) 17.0 Hz. Compound (XIVb) is also non-geminal [$^3J^*$(P–H) 16.0 Hz] but the resonance position of the dimethylamino-protons was shifted upfield from that observed for compound (XIVa). The anticipated shielding of a *cis*-benzylamino-group would explain this observation and consequently we assign a *cis*-non-geminal structure to compound (XIVb) and a *trans*-non-geminal structure to compound (XIVa).

Reactions of $N_3P_3Cl_6$ (I) with ethylamine, isopropylamine, and t-butylamine were discussed [10] in Part XXXIV. The more reactive amines, ethylamine and isopropylamine, give rise to non-geminal products during the earlier stages of replacement (bis) and to

[17] W. Lehr, *Z. anorg. Chem.*, 1967, **352**, 27; C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1965, **4**, 890.

TABLE 3

Preparation of dibenzylamino- and benzylamino-cyclotriphosphazatrienes

Amount of phosphazatriene			Amount of amine[f]			Solvent				Yield		
	g	mmol		g	mmol		V/cm^3	θ_c/°C	t/h	g		%
(I)	5	14	$HN(CH_2Ph)_2$	5.7	28	Et_2O	150	35	3	3.9 *a*	(I)	
										1.3 *a*	(II)	24
						$CHCl_3$	100	60	3	1.3 *a*	(I)	
										1.76 *a*	(II)	32
				11.3	56		75		6	1.1	(I)	
										0.9 *b*	(II)	18
										2.7	(III)	26
				17.0	84		100		6	3.0 *a*	(III)	29
(II)	1	2	$HNMe_2$	1.8	40	PhMe	20	90	3	0.3 *b*	(II)	
										0.45 *b*	(IV)	40
	2	4		1.4	32		5	80 [c]	6	1.3	(IV)	60
	1	2		1.8	40			110 [c]	5	0.85	(V)	82
(III)	2	3	$HNMe_2$	0.9	20	$CHCl_3$	20	70 [c]	8	0.8 *a*	(III)	
										0.22 *a*	(VI)	10
				0.54	12	MeCN	5	100 [c]	72	0.9 *b*	(III)	
										0.27 *b*	(VI)	13
										0.15	(VII)	7
			NaOMe	0.55	10	PhH	50	75	1	1.25	(VIII)	65
$N_3P_3Cl_5(NMe_2)$	3	8	$HN(CH_2Ph)_2$	3.2	16	MeCN	50	80	1	0.2 *d*	(IXa)	
										0.2 *d*	(IXb)	
(I)	17.4	50	H_2NCH_2Ph	10.8	100	Et_2O	400	35	3	2.1	(I)	
										14.9 *a, b*	(X)	71
										1.0	(XIa)	5
	9	26		11.0	104		500		6	1.0 *a, e*	(I)	
										4.25 *a, e*	(XIa)	39
	5	14		9.3	86	PhMe	150	100	8	1.8	(X)	25
										2.3 *b, e*	(XIa)	32
										0.9	(XIb)	12
	2	6		5.3	49		100		8	0.02	(X)	
										0.05 *b, e*	(XIa)	<1
										0.03	(XII)	
				7.9	72		10	150 [c]	36	1.5	(XIII)	50
(XIa)	0.5	1	$HNMe_2$	1.8	40	$CHCl_3$	10	60	2	0.38	(XVa)	72
(XIb)	0.25	0.5	$HNMe_2$	1.8	40	$CHCl_3$	10	60	2	0.21	(XVb)	43
$N_3P_3Cl_5(NMe_2)$	1.1	3	H_2NCH_2Ph	0.64	6	PhMe	25	100	2	0.6 *b*	(XIVa)	50
										0.25 *b*	(XIVb)	21

[a] Fractional crystallisation. [b] Column chromatography (silica gel). [c] Sealed tube. [d] Preparative-scale t.l.c. on 500 mg of sample. [e] Unidentified resin was also obtained. [f] Benzylamine and dibenzylamine were initially added dropwise at *ca.* 0 °C, dimethylamine at −78 °C. Reaction mixtures were then heated at the stated temperature.

TABLE 4

Analytical data (%)

	Found				Calc.			
	C	H	Cl	N	C	H	Cl	N
$C_{14}H_{14}Cl_5N_4P_3$ (II)	33.2	2.7	34.8	11.1	33.1	2.8	34.9	11.0
$C_{28}H_{28}Cl_4N_5P_3$ (III)	50.3	4.3	21.2	10.6	50.3	4.2	21.2	10.5
$C_{22}H_{36}ClN_5P_3$ (IV)	48.4	7.2	6.7	20.5	48.6	7.1	6.5	20.6
$C_{24}H_{44}N_9P_3$ (V)	52.2	8.0		22.8	52.3	8.0	0.0	22.8
$C_{30}H_{34}Cl_3N_6P_3$ (VI)	53.1	5.0	15.6	12.3	53.1	5.0	15.7	12.4
$C_{32}H_{40}Cl_2N_7P_3$ (VII)	55.8	5.8		14.4	56.0	5.9		14.3
$C_{32}H_{40}N_5O_4P_3$ (VIII)	59.0	6.3		10.7	59.0	6.2	0.0	10.7
$C_{16}H_{20}Cl_4N_5P_3$ (IXa)	37.0	4.2		13.4	36.5	3.8		13.3
(IXb)	37.0	4.2		13.4	36.5	3.8		13.3
$C_7H_8Cl_5N_4P_3$ (X)	20.0	1.9	42.8	13.4	20.1	2.1	42.3	13.2
$C_{14}H_{16}Cl_4N_5P_3$ (XIa)	34.4	3.3	29.0	14.2	34.4	3.3	29.0	14.3
(XIb)	34.3	3.4	29.0	14.2	34.4	3.3	29.0	14.3
$C_{28}H_{32}Cl_2N_7P_3$ (XII)	53.9	5.3		15.6	53.3	5.1		15.5
$C_{42}H_{48}N_9P_3$ (XIII)	65.3	6.3		16.3	65.6	6.3	0.0	16.4
$C_9H_{14}Cl_4N_5P_3$ (XIVa)	25.1	3.3	33.0	16.2	25.3	3.3	33.0	16.4
(XIVb)	25.1	3.2		16.3	25.3	3.3	33.0	16.4
$C_{22}H_{40}N_9P_3$ (XVa)	50.8	7.8		23.7	50.5	7.6	0.0	24.1
(XVb)	50.2	7.3		23.9	50.5	7.6	0.0	24.1

geminal products at the tris (not isolated) and tetra stage. Less reactive amines, *i.e.* t-butylamine and aniline, give geminal products. Hypotheses based on hydrogen bonding were suggested to explain the ready formation of the geminal derivatives, $N_3P_3Cl_2R_4$ (R = Et, Pr^i, or Bu^t). The only major difference between benzylamine and *all other* primary amines is that substantial quantities of both geminal and non-geminal bis isomers can be isolated.

The reactions involving dibenzylamine show that steric effects need to be given more prominence than previously. (Comparison with other secondary amines is not particularly meaningful as only two chlorodibenzylamino-derivatives were obtained.) However, the major point of interest in steric effects is likely to be the relative importance of bulky groups already attached to the phosphazene ring and the simultaneous presence in the reaction medium of bulky reagents that are potential nucleophiles.

EXPERIMENTAL

Dibenzylamino- and benzylamino-cyclotriphosphazatrienes and their derivatives were prepared by standard methods (see, for example, refs. 3, 5, 7, 10, 15, and 16). A summary is given in Table 3. Analytical data are reported in Table 4. ^1H N.m.r. spectra were recorded with a Varian A-60D spectrometer.

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