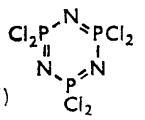
19. *Phosphorus–Nitrogen Compounds. Part VI.*[1] *Alkylamino- and Dialkylamino-derivatives of Geminal Phenylchlorocyclotriphosphazatrienes.*

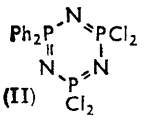
By K. Hills and R. A. Shaw.

Primary and secondary alkylamines react with 2,2,4,4-tetrachloro-6,6-diphenyl- and 2,2-dichloro-4,4,6,6-tetraphenyl-cyclotriphosphazatrienes to give partially and fully aminolysed derivatives. Two pairs of isomers of diaminodichlorodiphenylcyclotriphosphazatrienes have been characterised, and their structures are discussed. A tentative explanation for the absence of certain aminochlorophosphazenes is offered.

After detailed investigations [2] of the aminolysis of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (I),[2] and octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$,[3] use was made of the now available 2,2,4,4-tetrachloro-6,6-diphenyl-, $N_3P_3Ph_2Cl_4$ (II), and 2,2-dichloro-4,4,6,6-tetraphenyl-cyclotriphosphazatrienes,[1] $N_3P_3Ph_4Cl_2$ (III), for similar studies.

Prior studies of the ammonolysis and aminolysis of the diphenylphosphazene (II) led


(I)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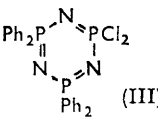
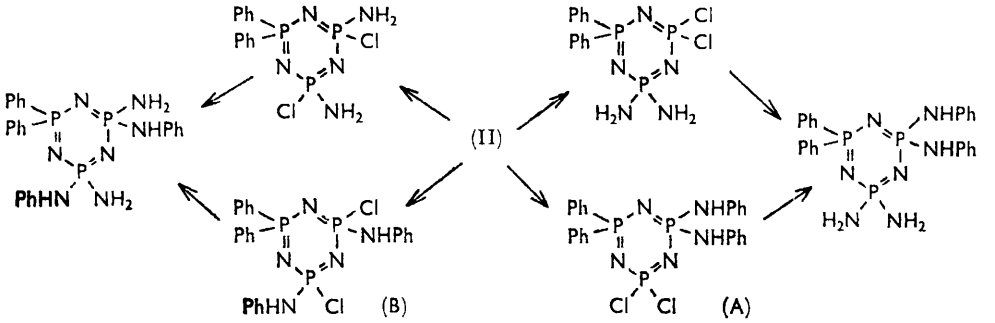

(III)

[1] Part V, Acock, Shaw, and Wells, preceding paper.
[2] Ray and Shaw, *Chem. and Ind.*, 1959, **53**; *J.*, 1961, 872.
[3] Ray, Shaw, and Smith, *J.*, 1963, 3236.

to di- and tetra-amino-derivatives.[4,5] Bode, Bütow, and Lienau [4] isolated the same diaminodianilino-6,6-diphenylcyclotriphosphazatriene, $N_3P_3Ph_2(NH_2)_2(NHPh)_2$, independently of the order in which the two different base residues (two at a time) were introduced; geminal reaction (A) was assumed throughout. Identical compounds would also be obtained if a non-geminal reaction pattern (B) is followed. More recently, Becke-Goehring and John [5] ascribed a non-geminal structure to the diaminodichloro-6,6-di-



phenyl compound, $N_3P_3Ph_2Cl_2(NH_2)_2$, reported by the earlier workers.[4] Reaction of this with aniline would lead to the non-geminal end-product $N_3P_3Ph_2(NH_2)_2(NHPh)_2$ in pattern (B). As it has been suggested that replacement of chlorine atoms by arylamino-residues is geminal,[5,6] ammonolysis of the dianilinodichloro-6,6-diphenyl derivative, $N_3P_3Ph_2Cl_2(NHPh)_2$ should lead to the end-product of scheme (A). Yet it has been reported (cf. above) that regardless of the order of introduction of the base residues the same end-product is obtained.[4] Not all the above can be easily reconciled and it therefore merits further study.

Our work with primary, NH_2R (R = Me, Et, Bu^t, Ph·CH_2, or cyclohexyl) and secondary alkylamines NHR_2 (R = Me, Et, or piperidino) has revealed a complex pattern. In reactions of the diphenyl derivative (II) mono-, di-, and tetra-amino-derivatives, $N_3P_3Ph_2Cl_{4-n}(NRR')_n$ (n = 1, 2, and 4), were isolated; in addition, monohydrochlorides of the last-mentioned, $N_3P_3Ph_2(NRR')_4$,HCl (R = Alk, R′ = H), were obtained from reactions with primary amines in the presence of an excess of the latter. All attempts to isolate triamino-derivatives, $N_3P_3Ph_2Cl(NRR')_3$ (R = Alk, R′ = H or R) under our reaction conditions were abortive. However, two crystalline isomer pairs of diamino-dichloro-6,6-diphenylcyclotriphosphazatriene, $N_3P_3Ph_2Cl_2(NRR')_2$, were obtained when the base was methylamine or piperidine. These can be distinguished, not only by their melting points and infrared spectra, but also by their basicities in nitrobenzene solution.[7] Thus, the diamino-isomers which were obtained in larger yields were about 2·5 pK_a' units weaker than the corresponding isomers obtained in smaller yields.

The less basic isomers were obtained from reactions with four equivalents of amine, usually accompanied by some monoamino-derivative, $N_3P_3Ph_2Cl_3(NRR')$. The more basic isomers were obtained by using six equivalents of amine in abortive attempts to make the triamino-compounds, $N_3P_3Ph_2Cl(NRR')_3$; other products obtained from the methylamine reaction included the tetra-amino-compound, $N_3P_3Ph_2(NHMe)_4$, and its monohydrochloride. The more basic isomers are formed under what appear to be more forcing conditions, and are usually accompanied by the fully aminolysed product. A similar observation was made in connection with the isomeric dichlorohexakisdimethyl-aminocyclotetraphosphazatetraenes, $N_4P_4Cl_2(NMe_2)_6$,[3] suggesting that in some aminolysis reactions at least, the more basic isomers are formed, and react further, less readily than

[4] Bode, Bütow, and Lienau, *Chem. Ber.*, 1948, **81**, 547.
[5] Becke-Goehring and John, *Angew. Chem.*, 1958, **70**, 657; *Z. anorg. Chem.*, 1960, **304**, 126.
[6] Becke-Goehring, John, and Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.
[7] Feakins, Last, Neemuchwala, and Shaw, unpublished results.

the less basic ones. In the light of our studies on the basicities of various phosphazenes,[7-9] we tentatively ascribe a non-geminal structure to the more prevalent, less basic, isomers and a geminal structure to the others. The occurrence of competing geminal and non-geminal reaction patterns has so far not been reported.

An aminotrichloro-6,6-diphenyl derivative, $N_3P_3Ph_2Cl_3(NRR')$, with a functional group in the side chain (NRR′ = 4′-methylpiperazino), has been synthesised and the purely organic tertiary amino-group converted into a hydrochloride and a methiodide.

From reactions of the dichlorotetraphenylphosphazene (III), monoamino-derivatives, $N_3P_3Ph_4Cl(NRR')$ (R = Alk, R′ = H or R), were occasionally isolated, although usually in relatively poor yields. Fully aminolysed compounds were obtained more readily and in good yields, although fairly vigorous reaction conditions were required. No hydrochloride formation in the presence of an excess of amine was observed in this series.

In general, in preparative work with a given amine, the ease of reaction decreases sharply in the series $N_3P_3Cl_6 > N_3P_3Ph_2Cl_4 > N_3P_3Ph_4Cl_2$. Preliminary kinetic work confirms this.[10] This parallels a similar decrease in hydrolytic susceptibility in this series.[1] Detailed investigations of several chlorophosphazene systems with a given reagent (*e.g.*, dimethylamine) led to the isolation of a number of partial replacement products, whilst the apparent absence of others was noted.[2,3] This coupled with results obtained from basicity studies [7-9] enables us to offer a tentative explanation of these observations.

One must attempt to explain the absence (under the stated reaction conditions) of triaminochlorodiphenyl derivatives, $N_3P_3Ph_2Cl(NRR')_3$, of penta-aminochlorocyclotriphosphazatrienes, $N_3P_3Cl(NRR')_5$ [2,11] [three apparent exceptions to this are reported in a recent review; [12] one of these is due to an error, the hydrochloride of the hexa-n-butylamino-derivative, $N_3P_3(NHBu^n)_6,HCl$,[13] being mistaken for the penta-aminochloro-compound $N_3P_3Cl(NHBu^n)_5$; for the other two no analytical figures or methods of preparation are given], and of hepta-aminochlorocyclotetraphosphazatetraenes,[3] $N_4P_4Cl(NRR')_7$, together with the isolation (albeit in low yields) of aminochlorotetraphenyl-derivatives, $N_3P_3Ph_4Cl(NRR')$.

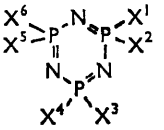
Three possible explanations of the above phenomena will be considered here, the two more probable ones being based on the differing electron supply of the various substituents to the phosphazene ring, the third, less likely one, on the known difference in the relative positions of the last two chlorine atoms in some of the systems discussed.

Basicity studies with nitrobenzene solutions [8] have shown the remarkably high contribution of alkylamino-groups to the base strength of phosphazenes. Thus hexa-aminocyclotriphosphazatrienes, $N_3P_3(NRR')_6$, and octa-aminocyclotetraphosphazatetraenes, $N_4P_4(NRR')_8$, have pK_a' values of 7·5—9·0,[7,8] tetra-aminodiphenyl derivatives, $N_3P_3Ph_2(NRR')_4$, values of 6·0—7·5,[7] and diaminotetraphenyl compounds, $N_3P_3Ph_4(NRR')_2$, values of 4·5—5·5 [7] (R = Alk, R′ = H or R). Fully phenylated derivatives, $N_3P_3Ph_6$ and $N_4P_4Ph_8$, possess pK_a' values in the region of 1·5—2·0,[9] whilst those of the chlorophosphazenes, $N_3P_3Cl_6$ and $N_4P_4Cl_8$, are very much below the present lower limit (−6·0) [9] of detection by our method.

The systems can be described by the general formula, $N_xP_xR''_yCl_z(NRR')_{2x-y-z}$ ($x = 3$ or 4; R″ = *e.g.*, Ph, R = Alk, R′ = H or R). In all these systems the dichloro-compounds ($z = 2$) can be readily isolated; the monochloro-derivatives ($z = 1$), however, have so far been obtained in only one of the above groups ($x = 3$; R″ = Ph; $y = 4$). It has also been shown that in nitrobenzene solution the parent alkylamines, NHRR′, are weaker bases (pK_a' 6·5—7·5) than the hexa-amino-,$N_3P_3(NRR')_6$ (IV)

[8] Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510.
[9] Feakins, Last, Neemuchwala, and Shaw, *Chem. and Ind.*, 1963, 164.
[10] Capon, Hills, and Shaw, *Proc. Chem. Soc.*, 1962, 390; and unpublished results.
[11] Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.
[12] Schmulbach in "Progress in Inorganic Chemistry," ed. Cotton, Interscience Publ., Inc., New York, 1962, Vol. IV, p. 366.
[13] Ray and Shaw, *Chem. and Ind.*, 1961, 1173.

(X^1—X^6 = NRR'), and octa-amino-derivatives, $N_4P_4(NRR')_8$, prepared from them, whilst they are of the same order of strength as the corresponding tetra-amino-diphenyl derivatives (IV; X^1—X^4 = NRR'; $X^5 = X^6$ = Ph), and somewhat stronger than the diaminotetraphenyl compounds (IV; $X^1 = X^2$ = NRR'; X^3—X^6 = Ph). Protonation at the ring-nitrogen atom has been already suggested,[8] and it is probable that it will be that ring-nitrogen atom which is flanked by the two phosphorus atoms carrying the four most electron-supplying substituents. Whilst the chlorine atom in the monochloro-compounds (V) will undoubtedly lower the basicity of all the ring-nitrogen atoms, it will probably affect the adjacent ring-nitrogen atoms more than the non-adjacent one, the latter, it is suggested, being the site of greatest basicity. It seems, therefore, possible that when the dichloro-precursors (VI) or (VII) have the penultimate chlorine atom replaced by an amino-group, the resultant monochloro-derivative (V) is now in some cases a sufficiently strong base to compete with the excess of amine for the proton liberated. If successful, there should be a percentage of a protonated monochloro-derivative, $N_3P_3ClX_5H^+$, which by analogy with nucleophilic substitution in nitrogen-containing aromatic compounds, would be very much more reactive towards further aminolysis than its conjugate base.[14] If the conjugate acid is also more reactive than the dichloro-precursor (VI) or (VII), this would account for the lack of success in obtaining monochloro-derivatives in two out of three six-membered ring series under the reaction conditions investigated.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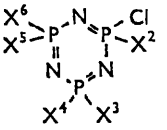
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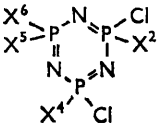
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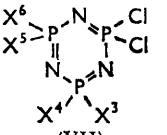
(VII)

With the tetraphenyl derivatives, the cumulative effect of four phenyl groups has considerably depressed the basicity of this type of molecule, and thus the proton affinity of the free amine is probably a good deal more favourable than that of the monochloro-compound (V) and hence allows the isolation of aminochloro-derivatives (V; X^2 = NRR', X^3—X^6 = Ph).

The above observations on the absence or presence of monochloro-derivatives are parallelled by the isolation of monohydrochlorides in the presence of an excess of amine, of the fully aminolysed primary alkylamino-derivatives, $N_3P_3(NRR')_6$,HCl [13] and $N_3P_3Ph_2(NRR')_4$,HCl, but not of those in the tetraphenyl series, $N_3P_3Ph_4(NRR')_2$ (R = Alk, R' = H).

Aminolysis studies with dimethylamine and tetrachlorodiphenoxyphosphazenes, $N_3P_3Cl_4(OPh)_2$,[15] have shown that monochloro-compounds, $N_3P_3R_2''Cl(NMe_2)_3$ (R'' = OPh) can be readily obtained. The common feature of all the monochloro-compounds isolated in the aminolysis experiments discussed is the relatively low basicity ($pK_a' \sim 4{\cdot}5$) of their fully aminolysed derivatives, *e.g.*, $N_3P_3Ph_4(NMe_2)_2$ and $N_3P_3(OPh)_2(NMe_2)_4$, compared with that of the parent amines ($pK_a' = 6{\cdot}5$—$7{\cdot}5$). Whilst obviously the basicity of the monochloro-compounds themselves would have been more revealing, insufficient are as yet available for a comprehensive study. Where the corresponding structures (IV) [$N_3P_3Ph_4(NRR')_2$] and (V) [$N_3P_3Ph_4Cl(NRR')$] are available and their basicities have been measured, the monochloro-compound (V) is weaker by about 5 pK_a' units than the fully aminolysed derivative (IV).

In the second of the more likely explanations, the measured basicities of the above systems are merely taken as indications of the changes in electron supply to the ring affecting the phosphorus as well as the nitrogen atoms. An increased electron supply

[14] Reinheimer, Gerig, Garst, and Schrier, *J. Amer. Chem. Soc.*, 1962, **84**, 2770, and references quoted therein; Chapman and Rees, *J.*, 1954, 1190.

[15] Dell, Fitzsimmons, and Shaw, presented at the XIXth Congress I.U.P.A.C., London, 1963.

with *e.g.*, increased replacement of chlorine atoms by amino-groups, may favour a change in mechanism from an S_N2 reaction to an ionisation process, which in some of the above-mentioned systems may cause the sixth chlorine atom to react faster than the fifth.

Whilst the third possible explanation based on the established difference in structure of some of the dichloro-precursors (VI) (X^2, X^4—X^6 = NMe_2) (non-geminal) and (VII) (X^3—X^6 = Ph) (geminal) cannot be at present dismissed, the above results make an explanation based on the increased reactivity of the conjugate acid or a change in mechanism (*e.g.*, ionisation) the more attractive, with the proviso that the basicity values were obtained for nitrobenzene solutions, whilst most of the preparative work was carried out in solvents such as ether or benzene.

It is probable that similar arguments can be applied to the, so far, less well-investigated eight-membered ring system.

Experimental

Ether, light petroleum (unless otherwise stated of b. p. 60—80°), and benzene were dried with sodium wire. The ratio, by volume of the light petroleum–chloroform mixtures used for recrystallisation was 9 : 1, unless otherwise stated. Hexachlorocyclotriphosphazatriene was recrystallised to constant m. p. from light petroleum. Triethylamine was purified by Swift's method.[16] Other amines were distilled from sodium. Silica gel (M.F.C. grade from Messrs. Hopkins and Williams) was used unactivated. Chromatographic separations were carried out on a column (30 × 2·5 cm.) containing about 45 g. of silica gel, with stepwise elution by the following solvent sequence: (*a*) light petroleum, (*b*) benzene, (*c*) ether, (*d*) chloroform, (*e*) methanol. The change from one solvent to the next was made through mixtures containing 2, 5, 10, 20, and 50% of the latter. The composition of the eluting solvent is indicated after the product obtained. 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene (II) and 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene (III) were prepared by a Friedel–Crafts reaction from hexachlorocyclotriphosphazatriene by the method of Acock, Shaw, and Wells.[1] M. p.s were determined on the hot-stage of a Reichert–Kofler polarising microscope. For the phosphazene hydrochlorides the m. p.s recorded represent the highest temperature at which any solid remained; sublimation was observed in every case at much lower temperatures.

2,2,4-*Trichloro*-4-*methylamino*-6,6-*diphenylcyclotriphosphazatriene*.—The diphenyl compound (II) (2·08 g., 0·00483 mole) in ether (25 ml.) was shaken for 5 hr. with an excess of aqueous methylamine. The organic layer was washed with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, dried (Na_2SO_4), and evaporated. The residue recrystallised from light petroleum–chloroform gave 2,2,4-*trichloro*-4-*methylamino*-6,6-*diphenylcyclotriphosphazatriene*, m. p. 151° (1·3 g., 63%) (Found: C, 36·4; H, 3·8; Cl, 25·7; N, 13·4. $C_{13}H_{14}Cl_3N_4P_3$ requires C, 36·7; H, 3·3; Cl, 25·0; N, 13·2%).

Dichlorobismethylamino-6,6-*diphenylcyclotriphosphazatriene*, *m. p.* 171°.—Anhydrous methylamine (0·8 ml., 0·02 mole) was added to a solution of the diphenyl derivative (II) (2·136 g., 0·00495 mole) in ether (40 ml.) at −78°, and the mixture set aside for 24 hr. The amine hydrochloride was filtered off and the filtrate evaporated. The solid residue was recrystallised from light petroleum–chloroform to give *dichlorobismethylamino*-6,6-*diphenylcyclotriphosphazatriene* m. p. 170—171° (0·51 g., 24%) (Found: C, 40·1; H, 4·7; Cl, 16·8; N, 16·6. $C_{14}H_{18}Cl_2N_5P_3$ requires C, 40·0; H, 4·3; Cl, 16·9; N, 16·7%). The mother-liquor yielded 1·31 g. of an oil, which was chromatographed. Elution gave starting material (30 mg., 2%) (benzene) and the monomethylamino-derivative, m. p. 151° (0·61 g., 29%) (benzene–ether 49 : 1).

Dichlorobismethylamino-6,6-*diphenylcyclotriphosphazatriene*, *m. p.* 103°, *and* 2,2,4,4-*Tetrakismethylamino*-6,6-*diphenylcyclotriphosphazatriene and its Hydrochloride*.—Anhydrous methylamine (1·6 ml., 0·04 mole) and compound (II) (2·85 g., 0·0066 mole) were allowed to react in ether at −78° in the manner described above. After 24 hr. the mixture was filtered and the precipitate extracted with chloroform, the residue being methylamine hydrochloride. From the chloroform extract, after recrystallisation from light petroleum–chloroform, 2,2,4,4-*tetrakismethylamino*-6,6-*diphenylcyclotriphosphazatriene hydrochloride*, m. p. 195° (0·81 g., 27%) was obtained (Found: C, 42·9; H, 5·8; Cl, 8·6; N, 21·2. $C_{16}H_{27}ClN_7P_3$ requires C, 43·1; H, 6·1; Cl, 8·0; N, 22·0%). 2,2,4,4-Tetrakismethylamino-6,6-diphenylcyclotriphosphazatriene, m. p. and mixed m. p. 174° (lit.,[5] 174°), was obtained in quantitative yield by boiling a chloroform

[16] Swift, *J. Amer. Chem. Soc.*, 1942, **64**, 115.

solution of the hydrochloride with an excess of triethylamine. The white solid from the ether mother-liquor was chromatographed. Starting material (50 mg., 2%) (benzene) and a new crystalline compound (benzene–ether 4 : 1) were obtained. This gave on recrystallisation from light petroleum an isomeric *dichlorobismethylamino*-6,6-*diphenylcyclotriphosphazatriene*, m. p. 102—103° (0·16 g., 6%) (Found: C, 39·3; H, 4·2; Cl, 16·4; N, 17·0%).

2,2,4-*Trichloro*-4-*ethylamino*- *and Dichlorobisethylamino*-6,6-*diphenylcyclotriphosphazatriene and* 2,2,4,4-*Tetrakisethylamino*-6,6-*diphenylcyclotriphosphazatriene Hydrochloride*.—The diphenyl compound (II) (2·03 g., 0·0047 mole) in ether (50 ml.) was treated with ethylamine (1·2 ml., 0·0188 mole) at −78° and set aside for 24 hr. Removal of the amine hydrochloride and evaporation of the filtrate gave a mixture of oil and crystals, which was extracted with light petroleum. The petroleum-insoluble oil was dissolved in ether (25 ml.), and pentane (6 ml.) was added. 2,2,4,4-*Tetrakisethylamino*-6,6-*diphenylcyclotriphosphazatriene hydrochloride* separated (0·201 g., 8·5%) and, recrystallised from light petroleum–chloroform (1 : 2), had m. p. 217° (Found: C, 46·9; H, 6·8; Cl, 6·9; N, 19·3; P, 19·1. $C_{20}H_{35}ClN_7P_3$ requires C, 47·9; H, 6·9; Cl, 7·1; N, 19·5; P, 18·5%). The monoethylamino-derivative, m. p. and mixed m. p. 96—97° (0·42 g., 20%), crystallised from the petroleum-soluble fraction. The mother-liquor was chromatographed, to yield the above monoethylamino-compound (0·26 g., 12%) (benzene) and *dichlorobisethylamino*-6,6-*diphenylcyclotriphosphazatriene*, m. p. 93° (recrystallised from light petroleum–chloroform) (0·55 g., 26%) (benzene–ether 19 : 1) (Found: C, 43·2; H, 4·9; N, 15·7. $C_{16}H_{22}Cl_2N_5P_3$ requires C, 42·9; H, 4·9; N, 15·6%).

2,2,4,4-*Tetrakisethylamino*-6,6-*diphenylcyclotriphosphazatriene and its Hydrochloride*.—The diphenyl compound (II) (1·55 g., 0·0036 mole) was treated with an excess of ethylamine (5 ml.) in boiling ether (1 hr.). The precipitate was filtered off and extracted with water, giving a residue of 2,2,4,4-tetrakisethylamino-6,6-diphenylcyclotriphosphazatriene hydrochloride, m. p. and mixed m. p. 217° (1·08 g., 60%). The ether solution yielded 2,2,4,4-*tetrakisethylamino*-6,6-*diphenylcyclotriphosphazatriene*, m. p. 121—122° (light petroleum, b. p. 80—100°) (0·443 g., 27%) (Found: C, 51·8; H, 7·4; N, 20·6; P, 20·6. $C_{20}H_{34}N_7P_3$ requires C, 51·6; H, 7·4; N, 21·1; P, 20·0%). The above hydrochloride was converted into the free aminophosphazene (m. p. and mixed m. p. 121°) by treatment with an excess of triethylamine in boiling chloroform.

6,6-*Diphenyl*-2,2,4,4-*tetrakis*-*t*-*butylaminocyclotriphosphazatriene and its Hydrochloride*.—A sealed tube containing a benzene solution (5 ml.) of diphenyl compound (II) (3·0 g., 0·0070 mole) and an excess of t-butylamine (7 ml.) was heated at 190° for 6 hr. Removal of the amine hydrochloride and of the solvent left an oil, which dissolved in hot aqueous alcohol from which were then deposited flakes of 6,6-*diphenyl*-2,2,4,4-*tetrakis*-*t*-*butylaminocyclotriphosphazatriene hydrochloride*, m. p. 290° (sealed tube) (3·2 g., 75%) (Found: C, 54·5; H, 8·3; Cl, 5·3; N, 15·5; P, 15·2. $C_{28}H_{51}ClN_7P_3$ requires C, 54·7; H, 8·4; Cl, 5·8; N, 16·0; P, 15·1%). The free tetra-amino-compound was not observed in this reaction. Boiling a chloroform solution of the hydrochloride with an excess of triethylamine gave a quantitative yield of 6,6-*diphenyl*-2,2,4,4-*tetrakis*-*t*-*butylaminocyclotriphosphazatriene*, m. p. 132—133° (from aqueous alcohol) (Found: C, 58·6; H, 8·7; N, 17·3. $C_{28}H_{50}N_7P_3$ requires C, 58·2; H, 8·7; N, 17·0%).

2,2,4-*Trichloro*-6,6-*diphenyl*-4-*piperidino*- *and Dichloro*-6,6-*diphenyldipiperidinocyclotriphosphazatriene, m. p.* 146°.—The diphenyl compound (II) (3·0 g., 0·007 mole) in ether (150 ml.) was treated with piperidine (2·37 g., 0·028 mole) in ether (50 ml.) at −78°. The residue, after removal of the amine hydrochloride and solvent, was dissolved in light petroleum (30 ml.). Fractional crystallisation gave starting material (0·31 g., 10%), the monopiperidino-derivative, m. p. and mixed m. p. 126° (1·13 g., 34%), and *dichloro*-6,6-*diphenyldipiperidinocyclotriphosphazatriene*, m. p. 145—146° (1·21 g., 33%) (Found: C, 50·1; H, 5·9; Cl, 13·6; N, 13·2. $C_{22}H_{30}Cl_2N_5P_3$ requires C, 50·0; H, 5·7; Cl, 13·4; N, 13·3%). Chromatography of the mother-liquor yielded the monopiperidino-derivative (0·110 g., 3·3%) (benzene–ether 49 : 1).

Dichloro-6,6-*diphenyldipiperidinocyclotriphosphazatriene, m. p.* 131°.—Piperidine (3·617 g., 0·043 mole) in ether (100 ml.) was allowed to react with an ether solution (200 ml.) of the diphenyl compound (II) (3·052 g., 0·0071 mole) in the manner described above. Removal of the amine hydrochloride and solvent left an oil which on chromatography yielded an isomeric *dichloro*-6,6-*diphenyldipiperidinocyclotriphosphazatriene*, m. p. 130—131° (from light petroleum–chloroform) (0·60 g., 16%) (benzene–ether 19 : 1) (Found: C, 50·2; H, 6·0; Cl, 13·4; N, 13·3%).

Dichlorobiscyclohexylamino-6,6-*diphenylcyclotriphosphazatriene and* 2,2,4,4-*Tetrakiscyclohexylamino*-6,6-*diphenylcyclotriphosphazatriene Hydrochloride*.—The diphenyl compound (II), (2·17 g., 0·0050 mole) in benzene (25 ml.) was boiled under reflux for 4 hr. with cyclohexylamine

(1·995 g., 0·020 mole). The amine hydrochloride was filtered off. The residue after evaporation of the solvent was extracted with light petroleum. *Dichlorobiscyclohexylamino-6,6-diphenylcyclotriphosphazatriene*, m. p. 144—145° (0·95 g., 34%), was isolated from the light petroleum extract (Found: C, 51·7; H, 6·0; Cl, 13·0; P, 16·7. $C_{24}H_{34}Cl_2N_5P_3$ requires C, 51·8; H, 6·2; Cl, 12·8; P, 16·7%). The petroleum-insoluble part of the product was recrystallised from light petroleum–chloroform (1 : 1), to give 2,2,4,4-*tetrakiscyclohexylamino*-6,6-*diphenylcyclotriphosphazatriene hydrochloride*, m. p. 243° (0·72 g., 20%) (Found: C, 60·1; H, 8·3; Cl, 4·8; N, 13·1. $C_{36}H_{59}ClN_7P_3$ requires C, 60·2; H, 8·3; Cl, 4·9; N, 13·7%).

2,2,4,4-*Tetrakiscyclohexylamino*-6,6-*diphenylcyclotriphosphazatriene and its Hydrochloride*.—The diphenyl derivative (II) (2·227 g., 0·0052 mole) was treated with an excess of cyclohexylamine (6 ml.) in boiling benzene (30 ml.) for 4 hr. The amine hydrochloride and solvent were removed and the product was worked up in the manner described immediately above. The aminophosphazene hydrochloride, m. p. and mixed m. p. 243° (1·0 g., 27%), was isolated together with the light petroleum-soluble 2,2,4,4-*tetrakiscyclohexylamino*-6,6-*diphenylcyclotriphosphazatriene*, m. p. 138° (1·23 g., 35%) (Found: C, 63·5; H, 8·6; N, 14·7; P, 14·2. $C_{36}H_{58}N_7P_3$ requires C, 63·4; H, 8·6; N, 14·4; P, 13·6%). The free aminophosphazene was also obtained from its hydrochloride by treatment with an excess of triethylamine in chloroform in the usual manner.

2,2,4-*Trichloro*-4-(4-*methylpiperazin*-1-*yl*)-6,6-*diphenylcyclotriphosphazatriene and its Hydrochloride and Methiodide*.—The diphenyl compound (II) (3·33 g., 0·0077 mole) in ether (75 ml.) was treated with 1-methylpiperazine (1·16 g., 0·116 mole) in ether (75 ml.) at −78°. The precipitate was filtered off and the solution diluted with more ether. Dry hydrogen chloride was bubbled through the solution, giving a precipitate of aminophosphazene hydrochloride, which was shaken with 0·1N-sodium hydroxide (100 ml.); the alkaline solution was extracted with ether. The free base was obtained by evaporating the ether solution and crystallising the oil from isopropyl acetate, to give 2,2,4-*trichloro*-4-(4-*methylpiperazin*-1-*yl*)-6,6-*diphenylcyclotriphosphazatriene*, m. p. 102·5—103·5° (0·95 g., 25%) (Found: C, 41·3; H, 4·4; Cl, 21·8; N, 14·2. $C_{17}H_{21}Cl_3N_5P_3$ requires C, 41·3; H, 4·3; Cl, 21·5; N, 14·2%). From this were prepared in quantitative yields the *hydrochloride*, m. p. 211—213° (Found: C, 38·5; H, 4·2; Cl, 26·2; N, 13·2. $C_{17}H_{22}Cl_4N_5P_3$ requires C, 38·4; H, 4·2; Cl, 26·7; N, 13·2%), and *methiodide*, m. p. 235° (decomp.) (Found: C, 34·4; H, 4·1; N, 11·7. $C_{18}H_{24}Cl_3IN_5P_3$ requires C, 34·0; H, 3·8; N, 11·0%).

2-*Chloro*-2-*methylamino*-4,4,6,6-*tetraphenylcyclotriphosphazatriene*.—Methylamine (0·3 ml., 0·0075 mole) was added to the tetraphenyl compound (III) (1·911 g., 0·0037 mole) in ether (40 ml.) at −78°, and the mixture set aside (18 hr.) and then filtered. The solid obtained from the filtrate was recrystallised from light petroleum–chloroform to give 2-*chloro*-2-*methylamino*-4,4,6,6-*tetraphenylcyclotriphosphazatriene*, m. p. 165—166° (0·51 g., 41%) (Found: C, 58·9; H, 4·9; N, 10·8. $C_{25}H_{24}ClN_4P_3$ requires C, 59·0; H, 4·8; N, 11·0%).

2-*Chloro*-2-*dimethylamino*-4,4,6,6-*tetraphenylcyclotriphosphazatriene*.—Dimethylamine (0·3 ml., 0·0046 mole) was caused to react with the tetraphenyl compound (III) (1·164 g., 0·0023 mole) in ether (30 ml.) at −78°. After 48 hr., the precipitate of amine hydrochloride was filtered off and the filtrate evaporated, leaving a solid residue. Crystallisation from light petroleum yielded two crystalline forms: (*a*) fine needles, m. p. 140—150°; (*b*) clusters, m. p. 130—140°. These were separated manually. Repeated recrystallisation of fraction (*a*) from light petroleum gave 2-*chloro*-2-*dimethylamino*-4,4,6,6-*tetraphenylcyclotriphosphazatriene*, m. p, 164—165° (0·105 g., 9%) (Found: C, 60·0; H, 5·0; Cl, 6·7; N, 10·75. $C_{26}H_{26}ClN_4P_3$ requires C, 59·7; H, 5·0; Cl, 6·8; N, 10·7%). Starting material, m. p. and mixed m. p. 142° (0·75 g., 65%) was recovered from fraction (*b*).

2-*Chloro*-2-*piperidino*-4,4,6,6-*tetraphenylcyclotriphosphazatriene*.—Piperidine (0·292 g., 0·0034 mole) in ether (10 ml.) was added with vigorous stirring to the tetraphenyl compound (III) (0·883 g., 0·0017 mole) in ether (25 ml.) at −78°, and the mixture was allowed to regain room temperature. The ether was removed by distillation at atmospheric pressure and benzene (30 ml.) was added. The solution was gently boiled under reflux (1 hr.), filtered, and evaporated, and the residue taken up in hot light petroleum. On cooling, 2-*chloro*-2-*piperidino*-4,4,6,6-*tetraphenylcyclotriphosphazatriene*, m. p. 175° (from light petroleum–chloroform) (0·145 g., 15%), was deposited (Found: C, 61·6; H, 5·3; Cl, 6·7; N, 10·0. $C_{29}H_{30}ClN_4P_3$ requires C, 61·9; H, 5·4; Cl, 6·3; N, 10·0%). Starting material, m. p. and mixed m. p. 142°, (0·22 g., 21%) was isolated from the mother-liquor by crystallisation.

Other Products.—Analogous reactions led to the *compounds* listed in Tables 1 and 2 in the conditions there outlined.

TABLE 1.

Amino- and aminochloro-derivatives of 2,2,4,4-tetrachloro-6,6-diphenyl- (II) and 2,2-dichloro-4,4,6,6-tetraphenyl-cyclotriphosphazatriene (III).

No.	Groups replacing Cl	Method *	Yield (%)	M. p.	Recryst. solvent †
		Compounds from (II).			
1	4-NHEt	Et_2O, at 0° ‡	84	97°	Pet.–$CHCl_3$
2	4-NMe_2	Et_2O, at 0° ‡	36	110	Pet.
3	4-Cyclohexylamino	Et_2O, b. p. ‡	27	111—112	,,
4	4-Piperidino	Et_2O, b. p. ‡	49	125—126	,,
5	$(NMe_2)_2$	Et_2O, at 0° §	60	143—144	Pet.–$CHCl_3$
6	$(NEt_2)_2$	C_6H_6, b. p., 24 hr.	31	66	Pentane
7	$(NHBu^t)_2$	C_6H_6, b. p., 24 hr.	30	108	Pet.
8	2,2,4,4-$(NMe_2)_4$	C_6H_6, 80°, 4 hr.¶	50	119—120 ‖	,,
9	2,2,4,4-$(NEt_2)_4$	C_6H_6, 180°, 6 hr.¶	61	76—77	Aq. EtOH
10	2,2,4,4-(Piperidino)$_4$	C_6H_6, b. p., 12 hr.	40	195—197	Pet.–$CHCl_3$
11	2,2,4,4-$(NH{\cdot}CH_2Ph)_4$	C_6H_6, b. p., 8 hr.	71	92·5	Pet.–C_6H_6
		Compounds from (III).			
12	2,2-$(NHMe)_2$	C_6H_6, 80°, 6 hr.¶	92	190—192	Pet.–$CHCl_3$
13	2,2-$(NMe_2)_2$	C_6H_6, 100°, 6 hr.¶	58	145	Pet.
14	2,2-$(NHEt)_2$	C_6H_6, 80°, 6 hr.¶	90	165	Pet.–$CHCl_3$
15	2-NEt_2	C_6H_6, 120°, 16 hr.¶	51	147·5	Pet.
16	2,2-$(NEt_2)_2$	C_6H_6, 190°, 16 hr.¶	35	122—123	,,
17	2,2-(Cyclohexylamino)$_2$	C_6H_6, b. p., 12 hr.	41	122—123	,,
18	2,2-(Piperidino)$_2$	C_6H_6, b. p., 12 hr.	60	180—181	Cyclohexane
19	2,2-$(NHBu^t)_2$	C_6H_6, 190°, 16 hr.¶	16	162—163	Aq. EtOH
20	2,2-$(NH{\cdot}CH_2Ph)_2$	C_6H_6, b. p. 12 hr.	73	133	Pet.

* Excess of amine used, unless otherwise stated. † Pet. = light petroleum of b. p. 60—80°. ‡ Two equivalents of amine used. § Four equivalents of amine used. ¶ Reaction carried out in a sealed tube. ‖ Lit.,[5] m. p. 120°.

TABLE 2.

Analyses of compounds in Table 1.

	Found (%)						Required (%)				
No.	C	H	Cl	N	P	Formula	C	H	Cl	N	P
1	37·8	3·8	24·2	13·5	—	$C_{14}H_{16}Cl_3N_4P_3$	38·2	3·7	24·2	12·7	—
2	38·1	3·5	24·4	13·5	—	,,	,,	,,	,,	,,	—
3	43·7	5·3	21·7	11·8	—	$C_{18}H_{22}Cl_3N_4P_3$	43·8	4·5	21·6	11·4	—
4	42·5	4·4	21·6	11·7	—	$C_{17}H_{20}Cl_3N_4P_3$	42·6	4·2	22·2	11·7	—
5	42·3	5·0	15·7	15·8	—	$C_{16}H_{22}Cl_2N_5P_3$	42·9	4·9	15·8	15·6	—
6	47·6	5·9	14·2	13·6	—	$C_{20}H_{30}Cl_2N_5P_3$	47·6	6·0	14·1	13·9	—
7	48·4	5·9	14·2	14·3	—	,,	,,	,,	,,	,,	—
8	52·0	7·7	—	—	—	$C_{20}H_{34}N_7P_3$	51·6	7·4	—	—	—
9	57·9	8·4	—	16·8	15·2	$C_{28}H_{50}N_7P_3$	58·2	8·7	—	17·0	16·1
10	61·6	8·1	—	15·4	—	$C_{32}H_{50}N_7P_3$	61·4	8·1	—	15·7	—
11	66·9	5·8	—	13·4	13·2	$C_{40}H_{42}N_7P_3$	67·3	5·9	—	13·7	13·0
12	61·7	5·7	—	13·7	—	$C_{26}H_{28}N_5P_3$	62·0	5·6	—	13·9	—
13	63·5	6·1	—	12·9	—	$C_{28}H_{32}N_5P_3$	63·3	6·1	—	13·2	—
14	63·2	6·0	—	12·1	18·1	,,	,,	,,	—	,,	—
15	61·0	5·7	6·5	10·1	—	$C_{28}H_{30}ClN_4P_3$	61·0	5·5	6·4	10·2	—
16	65·2	6·6	—	12·3	15·5	$C_{32}H_{40}N_5P_3$	65·4	6·9	—	11·9	15·8
17	68·3	7·1	—	11·0	—	$C_{36}H_{44}N_5P_3$	67·6	6·9	—	11·0	—
18	66·9	6·7	—	11·9	—	$C_{34}H_{40}N_5P_3$	66·8	6·6	—	11·5	—
19	65·0	6·8	—	11·8	—	$C_{32}H_{40}N_5P_3$	65·4	6·9	—	11·9	—
20	68·9	5·5	—	10·2	—	$C_{38}H_{36}N_5P_3$	69·6	5·5	—	10·7	—

We are indebted to Dr. F. B. G. Wells for the synthesis of the monopiperidino- and the 4-methylpiperazino-1-yl-phosphazenes. One of us (K. H.) gratefully acknowledges a maintenance grant from the D.S.I.R.

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[*Received, March 13th,* 1963.]