602. *Phosphorus–Nitrogen Compounds. Part IV.*[1] *Alkylamino- and Dialkylamino-derivatives of Cyclotetraphosphazatetraene.*

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Primary and secondary alkylamines react with octachlorocyclotetraphosphazatetraene to give aminocyclotetraphosphazatetraenes and the amine hydrochloride. Complete replacement of chlorine by a given amine occurs more readily than with hexachlorocyclotriphosphazatriene. Aminochlorocyclotetraphosphazatetraenes are obtained under suitable conditions. Dimethylamino-derivatives include several series of isomers.

Chlorophosphazenes react with primary or secondary amines to give aminophosphazenes and amine hydrochlorides.[2] Reactions of alkylamines with hexachlorocyclotriphosphazatriene were described in Part I of this series;[3] some reactions with octachlorocyclotetraphosphazatetraene are reported here.

[1] Part III, Miller and Shaw, preceding paper.
[2] Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.
[3] Ray and Shaw, *J.*, 1961, 872.

Replacement of all eight chlorine atoms occurs with stoicheiometric quantities or with an excess of an amine. The products are colourless crystalline solids, and melting points of octakisaminocyclotetraphosphazatetraenes derived from ten amines, *viz.*, NH_2Me, $NHMe_2$, NH_2Et, $NHEt_2$, NH_2Pr^n, NH_2Pr^i, NH_2Bu^n, NH_2Bu^i, NH_2Bu^s, and NH_2Bu^t, are recorded in the Table. Four of these compounds have been prepared previously.[4,5]

$$N_4P_4Cl_8 + 16NHRR' \longrightarrow N_4P_4(NRR')_8 + 8NH_2RR'Cl$$

(R = Alk, R' = R or H)

Octachlorocyclotetraphosphazatetraene reacts with many amines in boiling ether, but higher temperatures and pressures are required for complete replacement of chlorine by bulky groups such as t-butylamino and diethylamino. Complete replacement of chlorine atoms of hexachlorocyclotriphosphazatriene by reaction with secondary amines, NHR_2 (*e.g.*, R = Me or Et), and branched primary amines, NH_2R (*e.g.*, R = Pr^i, or Bu^s), occurs only on heating in an autoclave or sealed tube at fairly high temperatures;[3] and complete replacement by t-butylamine has not been achieved. It is clear that replacement reactions of chlorocyclotetraphosphazatetraenes are less susceptible to steric hindrance than similar reactions of cyclotriphosphazatrienes, perhaps because of puckering of the eight-membered ring. Kinetic studies[6] show that reaction of diethylamine with the first chlorine atom of octachlorocyclotetraphosphazatetraene is faster by a factor of 10^2—10^3 than similar reaction with the first chlorine atom of hexachlorocyclotriphosphazatriene.

A further difference between aminocyclotriphosphazatrienes and aminocyclotetraphosphazatetraenes concerns the formation of hydrochlorides. Hexakisaminocyclotriphosphazatriene hydrochlorides are formed in the presence of an excess of the parent primary alkylamine.[7] Octakisaminocyclotetraphosphazatetraenes have similar basic strengths in water and nitrobenzene,[8] but hydrochlorides have not been isolated in the presence of an excess of amine.

Reaction of chlorocyclotetraphosphazatetraene with limited amounts of dimethylamine, diethylamine, isopropylamine, or t-butylamine leads to partial replacement of the chlorine. The resulting aminochlorocyclotetraphosphazatetraenes are generally colourless and crystalline; melting points are recorded in the Experimental section. Hexachloro-bis-t-butylaminocyclotetraphosphazatetraene, m. p. 168°, appears to be different from the similar compound, m. p. 124°, reported previously.[9]

Reactions of dimethylamine have been investigated in considerable detail:

$$N_4P_4Cl_8 + 2n NHMe_2 \longrightarrow N_4P_4Cl_{8-n}(NMe_2)_n + n NH_2Me_2Cl$$

Ten partially replaced crystalline chlorodimethylaminocyclotetraphosphazatetraenes, including one mono-, one bis-, one tris-, three tetrakis-, two pentakis-, and two hexakis-dimethylamino-derivatives have been prepared by reaction with octachlorocyclotetraphosphazatetraene or lower chlorodimethylaminocyclotetraphosphazatetraenes. In addition, an oily fraction has been isolated whose analysis corresponds to that of a third pentakisdimethylamino-derivative. The three sets of isomers are the first prepared by aminolytic replacements in the cyclotetraphosphazatetraene series. Isomers can be distinguished by physical properties including m. p., infrared spectra, and, in some cases, pK values in nitrobenzene solution.[10] In the preparation of two isomeric dichlorohexakisdimethylaminocyclotetraphosphazatetraenes by reaction of octachlorocyclotetraphosphazatetraene with stoicheiometric quantities of dimethylamine, the more basic isomer [10]

[4] John, Moeller, and Audrieth, *J. Amer. Chem. Soc.*, 1961, **83**, 2608.
[5] Ray and Shaw, *Chem. and Ind.*, 1959, 53.
[6] Capon, Hills, and Shaw, *Proc. Chem. Soc.*, 1962, 390.
[7] Ray and Shaw, *Chem. and Ind.*, 1961, 1173.
[8] Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510.
[9] John, Moeller, and Audrieth, *J. Amer. Chem. Soc.*, 1960, **82**, 5616.
[10] Feakins, Last, Neemuchwala, and Shaw, unpublished results.

was obtained in lower yield. One hexachlorobisdimethylaminocyclotetraphosphazatetraene has been reported previously.[9] The compounds $N_4P_4Cl_7{\cdot}NMe_2$, $N_4P_4Cl_5(NMe_2)_3$, and $N_4P_4Cl_3(NMe_2)_5$ are the first cyclotetraphosphazatetraene derivatives of this type in which odd numbers of chlorine atoms have been replaced. Attempted preparations of the compound $N_4P_4Cl(NMe_2)_7$ were unsucessful.

Two main types of reaction pattern, geminal and non-geminal, have been considered in replacement reactions of chlorophosphazenes.[2,3] Proton magnetic resonance spectra of a series of compounds $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 1—4, 6) established that the pattern of reaction of dimethylamine with hexachlorocyclotriphosphazatriene is non-geminal.[3] Cyclotetraphosphazatetraenes have been studied less than cyclotriphosphazatrienes, and reaction schemes are more complicated. Possible isomeric structures are listed elsewhere.[2] There is no compelling evidence that a non-geminal reaction pattern is not followed with dimethylamine, but no attempt is made to assign configurations to the compounds reported here. A series of bis- and tetrakis-amino-derivatives of chlorocyclotetraphosphazatetraenes was prepared recently and the phosphorus nuclear magnetic resonance spectra of some of these compounds were reported.[4,9] Three bisarylamino-derivatives showing two triplet bands of equal intensity were assigned 2,6-bisamino-structures. Spectra of another six bisamino-derivatives of aliphatic and heterocyclic amines showed only one line, but non-geminal structures were assigned by analogy.[9] One line was observed in the spectra of two tetrakisamino-derivatives, and 2,4,6,8-tetrakisamino-structures were assigned to these compounds. Derivatives of cyclotriphosphazatrienes which are known to contain phosphorus in different chemical environments show only a single line,[11] and data compiled by Van Wazer and his co-workers [12] show that replacement by nitrogen of chlorine attached to phosphorus is particularly unfavourable for the observation of differences in chemical shifts.

Experimental

Octachlorocyclotetraphosphazatetraene, m. p. 124°, was recrystallised from light petroleum. Amines were purified by distillation from potassium hydroxide. Organic solvents were dried by conventional methods. Light petroleum was of b. p. 60—80°.

Preparation of Octakisaminocyclotetraphosphazatetraenes.—Quantities, yields, and analytical data are recorded in the Table. Four experimental procedures (*A*—*D*) are described below.

(*A*) An excess of methylamine reacted vigorously when added to a solution of octachlorocyclotetraphosphazatetraene in diethyl ether at room temperature. The colourless solid product was collected and extracted with boiling chloroform. Evaporation of the solvent and recrystallisation from chloroform–light petroleum gave colourless *octakismethylaminocyclotetraphosphazatetraene.*

(*B*) An excess of diethylamine was heated with octachlorocyclotetraphosphazatetraene in benzene (100 ml.) in an autoclave at 120° for 12 hr. Diethylamine hydrochloride was removed by filtration. Evaporation of the solvent and recrystallisation from aqueous methanol gave colourless *octakisdiethylaminocyclotetraphosphazatetraene.*

(*C*) Similar reaction with an excess of t-butylamine in a sealed tube at 140° for 16 hr. and recrystallisation from benzene–light petroleum gave colourless *octakis-t-butylaminocyclotetraphosphazatetraene.*

(*D*) Ether solutions of octachlorocyclotetraphosphazatetraene were boiled under reflux with an excess of other amines, and amine hydrochlorides were removed by filtration. *Octakisaminocyclotetraphosphazatetraenes* were obtained by evaporation of the solvent and recrystallisation from light petroleum.

Reactions of Octachlorocyclotetraphosphazatetraene.—(*a*) *With two equivalents of dimethylamine.* Anhydrous dimethylamine (0·9 g., 0·02 mole) was added to a solution of octachlorocyclotetraphosphazatetraene (4·64 g., 0·01 mole) in ether (100 ml.). Dimethylamine hydrochloride was filtered off and ether was evaporated *in vacuo*. The residual colourless oil was dissolved in

[11] Becke-Goehring, John, and Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.
[12] Van Wazer, Callis, Shoolery, and Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 5715; Van Wazer, "Phosphorus and its Compounds," Interscience Publ., Inc., New York, 1958, p. 47.

Octakisaminocyclotetraphosphazatetraenes.

	$N_4P_4Cl_8$			Aminophosphazene			
No.	(g.)	(mole)	Method		m. p.	(g.)	(%)
1	10·0	0·0216	*A*	$N_4P_4(NHMe)_8$	206° *	6·3	68
2	10·0	0·0216	*D*	$N_4P_4(NMe_2)_8$	237 (decomp.) †	9·9	86
3	23·2	0·0500	*D*	$N_4P_4(NHEt)_8$	116 ‡	22·0	83
4	46·4	0·1000	*B*	$N_4P_4(NEt_2)_8$	200	42·1	56
5	10·0	0·0216	*D*	$N_4P_4(NHPr^n)_8$	98 §	10·9	79
6	23·2	0·0500	*D*	$N_4P_4(NHPr^i)_8$	170	14·8	46
7	23·2	0·0500	*D*	$N_4P_4(NHBu^n)_8$	81 ¶	36·0	95
8	23·2	0·0500	*D*	$N_4P_4(NHBu^i)_8$	94	26·8	71
9	4·64	0·0100	*D*	$N_4P_4(NHBu^s)_8$	111	1·6	21
10	10·0	0·0216	*C*	$N_4P_4(NHBu^t)_8$	300 (decomp.)	1·1	7

	Found (%)					Required (%)			
No.	C	H	N	P	Formula	C	H	N	P
1	22·85	8·8	39·4	—	$C_8H_{32}N_{12}P_4$	22·9	7·7	40·0	29·6
2	36·9	8·7	31·3	23·3	$C_{16}H_{48}N_{12}P_4$	36·1	9·0	31·6	23·3
3	35·7	9·3	32·3	23·4	$C_{16}H_{48}N_{12}P_4$	36·1	9·0	31·6	23·3
4	50·9	10·5	21·5	16·45	$C_{32}H_{80}N_{12}P_4$	50·8	10·6	22·2	16·5
5	44·95	10·0	25·8	18·95	$C_{24}H_{64}N_{12}P_4$	44·7	10·0	26·1	19·2
6	43·6	9·4	26·4	—	$C_{24}H_{64}N_{12}P_4$	44·7	10·0	26·1	19·2
7	50·6	10·5	22·0	16·3	$C_{32}H_{80}N_{12}P_4$	50·8	10·6	22·2	16·5
8	50·8	10·9	22·1	16·3	$C_{32}H_{80}N_{12}P_4$	50·8	10·6	22·2	16·5
9	51·4	10·5	22·05	—	$C_{32}H_{80}N_{12}P_4$	50·8	10·6	22·2	16·5
10	50·05	10·4	22·2	—	$C_{32}H_{80}N_{12}P_4$	50·8	10·6	22·2	16·5

* Lit.,[4] m. p. 201°. † Cf. ref. 5. ‡ Lit.,[4] m. p. 122°. § Lit.,[4] m. p. 96°. ¶ Lit.,[4] m. p. 86°.

pentane (30 ml.) and left in a refrigerator for 12 hr. Crystals of octachlorocyclotetraphosphazatetraene (1·5 g.) were removed. The residual oil was eluted with light petroleum from a silica-gel chromatography column. Four fractions were obtained: (i) colourless crystals of octachlorocyclotetraphosphazatetraene (0·75 g.); (ii) colourless crystals mixed with oil (1·2 g.); (iii) a colourless oil which crystallised in a refrigerator in 48 hr.; recrystallisation from pentane gave *heptachlorodimethylaminocyclotetraphosphazatetraene* (0·95 g., 19%), m. p. 61° (Found: C, 5·4; H, 1·5; Cl, 52·05; N, 15·3; P, 26·5. $C_2H_6Cl_7N_5P_4$ requires C, 5·1; H, 1·3; Cl, 52·5; N, 14·8; P, 26·3%); (iv) colourless crystals (0·65 g., 14%), m. p. 160—165°; recrystallisation from pentane gave colourless crystals of hexachlorobisdimethylaminocyclotetraphosphazatetraene, m. p. 171° [lit.[9] m. p. 171° (sublimes)].

(*b*) *With four equivalents of dimethylamine.* Similar reaction of dimethylamine (1·8 g., 0·04 mole) with octachlorocyclotetraphosphazatetraene (4·64 g., 0·01 mole), and recrystallisation of the product from light petroleum, gave colourless hexachlorobisdimethylaminocyclotetraphosphazatetraene (2·7 g., 56%), m. p. and mixed m. p. 171° (Found: C, 10·2; H, 2·6; Cl, 43·9; N, 17·6. Calc. for $C_4H_{12}Cl_6N_6P_4$: C, 10·0; H, 2·5; Cl, 44·4; N, 17·5%).

(*c*) *With six equivalents of dimethylamine.* An aqueous solution of dimethylamine (100 ml., 0·13 mole) was added slowly to a solution of octachlorocyclotetraphosphazatetraene (10·0 g., 0·0216 mole) in ether (150 ml.). The mixture was stirred for ½ hr. and the ether layer was separated and dried (Na_2SO_4). Evaporation of the ether and recrystallisation of the product from pentane gave colourless *pentachlorotrisdimethylaminocyclotetraphosphazatetraene* (1·58 g., 15%), m. p. 91° (Found: C, 14·7; H, 3·5; Cl, 36·1; N, 20·0. $C_6H_{18}Cl_5N_7P_4$ requires C, 14·7, H, 3·7; Cl, 36·3; N, 20·0%) (correct carbon analyses of these aminochlorocyclophosphazapolyenes cannot always be obtained).

(*d*) *With eight equivalents of dimethylamine.* Reaction of dimethylamine (7·8 g., 0·173 mole) with octachlorocyclotetraphosphazatetraene (10·0 g., 0·0216 mole) in ether (200 ml.) gave a precipitate of dimethylamine hydrochloride which was removed and extracted with hot ether. The filtrate and the ether extract were concentrated to 100 ml. and left overnight in a refrigerator. Colourless crystals appeared, and recrystallisation from pentane gave *tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene* (5·75 g., 53%), m. p. 199—200° (Found: C, 19·45; H, 5·0; Cl, 29·0; N, 22·8. $C_8H_{24}Cl_4N_8P_4$ requires C, 19·3; H, 4·85; Cl, 28·5; N,

22·5%). Evaporation of the mother-liquor gave colourless crystals mixed with oil. Recrystallisation from pentane at 0° gave an isomeric *tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene* (1·95 g., 18%), m. p. 148° (Found: C, 19·8; H, 5·0; Cl, 28·6; N, 22·15%).

(*e*) *With ten equivalents of dimethylamine.* Similar reaction of dimethylamine (9·5 g., 0·216 mole) with octachlorocyclotetraphosphazatetraene (10·0 g., 0·0216 mole) in ether (250 ml.) gave a colourless oil. Trituration with pentane gave colourless crystals of tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene (0·57 g., 5·3%), m. p. and mixed m. p. 200°. Evaporation of pentane from the filtrate gave a colourless oil. Distillation gave two fractions: (i) an oil, b. p. 140—174°/0·6 mm.; (ii) an oil, b. p. 174°/0·6 mm., whose analysis on redistillation corresponded to that of *trichloropentakisdimethylaminocyclotetraphosphazatetraene* (1·2 g., 11·8%) (Found: C, 23·4; H, 6·1; Cl, 21·4; N, 23·3. $C_{10}H_{30}Cl_3N_9P_3$ requires C, 23·6; H, 5·9; Cl, 21·0; N, 24·95%). Fraction (i) was eluted from a chromatography column containing silica gel (40 g.) which had been heated at 160° for 24 hr. Three fractions were obtained: (*A*) light petroleum eluant, a colourless oil (1·9 g.) which gave colourless crystals when kept overnight in a refrigerator; recrystallisation gave an isomeric *tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene* (0·3 g., 2·8%), m. p. 103° (Found: C, 20·0; H, 4·9; Cl, 27·9; N, 22·2%); (*B*) light petroleum (90%)–benzene (10%) eluant, a pale yellow oil (0·5 g.), b. p. 174°/0·6 mm.; (*C*) benzene (95%)–chloroform (5%) eluant, a brown solid (0·4 g.), m. p. 113—140°. Recrystallisation of fraction (*C*) from light petroleum (b. p. 60—80°) gave colourless *trichloropentakisdimethylaminocyclotetraphosphazatetraene* (0·15 g., 1·3%), m. p. 146° (Found: C, 24·1; H, 6·4; Cl, 20·8; N, 25·6%).

(*f*) *With twelve equivalents of dimethylamine.* Similar reaction of dimethylamine (11·7 g., 0·26 mole) with octachlorocyclotetraphosphazatetraene (10·0 g., 0·0216 mole) in ether (200 ml.) gave crystals which, when redissolved in light petroleum (30 ml.) and kept in a refrigerator overnight, gave colourless crystals of *dichlorohexakisdimethylaminocyclotetraphosphazatetraene* (5·7 g., 51%), m. p. 168° (Found: C, 27·8; H, 6·85; Cl, 14·05; N, 27·2. $C_{12}H_{36}Cl_6N_{10}P_4$ requires C, 28·0; H, 7·0; Cl, 13·8; N, 27·2%). Evaporation of the filtrate and fractional crystallisation of the product from pentane gave an isomeric *dichlorohexakisdimethylaminocyclotetraphosphazatetraene* (1·45 g., 13%), m. p. 83° (Found: C, 27·7; H, 7·5; Cl, 13·4; N, 27·35%).

(*g*) *With fourteen equivalents of dimethylamine.* Dimethylamine (6·3 g., 0·14 mole) was added to a solution of octachlorocyclotetraphosphazatetraene (4·64 g., 0·01 mole) in ether (100 ml.). Dimethylamine hydrochloride was removed; evaporation of ether from the filtrate then gave colourless crystals mixed with oil. Recrystallisation from light petroleum gave octakisdimethylaminocyclotetraphosphazatetraene (1·9 g., 36%), m. p. and mixed m. p. 237° (decomp.). Evaporation of the solvent and recrystallisation of the residue from pentane gave dichlorohexakisdimethylaminocyclotetraphosphazatetraene (0·7 g., 13·5%), m. p. and mixed m. p. 83°.

Reaction of Tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene, m. p. 103°.—Similar reaction of dimethylamine (0·135 g., 0·003 mole) with tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene (0·75 g., 0·0015 mole), m. p. 103°, in ether (50 ml.) gave crystals mixed with oil. Recrystallisation from pentane gave trichloropentakisdimethylaminocyclotetraphosphazatetraene (0·15 g., 20%), m. p. and mixed m. p. 146°.

Reaction of Tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene, m. p. 200°.—Dimethylamine (0·27 g., 0·006 mole) was added slowly to a solution of tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene (1·5 g., 0·003 mole), m. p. 200°, in ether (150 ml.). Dimethylamine hydrochloride (0·09 g., 0·0011 mole) was removed, and ether was evaporated from the filtrate. Fractional crystallisation of the residue from pentane gave tetrachlorotetrakisdimethylaminocyclotetraphosphazatetraene (0·9 g., 60%), m. p. 200°, and an isomeric *trichloropentakisdimethylaminocyclotetraphosphazatetraene* (0·2 g., 13%), m. p. 99—99·5° (Found: C, 22·4; H, 5·8; Cl, 21·0; N, 22·05%).

Reaction of Dichlorohexakisdimethylaminocyclotetraphosphazatetraene, m. p. 168°.—Similar reaction of this phosphazene (2·0 g., 0·0039 mole) with dimethylamine (0·35 g., 0·0078 mole), m. p. 168°, in ether (50 ml.) gave dimethylamine hydrochloride which was removed. Colourless crystals obtained on evaporation of the filtrate gave octakisdimethylaminocyclotetraphosphazatetraene (0·7 g., 34%), m. p. 237° (decomp.), on recrystallisation from light petroleum. Dichlorohexakisdimethylaminocyclotetraphosphazatetraene (1·2 g., 60%), m. p. 168°, was recovered from the mother-liquor.

Tetrachlorotetrakisdiethylaminocyclotetraphosphazatetraene.—A solution of diethylamine (12·6

g., 0·173 mole) and octachlorocyclotetraphosphazatetraene (10·0 g., 0·216 mole) in ether was boiled under reflux for ½ hr., diethylamine hydrochloride was removed, and evaporation of the filtrate gave a colourless oil which crystallised at 0°. Recrystallisation from light petroleum gave *tetrachlorotetrakisdiethylaminocyclotetraphosphazatetraene* (3·4 g., 26%), m. p. 172° (Found: C, 31·45; H, 6·8; Cl, 22·8; N, 18·3. $C_{16}H_{40}Cl_4N_8P_4$ requires C, 31·5; H, 6·5; Cl, 23·3; N, 18·4%).

Tetrachlorotetrakisisopropylaminocyclotetraphosphazatetraene.—Similar reaction of isopropylamine (4·8 g., 0·08 mole) and octachlorocyclotetraphosphazatetraene (4·64 g., 0·1 mole) in ether (75 ml.) gave crystalline *tetrachlorotetrakisisopropylaminocyclotetraphosphazatetraene* (4·1 g., 74%), m. p. 187° (Found: C, 26·8; H, 6·1. $C_{12}H_{32}Cl_4N_4P_4$ requires C, 26·0; H, 5·8%).

Hexachlorobis-t-butylaminocyclotetraphosphazatetraene.—Similar reaction of t-butylamine (6·3 g., 0·0865 mole) and octachlorocyclotetraphosphazatetraene (10 g., 0·0216 mole) in ether (120 ml.) gave *hexachlorobis-t-butylaminocyclotetraphosphazatetraene* (4·6 g., 41%), m. p. 168° (Found: C, 18·4; H, 3·9. $C_8H_{20}Cl_6N_6P_4$ requires C, 17·9; H, 3·7%).

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