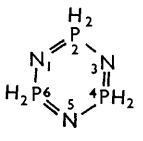
184. *Phosphorus–Nitrogen Compounds. Part I. Alkylamino- and Dialkylamino-derivatives of Cyclotriphosphazatriene.*

By S. K. Ray and R. A. Shaw.

Reaction of hexachlorocyclotriphosphazatriene with primary (Me—Bu^n) alkylamines results in complete aminolysis at or near room temperature. In similar circumstances branched alkylamines (Pr^i, Bu^i, Bu^s, Bu^t, cyclohexyl) yield partially substituted derivatives and higher temperatures are required for complete substitution. These effects are more pronounced with secondary amines (R in NHR_2 = Me, Et, Pr^n, Bu^n, Bu^i, Bu^s, cyclohexyl; piperidyl), and very bulky alkylamines failed to yield completely aminolysed compounds even under severe conditions. In reactions with dimethyl- and diethyl-amine, compounds $P_3N_3Cl_{6-n}(NR_2)_n$ were isolated with n = 1, 2, 3, 4, and 6. The stereochemistry of the ring system is discussed and structural assignments are made to some derivatives.

Nomenclature.—In this paper the hypothetical parent compound (I) is named cyclotriphosphaza-1,3,5-triene, with the numbering shown. Normally enumeration of the double bonds is omitted: Kekulé-type resonance is assumed. Substitution products from this parent are named by the usual methods of organic chemistry.



(I)

Although known since 1834,[1] phosphazenes have only lately been examined systematically. Until recently it was assumed [2,3] that replacement of chlorine in hexachlorocyclotriphosphazatriene occurred in geminal pairs although the only valid evidence related to two partially phenylated compounds [4] and few products had been identified where the chlorine had been partially or completely replaced.[2,5] Within the last year the isolation of products in which one [6] or three [7–10] chlorine atoms (as well as two, four, and six) had been replaced, and in particular the preparation by Becke-Goehring and John [8,9] of compounds containing both amino- and methylamino-groups, disproved the universality of pairwise replacement.

Nuclear magnetic resonance spectra of the protons in dimethylamino-derivatives,[11] and of phosphorus [9] in some other compounds, confirm the new reaction scheme proposed on chemical grounds. This proposal is that in reactions with some nitrogenous bases one chlorine on each phosphorus atom is replaced successively, and that the second chlorine atom of a pair is replaced only when no more geminal dichloro-groups are present.

Complete ammonolysis is relatively slow.[12] Although primary unbranched alkylamines (Me–Bu) react readily in ether at or near room temperature, to afford the hexasubstituted compound $P_3N_3(NHR)_6$, primary branched alkylamines (Pr^i, Bu^i, Bu^s, Bu^t, cyclohexyl) under similar conditions yield partially (usually tetra)substituted derivatives, and higher temperatures (boiling benzene, or 140—180° under pressure) are necessary for complete replacement, and from t-butylamine no product higher than the tetrasubstituted derivative could be obtained at all.

[1] Liebig, *Annalen*, 1834, **11**, 139.
[2] Cf. Audrieth, Steinman, and Toy, *Chem. Rev.*, 1943, **32**, 109.
[3] Bode, Bütow, and Lienau, *Chem. Ber.*, 1948, **81**, 547.
[4] Bode and Bach, *Ber.*, 1942, **75**, 215; Bode and Thamer, *Ber.*, 1943, **76**, 121.
[5] Cf. Steinman, Ph.D. Thesis, University of Illinois, 1942.
[6] Shaw, *Chem. and Ind.*, 1959, 412; Shaw, Conference on High Temperature Polymer and Fluid Research, Session VI, Inorganic Polymers, Dayton, Ohio, May 1959; Symposium on Macromolecules, Section IVB, Wiesbaden, October 1959.
[7] Ray and Shaw, *Chem. and Ind.*, 1959, 53.
[8] Becke-Goehring and John, *Angew. Chem.*, 1958, **70**, 657.
[9] Becke-Goehring, John, and Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.
[10] Audrieth, *Rec. Chem. Progr.*, 1959, **20**, 57; Bull, Ph.D. Thesis, University of Illinois, 1957.
[11] White, personal communication.
[12] Moureu and Rocquet, *Bull. Soc. chim. France*, 1936, **3**, 821; Audrieth and Sowerby, *Chem. and Ind.*, 1959, 748; Shaw, unpublished results.

These effects are more pronounced with secondary amines. Even dimethylamine yields, at room temperature, only a tetra-amino-compound and with most of the higher ones (Et, Pr^n, Bu^n, Bu^i, Bu^s, cyclohexyl) even the initial reaction in boiling ether is very slow. Complete substitution is achieved with dimethylamine and piperidine at 60—80°, but the others yield only partially (again usually tetra)substituted products. With diethylamine aminolysis was complete after 24 hours' heating at 150°, but with di-s-butylamine even under the most drastic conditions investigated over 95% of the starting material was recovered.

In a study with dimethyl- and diethyl-amine derivatives, $P_3N_3Cl_{6-n}(NR_2)_n$ were in each case obtained with $n = 1$, 2, 3, 4, and 6. (There were indications of isomeric compounds with NMe_2, $n = 4$, and with NEt_2, $n = 3$.)

The replacement is visualised as occurring in the stages: 2-mono, 2,4-di, 2,4,6-tri, 2,2,4,6-tetra, 2,2,4,4,6-penta, and 2,2,4,4,6,6-hexa. Proton magnetic resonance spectra of the compounds [11] in the dimethylamino-series confirm this (see Table). The mono-, di-, and tri-amino-compounds have only the amino-grouping $PCl{\cdot}NMe_2$ and give only one band. The hexa-amino-derivative, having only $P(NMe_2)_2$, gives only one, but a different band. The tetra-amino-compound, containing both groupings, shows both bands.

The reported aminocyclotriphosphazatrienes show a definite pattern. There are only two (oily) monosubstituted derivatives; this may be in part due to experimental difficulties, for there is a relatively small difference in the ease of reaction of the hexachloro- and monoamino-compounds described by us and unless great care is taken the reaction proceeds readily to the disubstituted stage. Nine disubstituted examples are available. The number of triamino-derivatives is only five, but growing, and ten tetra-amino-com-

Proton magnetic resonance spectra.

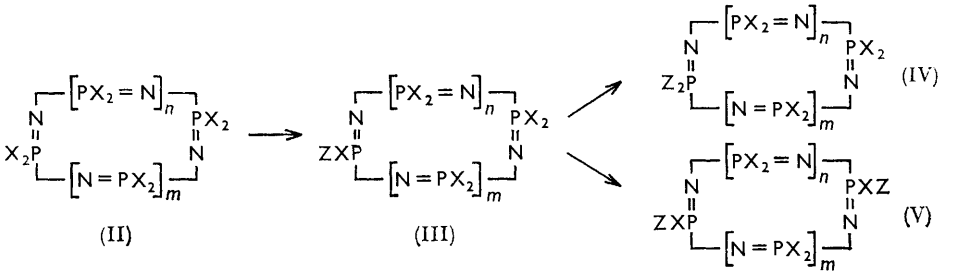
Compound	c./sec.	Compound	c./sec.
$P_3N_3Cl_5{\cdot}NMe_2$	83	$P_3N_3Cl_2(NMe_2)_4$	81 93
$P_3N_3Cl_4(NMe_2)_2$	84	$P_3N_3(NMe_2)_6$	91
$P_3N_3Cl_3(NMe_2)_3$	84		

Shifts are quoted on the high field side of water. The bands show triplet structure and the values quoted represent the mean.

pounds are known, but no penta-amino-derivatives. Twenty-four completely aminolysed compounds have been reported.

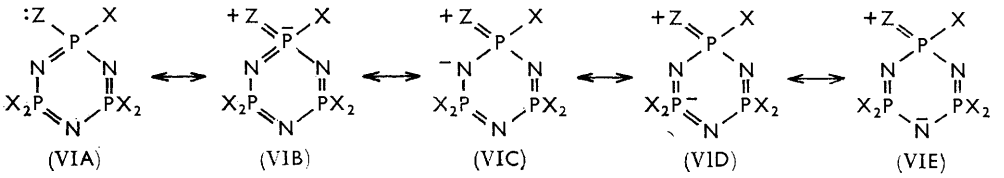
Except for a pair of tetrakisdimethylamino-derivatives and a pair of trisdiethylamino-compounds (both cases not rigidly established), no isomers have been reported in the reactions of the six-membered ring system with one reagent: it appears that one isomer is preferentially formed (or, at least, isolated). This indicates a directing effect, which could be steric and/or polar. Electronegativity considerations and the ability of phosphorus to accommodate up to twelve electrons in its valency shell point to it as the centre for nucleophilic attack. In reaction of a nucleophile Z with a cyclic structure (II), monosubstitution will yield only one product (III) (here $n = 1$, $m = 0$) (conformational isomerism being neglected). In the extreme case, where the steric requirements of X and Z are the same, disubstitution will occur at that phosphorus atom which has the lowest electron-density, *i.e.*, if Z decreases the electron-supply (relative to X) to the phosphorus atom to which it is attached [and if the assumption made below is correct that structure (VIB) is more important than (VID)], geminal disubstitution will lead to (IV); if it increases it, the second replacement will occur preferentially on another atom, leading to (V). This type of positional isomerism will be at its simplest in the six-membered ring, as the PCl_2 groups at position 4 and 6 are equivalent. In the other extreme case, with the polar effects of X and Z identical, steric requirements will predominate. With most reagents both steric and polar factors will simultaneously play a part, as well as others such as the nature of the reaction medium.

In benzenoid chemistry polar effects can be transmitted to the *meta*-position,[13] and similar effects may operate in the cyclophosphazene system where the negative charge produced by double-bond formation with the substituents could reside on the phosphorus



(II) (III) (IV) (V)

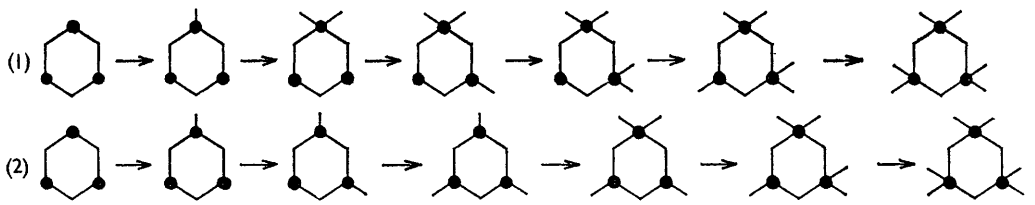
(VIB) or be transmitted (VIC, D, and E). The analogy must not be pressed too far: not only is the stereochemistry different, but whereas the benzene system contains $p\pi$–$p\pi$-bonds, the cyclophosphazenes contain $d\pi$–$p\pi$-bonds.[14] It is not known how the latter type of ring relays electronic effects, in particular whether a preferential *cis*- or *trans*-effect is exerted. Steric effects to the *meta*-position were not considered in benzene chemistry. But in the phosphazene system, where the substituents are not in the plane of the ring



(VIA) (VIB) (VIC) (VID) (VIE)

(or, more generally, not in the plane of the grouping NPN), steric effects may exert some influence to the *meta*-position, in particular in the transition state, and this might be further enhanced by puckering of the ring. Non-planarity has been established for the solid state of a number of derivatives based on the eight-membered ring,[15,16] and there is *X*-ray evidence [16,17] for it in the six-membered ring system.

For successive reactions of cyclotriphosphazatrienes with one reagent, two mechanisms (1) and (2) need consideration, where ● denotes a phosphorus atom. Scheme (1) will be discussed in a later paper. The present work deals mainly with compounds derived by scheme (2).



That the amino-group produces a higher electron-density at an adjacent unsaturated centre than a chlorine atom has been shown in a number of systems; [13] and this applies more powerfully to alkylamino- and dialkylamino-groups. A phosphorus atom carrying

[13] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons Ltd., London, 1953.
[14] Craig, *Chem. and Ind.*, 1958, 3; *J.*, 1959, 997; Craig and Paddock, *Nature*, 1958, **181**, 1052.
[15] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081; Tromans, referred to by Paddock and Searle in " Advances in Inorganic Chemistry and Radiochemistry " (ed. Emeléus and Sharpe), Academic Press Inc., New York, 1959, Vol. I, p. 368; Bullen, personal communication.
[16] Jagodzinski, Langer, Oppermann, and Seel, *Z. anorg. Chem.*, 1959, **302**, 81.
[17] Pompa and Ripamonti, *Ricerca Sci.*, 1959, **29**, 1516.

an amino-group (PNR_2·Cl), thus tends, by both its polar and its steric effect, to direct another molecule of a nucleophilic reagent to another PCl_2 centre, *i.e.*, in the reactions of the chlorophosphazenes with ammonia and aliphatic amines mechanism (2) would be preferred. Nuclear magnetic resonance spectra of dimethylamino-,[11] methylamino-, and amino-derivatives [9] of cyclotriphosphazatriene confirm these deductions, which must apply with greater certainty to higher amino-derivatives whose polar and steric effects would be more pronounced. The position with arylamines is less clear. Although steric factors are here less potent, polar factors are more favourable to geminal disubstitution than with ammonia. At present all results with arylamines [2,3,8] can be equally explained by either scheme. With *ortho*-diamines, especially favourable steric factors are present which may lead to the suggested spiran structure [3] [scheme (1)].

Individual differences amongst the reagents can now be considered. Correlations between the basic strengths of the amines in aqueous solution and their relative ease of reaction with the chlorophosphazenes are of little value. Brown,[18] in particular, has pointed out, that basic strength has a meaning only with reference to a given acid. Basicity in aqueous media is a measure of the polar effects. With bulkier reference acids steric effects will become increasingly important. At present no kinetic data are available for reactions of phosphazenes. In particular, as six reacting groups are available in the molecule, no strict comparison is possible after the replacement of the first chlorine atom as products $P_3N_3ZCl_5$ and $P_3N_3Z'Cl_5$ are no longer equivalent. All that can be discussed at this stage is ease of complete substitution. The results reported above show the importance of the steric factor. (Trimethylamine reacts in a superficially similar manner,[19] but a nitrogen–carbon, instead of a nitrogen–hydrogen bond is being broken.)

The small number of monoamino- and triamino-compounds isolated and the absence of a penta-amino-derivative, may be in part due to experimental difficulties. Not all the reaction mixtures were examined in the same detail as those from dimethylamine and diethylamine, and some of the compounds isolated need not represent the major products. Nevertheless the isolation of tetra-amino-derivatives, often in excellent yield, where one would have expected tri- or hexa-amino-derivatives, points to the particular stability of this structure. This is strikingly demonstrated with t-butylamine. In boiling ether a tetra-amino-compound was obtained in excellent yield, and there was no further reaction even in sealed tubes at 140—160°. Under the latter conditions, other less sterically hindered compounds, such as the tetraisopropylamino-derivative, were converted into the corresponding completely substituted hexa-amino-compound; and the tetra-t-butylamino-derivative, although resistant to further reaction with t-butylamine, reacts readily with methylamine, showing that its behaviour is largely governed by steric factors.

It has been known for some time that the phosphorus–nitrogen bonds in hexachlorocyclotriphosphazatriene are all equal, *i.e.*, resonance occurs.[20] Until recently too, all evidence pointed to the planarity of the six-membered ring.[20] However, crystallographic results [17] obtained with the chloride now indicate a planar ring slightly distorted towards a chair form. There is also possibly puckering in the corresponding fluoride.[16] If the ring is planar or near-planar the 2,2,4,6-tetra-amino-compound will probably have the 4- and the 6-group *trans* to each other. Two bulky groups would then project on either side of the ring and could present steric hindrance to a third, particularly in the transition state. (For some conformations, models show considerable interaction of bulky groups *cis* to each other.) If the ring is flexible, bulky groups may well " freeze " it into a preferred conformation (where the non-geminal groups need not be *trans* to one another), which again may hinder further reaction. Similar arguments can be invoked to a smaller extent for the prevalence of di- and the absence of penta-amino-derivatives. Thus we are dealing with a

[18] Brown, *J.*, 1955, 1248.
[19] Burg and Caron, *J. Amer. Chem. Soc.*, 1959, **81**, 836.
[20] Brockway and Bright, *J. Amer. Chem. Soc.*, 1943, **65**, 1551; Daasch, *ibid.*, 1954, **76**, 3403; Wilson and Carroll, *Chem. and Ind.*, 1958, 1558.

structure which possesses some resemblance to benzene (unsaturation and resonance), as well as to cyclohexane (two substituents on some of the ring atoms, and the possibility of conformational isomerism). In the chemistry of carbon compounds, the directing effect of a particular group is often not exclusively to one position, and mixtures of isomers are formed; [13] the same is probably true for the phosphazenes.

Experimental

Microanalyses for carbon, hydrogen, nitrogen, and chlorine, and molecular-weight determinations were carried out by the Microanalytical Laboratory, Imperial College of Science and Technology, London.

Ether, light petroleum (unless otherwise stated of b. p. 60—80°), and benzene were dried with sodium wire. Hexachlorocyclotriphosphazatriene was prepared by Schenk and Römer's method [21] and separated by vacuum-sublimation. This product, as well as material purchased from Albright & Wilson Ltd., was recrystallised to constant m. p. from light petroleum. Silica gel (M.F.C. grade from Hopkin & Williams) was heated to the temperature and for the time stated. Amines were distilled from sodium.

2,2,4,6-*Tetrachloro*-4,6-*bismethylaminocyclotriphosphazatriene*.—Prepared by the method of Bode *et al.*[3] in 23% yield, this had m. p. 100—100·5° [from light petroleum (b. p. 40—60°)] (Found: C, 7·7; H, 2·5; Cl, 41·25; N, 21·2. Calc. for $C_2H_8Cl_4N_5P_3$: C, 7·1; H, 2·4; Cl, 42·2; N, 20·8%).

Hexamethylaminocyclotriphosphazatriene.—Excess of methylamine was added to hexachlorotriphosphazatriene (5·0 g.) in ether (150 ml.) at −78° and the mixture was then allowed to regain room temperature and filtered. The residue was extracted with cold chloroform, and light petroleum added to the extract. The resultant precipitate, recrystallised from a mixture of these two solvents, had m. p. 258° (Becke-Goehring *et al.*[9] report m. p. 258°) (2·66 g., 65%) (Found: C, 23·4; H, 8·0; N, 39·9. Calc. for $C_6H_{24}N_9P_3$: C, 22·9; H, 7·7; N, 40·0%).

Hexaethylaminocyclotriphosphazatriene.—Excess of ethylamine was added to the hexachloro-compound (5·0 g.) in benzene (50 ml.). An exothermic reaction took place. The mixture was set aside for 12 hr., filtered, and evaporated, and the residue was washed with acid, base, and water, dried, and extracted with light petroleum which, on cooling, deposited *hexaethylaminocyclotriphosphazatriene*, m. p. 118—119° (2·48 g., 43%) (Found: C, 36·5; H, 9·0; N, 32·15. $C_{12}H_{36}N_9P_3$ requires C, 36·8; H, 9·1; N, 31·6%).

Similar methods gave the *amines* recorded in the Table where variations in the solvent and conditions are stated (excess of amine was used, unless otherwise noted).

2,4-*Bismethylamino*-2,4,6,6-*tetra-t-butylaminocyclotriphosphazatriene*.—Excess of methylamine was added to 2,4-dichloro-2,4,6,6-tetra-t-butylaminocyclotriphosphazatriene (2 g.) in ether (30 ml.). The solution was kept overnight and then refluxed for 1 hr. The amine hydrochloride was filtered off, and the solvent evaporated. The residue recrystallised from light petroleum (b. p. 40—60°), yielding starting material, m. p. and mixed m. p. 156° (1·2 g., 60%). Concentrating the mother-liquor gave a solid which on recrystallisation from light petroleum yielded 2,4-*bismethylamino*-2,4,6,6-*tetra-t-butylaminocyclotriphosphazatriene*, m. p. 199° (0·31 g., 16%) (Found: C, 44·4; H, 9·0. $C_{18}H_{48}N_9P_3$ requires C, 44·7; H, 9·9%).

Pentachlorodimethylamino- and 2,2,4,6-*tetrachloro*-4,6-*bisdimethylamino-cyclotriphosphazatriene*.—Dimethylamine (2·54 g., 0·0565 mole) was added to the hexachloro-compound (10 g., 0·0288 mole) in ether (100 ml.) cooled in ice–salt. After ½ hr. the precipitate of amine hydrochloride was filtered off and the filtrate evaporated. The residue was taken up in light petroleum (b. p. 60—80°), and some hexachloro-compound (2·3 g.) was recovered by crystallisation. The mother-liquor was chromatographed on silica gel (45 g., heated at 400° for 3½ hr.) with light petroleum as eluant. The first fraction yielded hexachloro-compound (3·33 g.), the second *pentachlorodimethylaminocyclotriphosphazatriene* (2·10 g., 20%), m. p. 12—14°, b. p. 70—72°/0·01 mm. (only one peak found on gas–liquid chromatography) (Found: C, 7·1; H, 1·7; Cl, 50·8; N, 15·9. $C_2H_6Cl_5N_4P_3$ requires C, 6·7; H, 1·7; Cl, 49·7; N, 15·7%), and the third 2,2,4,6-tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene, m. p. 103° (from light petroleum) (Becke-Goehring *et al.*[9] report m. p. 103°) (1·31 g., 12%) (Found: C, 13·8; H, 3·2; Cl, 38·5; N, 19·1. Calc. for $C_4H_{12}Cl_4N_5P_3$: C, 13·2; H, 3·3; Cl, 38·9; N, 19·2%). The last

[21] Schenk and Römer, *Ber.*, 1924, **57**, 1343.

Amino-chloro-cyclotriphosphazatrienes.

No.	Amino-groups	Condns. of prep.	Yield (%)	M. p.	Solvent for recrystn.[a]
1	2,4,6,6-$(NHPr^n)_4$	Et_2O, room temp.	9	93°	Pet-1
2	$(NHPr^n)_6$	Et_2O, b. p., 3 hr.	17	59	EtOAc
3	2,4,6,6-$(NHPr^i)_4$	Et_2O, room temp.	96	126	Pet-2
4	$(NHPr^i)_6$	C_6H_6, 120°, 16 hr.[b]	34	81	Pet-1
5	$(NHBu^n)_6$	Et_2O, room temp.	23	48	Pet-1
6	$(NHBu^i)_6$	C_6H_6, 120° 12 hr.[b]	77	59	Pet-1
7	2,4,6,6-$(NHBu^s)_4$	Et_2O, room temp.	14	71	Pet-2
8	2,4,6,6-$(NHBu^t)_4$	Et_2O, room temp.[c]	95	155·5	Pet-2
9	$(Cyclohexylamino)_6$	C_6H_6, b. p., 1 hr.	17	165	Pet-2
10	$(NEt_2)_6$	C_6H_6, 150°, 24 hr.[b]	62·5	205	aq. MeOH
11	4,6-$(NBu^i_2)_2$	Et_2O, b. p., 24 hr.	8	73	Pet-1
12	4,6-$(Dicyclohexylamino)_2$	C_6H_6, b. p., 150, hr.	2	200	Pet-2
13	2,4,6-$(NBu^n_2)_3$	C_6H_6, 140°, 48 hr.[b]	42	B. p. 170/0·01.	—
14	$(p$-Toluidino$)_4$[d]	C_6H_6, b. p., 1 hr.[e]	13·5	174	Et_2O
15	$(p$-Toluidino$)_6$[f]	C_6H_6, b. p., 1 hr.	64	243	Pet-2
16	$(NMe_2)_6$[g]	C_6H_6, 90°, 3 hr.[b]	91	104	Pet-2
17	$(Piperidino)_6$[h]	C_6H_6, b. p., 12 hr.	19	266	EtOH

	Found (%[i])						Required (%[i])				
No.	C	H	Cl	N	*M*	Formula	C	H	Cl	N	*M*
1	33·2	7·2	16·75	23·6	—	$C_{12}H_{32}Cl_2N_7P_3$	32·9	7·4	16·2	22·4	—
2	43·9	9·95	—	26·4	479	$C_{18}H_{48}N_9P_3$	44·7	10·0	—	26·1	484
3	33·3	7·2	16·3	22·65	—	$C_{12}H_{32}Cl_2N_7P_3$	32·9	7·4	16·2	22·4	—
4	44·65	9·5	—	25·6	—	$C_{18}H_{48}N_9P_3$	44·7	10·0	—	26·1	—
5	51·4	10·9	—	22·2	567	$C_{24}H_{60}N_9P_3$	50·8	10·6	—	22·2	568
6	50·1	9·9	—	—	—	$C_{24}H_{60}N_9P_3$	50·8	10·6	—	—	—
7	38·2	8·0	14·3	19·6	—	$C_{16}H_{40}Cl_2N_7P_3$	38·8	8·15	14·3	19·8	—
8	39·3	8·1	14·3	20·8	—	$C_{16}H_{40}Cl_2N_7P_3$	38·8	8·15	14·3	19·8	—
9	59·2	9·9	—	17·4	—	$C_{36}H_{72}N_9P_3$	59·7	10·0	—	17·3	—
10	50·8	10·7	—	22·1	—	$C_{24}H_{60}N_9P_3$	50·8	10·65	—	22·1	—
11	36·7	6·8	27·1	13·4	—	$C_{16}H_{36}Cl_4N_5P_3$	36·0	6·8	26·5	13·1	—
12	45·8	7·2	20·8	10·3	—	$C_{24}H_{44}Cl_4N_5P_3$	45·2	7·0	22·2	11·0	—
13	46·1	8·5	—	—	—	$C_{24}H_{54}Cl_3N_6P_3$	46·05	8·7	—	—	—
14	—	—	11·1	15·1	—	$C_{28}H_{32}Cl_2N_7P_3$	—	—	11·25	15·6	—
15	—	—	—	16·4	—	$C_{42}H_{48}N_9P_3$	—	—	—	16·3	—
16	36·6	9·1	—	31·7	—	$C_{12}H_{36}N_9P_3$	36·45	8·2	—	31·9	—[j]

[a] Pet-1 = light petroleum of b. p. 40—60°; Pet-2 = light petroleum of b. p. 60—80°. [b] Reaction carried out in autoclave or sealed tube. [c] 12 Hr. in benzene at 140° yielded 60% of tetrasubstituted product, the remainder being an insoluble material not melting below 360°. [d] Bode, Bütow, and Lienau (*Chem. Ber.*, 1948, **81**, 547) report m. p. 174°. [e] 8 Equivalents of *p*-toluidine used. [f] Hoffmann (*Ber.*, 1884, **17**, 1909) reports m. p. 243°. [g] Becke-Goehring, John, and Fluck (*Z. anorg. Chem.*, 1959, **302**, 103) report m. p. 100°. [h] Bode *et al.*[d] report m. p. 166°. [i] Except for *M*. [j] Found: P, 23·25; calc.: P, 23·5%.

compound, m. p. 103° (1·24 g., 23%), was also obtained from the reaction of the hexachloro-compound (5 g.) in ether (60 ml.) with 30% aqueous dimethylamine.

2,4,6-*Trichloro*-2,4,6-*trisdimethylaminocyclotriphosphazatriene*.—Dimethylamine (3·7 g., 0·082 mole) was added to the hexachloro-compound (5 g., 0·0144 mole) in ether (50 ml.) at −78°, and the mixture was set aside for 18 hr., then filtered. The solid obtained from the filtrate was recrystallised from light petroleum to give flakes of 2,4,6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene, m. p. 104·5—105·5° (lit.,[9] m. p. 107°) (3·15 g., 58·5%) (Found: C, 19·4; H, 5·0; Cl, 29·1; N, 22·9. Calc. for $C_6H_{18}Cl_3N_6P_3$: C, 19·3; H, 4·85; Cl, 28·5; N, 22·5%).

2,4-*Dichloro*-2,4,6,6-*tetrakisdimethylaminocyclotriphosphazatriene*.—(i) Excess of dimethylamine was added to the hexachloro-compound (10 g.) in ether (75 ml.) at 0°. After the vigorous reaction further amine was added until no more amine hydrochloride was precipitated. The solid obtained by evaporation of the filtrate recrystallised from light petroleum to give 2,4-*dichloro*-2,4,6,6-*tetrakisdimethylaminocyclotriphosphazatriene*, (A) m. p. 103·5—104° (8·7 g., 79%) (Found: C, 25·8; H, 6·2; Cl, 18·1; N, 25·8. $C_8H_{24}Cl_2N_7P_3$ requires C, 25·1; H, 6·3; Cl, 18·5; N, 25·65%).

(ii) Dimethylamine (5·2 g., 0·115 mole) was added to the hexachloro-compound (5 g., 0·144 mole) in ether (150 ml.) at −78°. After 36 hr. at room temperature the amine hydrochloride

was filtered off. Concentrating the filtrate yielded 2,4-*dichloro*-2,4,6,6-*tetradimethylaminocyclotriphosphazatriene* (B) (0·92 g., 7%), m. p. 101—101·5° (from light petroleum), mixed m. p. with (A) 71—87° (Found: C, 25·4; H, 6·1; Cl, 17·6; N, 25·0%). (This compound was observed in only one experiment.) From the mother-liquor, compound (A) (2·59 g., 45·5%) was obtained.

Attempted Preparation of Chloropentakisdimethylaminocyclotriphosphazatriene.—2,4-Dichloro-2,4,6,6-tetrakisdimethylaminocyclotriphosphazatriene (2 g., 0·0052 mole) in benzene (8 ml.) was heated in a sealed tube for 12 hr. at 90° with dimethylamine (0·5 g., 0·011 mole). After removal of dimethylamine hydrochloride (0·52 g., 0·0048 mole) and of the solvent, the solid residue was recrystallised from light petroleum to give hexadimethylaminocyclotriphosphazatriene (1·05 g., 0·0027 mole), m. p. and mixed m. p. 103—104°. The mother-liquor was chromatographed on silica gel (35 g., heated at 400° for 3 hr.). Benzene eluted starting material, m. p. and mixed m. p. 103·5° (0·63 g., 31·5%). Thus most of the amine (93%) and of the phosphazene (83·5%) were accounted for, but no pentasubstituted compound could be found.

Pentachlorodiethylaminocyclotriphosphazatriene.—Diethylamine (3·0 g., 0·041 mole) was added to the hexachloro-compound (10 g., 0·0288 mole) in ether (50 ml.). After 18 hr. the amine hydrochloride was filtered off and a colourless oil obtained from the solution. This was chromatographed on silica gel (45 g., heated at 400° for 3 hr.) with light petroleum as eluant. The first fraction was starting material (1·38 g.); the second yielded on distillation *pentachlorodiethylaminocyclotriphosphazatriene* (1·60 g., 14%), b. p. 81—83°/0·01 mm., n_D^{22} 1·5310 (Found: C, 13·2; H, 3·0; Cl, 46·5; N, 14·6. $C_4H_{10}Cl_5N_4P_3$ requires C, 12·5; H, 2·3; Cl, 46·1; N, 14·6%).

2,2,4,6-*Tetrachloro*-4,6-*bisdiethylaminocyclotriphosphazatriene.*—Diethylamine (6·5 g., 0·089 mole) was added to the hexachloro-compound (5 g., 0·0144 mole) in benzene (50 ml.) and the solution was boiled for 3 hr. The amine hydrochloride was filtered off and an orange oil obtained from the solvent. This was kept at −78° (30 hr.) and was then collected; recrystallised from light petroleum it gave 2,2,4,6-*tetrachloro*-4,6-*bisdiethylaminocyclotriphosphazatriene*, m. p. 134° (0·44 g., 7%) (Found: C, 22·3; H, 5·0; Cl, 32·9; N, 16·0. $C_8H_{20}Cl_4N_5P_3$ requires C, 22·8; H, 4·8; Cl, 33·7; N, 16·6%).

2,4,6-*Trichloro*-2,4,6-*trisdiethylaminocyclotriphosphazatriene.*—(*a*) Diethylamine (13·0 g.) and the hexachloro-compound (5 g.) in benzene (50 ml.) were boiled for 18 hr. Removal of the amine hydrochloride and evaporation yielded an orange oil which was chromatographed on silica gel (45 g., heated at 350° for 3½ hr.). Light petroleum eluted 2,4,6-*trichloro*-2,4,6-*trisdiethylaminocyclotriphosphazatriene*, b. p. 102°/2 mm., n_D^{23} 1·5100 (only one peak found in vapour-phase chromatography) (2·15 g., 33%). This product did not solidify even after 1½ years (Found: C, 31·45; H, 6·6; Cl, 22·8; N, 18·3. $C_{12}H_{30}Cl_3N_6P_3$ requires C, 31·5; H, 6·6; Cl, 23·2; N, 18·4%).

(*b*) Diethylamine (8·8 g., 0·12 mole) and the hexachloro-compound (3·5 g., 0·01 mole) in toluene (50 ml.) were boiled for 5 hr. Evaporation of the filtrate gave the above product, m. p. 162° (lit.,[10] m. p. 162°) (from light petroleum) (12%) (Found: C, 31·2; H, 6·3; N, 17·6%).

2,4-*Dichloro*-2,4,6,6-*tetrakisdiethylaminocyclotriphosphazatriene.*—The hexachloro-compound (5 g., 0·0144 mole) in benzene (25 ml.) was heated with diethylamine (8·5 g., 0·116 mole) in a sealed tube at 140° for 16 hr. After removal of the amine hydrochloride (6·8 g., 0·053 mole) and of solvent an orange oil remained, that was chromatographed in light petroleum on silica gel (45 g., heated at 450° for 3 hr.). Light petroleum eluted 2,4-*dichloro*-2,4,6,6-*tetrakisdiethylaminocyclotriphosphazatriene*, b. p. 125°/0·02 mm., n_D^{22} 1·5103 (2·2 g., 31%) (Found: C, 37·8; H, 7·5; N, 19·2. $C_{16}H_{40}N_7Cl_2P_3$ requires C, 38·9; H, 8·15; N, 19·85%).

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
MALET STREET, LONDON, W.C.1.

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