395. *Phosphorus–Nitrogen Compounds. Part IX.*[1] *The Reaction of Dimethylamine with Hexachlorocyclotriphosphazatriene: the Replacement Pattern and the Structure of the Products* *

By R. KEAT and R. A. SHAW

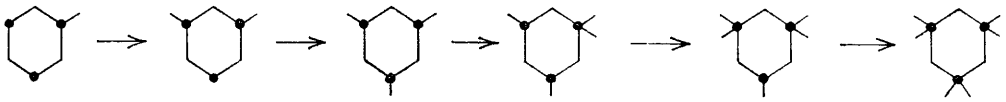
The reaction between dimethylamine and hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6 + NHMe_2 \longrightarrow N_3P_3Cl_{6-n}(NMe_2)_n$, has been subjected to a detailed investigation. Nine phosphazene derivatives were isolated, $N_3P_3Cl_{6-n}(NMe_2)_n$, [n = 1, 2 (three), 3 (three), 4, and 6]. By proton magnetic resonance spectroscopy, and basicity measurements, structures have been assigned. *cis*- and *trans*-Nongeminal, as well as geminal, compounds have been found. The reaction pattern is discussed.

HEXACHLOROCYCLOTRIPHOSPHAZATRIENE, $N_3P_3Cl_6$ (I), reacts readily with dimethylamine in ether to give chlorodimethylamino-derivatives, $N_3P_3Cl_6 + 2n NHMe_2 \longrightarrow N_3P_3Cl_{6-n}(NMe_2)_n + n NH_2Me_2Cl$.[2] Complete replacement of chlorine atoms has been achieved by use of benzene solutions in sealed tubes.[2] Systematic characterisations of dimethylamino- and other amino-derivatives[2–4] have been carried out, but as yet, few examples of geometrical isomers have been reported. Proton nuclear magnetic resonance spectra[2] of the previously isolated dimethylamino-derivatives indicated that a non-geminal reaction scheme is predominant[2] (Scheme 1).

* Presented in part during discussion at the XIXth Internat. Congress of Pure and Applied Chemistry, London, July 1963.

[1] Part VIII, B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J.*, 1964, 4459.
[2] S. K. Ray and R. A. Shaw, *J.*, 1961, 872.
[3] M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. Chem.*, 1959 **302** 103.
[4] R. A. Shaw B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

Scheme 1



Nongeminal replacement pattern of hexachlorocyclotriphosphazatriene; incoming group only is shown; • indicates phosphorus atom

Thin-layer chromatography has enabled a more detailed examination of the products of the reaction of dimethylamine with hexachlorocyclotriphosphazatriene (I) to be carried out. Nine phosphazene derivatives, $N_3P_3Cl_{6-n}(NMe_2)_n$ [n = 1, 2 (three), 3 (three), 4, and 6] (II ⟶ IX, XIII) were detected, isolated, and their structures investigated.

The initial investigations involved the reaction of hexachlorocyclotriphosphazatriene (I) with stoicheiometric quantities of dimethylamine under a variety of conditions. Subsequent studies dealt with the further reactions of isolated and purified individual chlorodimethylamino-derivatives. Both approaches throw significant light on this reaction system.

When hexachlorocyclotriphosphazatriene (I) is treated with two equivalents of dimethylamine in ether at −78° good yields of the monodimethylaminophosphazene (II) are obtained, whilst four equivalents of amine under similar conditions give, apart from traces of mono- (II) and *trans*-tris-derivatives * (VII), as main products the *cis*- (m. p. 86°) (III) and *trans*-bisdimethylamino- (m. p. 103°) (IV) isomers, the latter predominating. Structural evidence for all the compounds reported here (Scheme 2), is discussed later in this Paper.

In contrast to this, the reaction of the hexachloro-compound (I) with six equivalents of amine under a variety of conditions gives *trans* (VII) and geminal (VIII) tris-derivatives, in roughly equal proportions, as the major components of the reaction mixtures, invariably accompanied by varying, but small amounts of geminal bis- (V) and occasionally also by traces of *cis*-tris- (VI) derivatives. The formation of the geminal bis- (V) and especially of the geminal tris- (VIII) compounds seems to be somewhat favoured by an increase in the reaction temperature.

The reaction of excess of amine in refluxing ether with the chloro-compound (I) gives excellent yields of the tetrakis-derivative (IX). No other tetrakis-derivative was observed. Although detection and separation techniques more sensitive than previous ones were employed, the absence of a pentakis-compound (XII), noted earlier,[2] has been confirmed. Hexakisdimethylaminocyclotriphosphazatriene (XIII) is conveniently prepared from the chloro-compound (I) and an excess of dimethylamine in refluxing chloroform solution, obviating the sealed-tube methods previously employed.

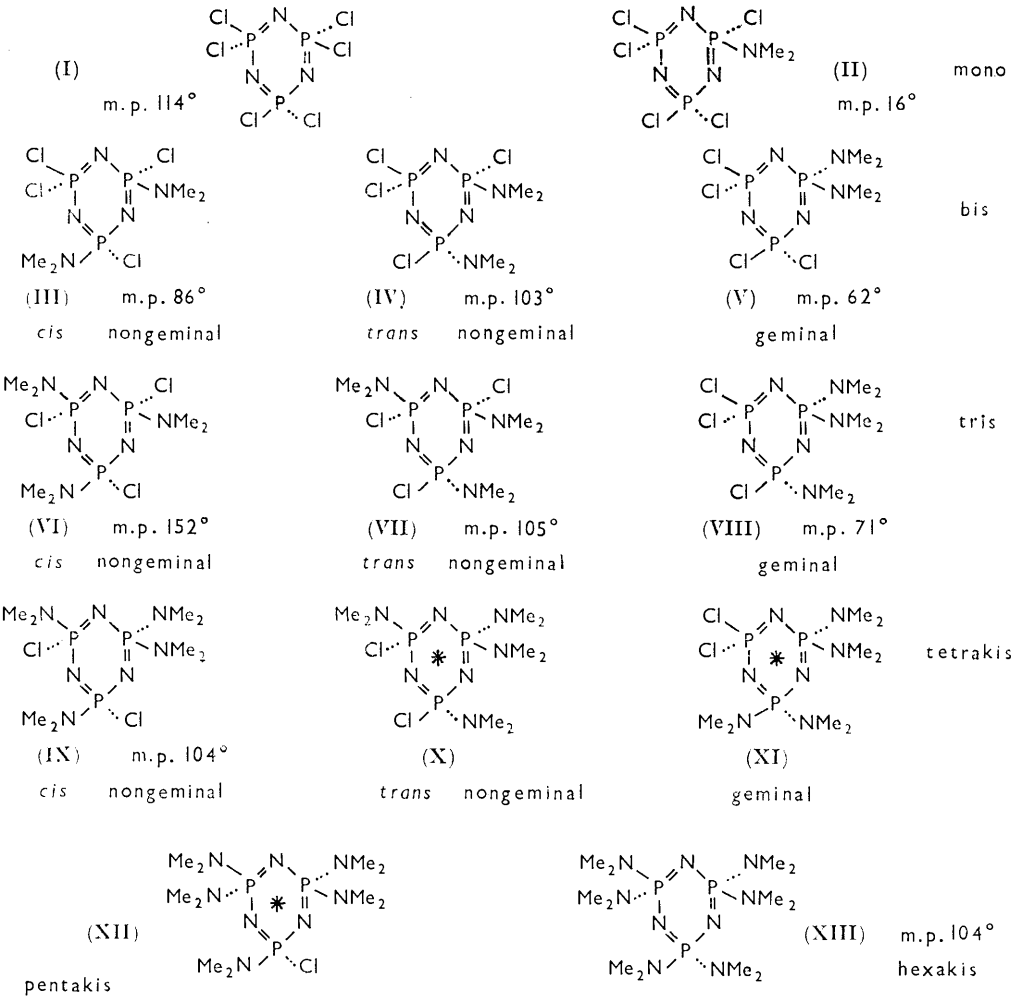
The effect of variations in the reaction conditions on the products formed and their relative proportions is summarised in Table 1, together with their order of elution in column and thin-layer chromatography.

It is convenient now to discuss some of the evidence on which the above structural assignments are based. The proton magnetic resonance spectra of all the dimethylaminolysis products were examined. Detailed interpretation is difficult, because of the great complexity of the spectra, probably owing to complex proton–phosphorus coupling, and is deferred until a later date.

The spectra occur in the region of τ 7·2—7·5 and their mean positions move up-field with increasing degree of aminolysis. At their simplest, the spectra consist of one sharp doublet with a separation varying between 11 and 18 c./sec. Between these doublets lie broad absorption regions whose integrated signals contain the bulk of the total absorption. Compounds (II, III, IV, V, VI, and XIII) give spectra of this type, suggesting that they

* For nomenclature see ref. 4. In the Discussion section of this Paper only shortened versions of the systematic names are used; for the full systematic names see Experimental section.

Scheme 2. Dimethylamino-derivatives of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_{6-n}(NMe_2)_n$



* Compound as yet not known.

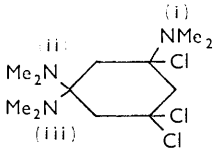
TABLE 1

The effect of solvent, reaction temperature, and stoicheiometry of the reagents on product distribution in the reaction of hexachlorocyclotriphosphazatriene with dimethylamine

Solvent	Temp.	Equivs. of amine	Dimethylaminocyclotriphosphazatrienes. Relative proportions formed: II	III	IV	V	VI	VII	VIII
Et_2O	−78°	4	<1	2	3	—	—	<1	—
Et_2O	−78	6	—	<1	<1	≪1	<1	2	2
Et_2O	~20	6	—	<1	1	<1	—	2	2
Et_2O	35	6	—	<1	1	<1	—	2	2
Pet.*	~70	6	—	1	2	<1	—	2	3
C_6H_6	78	6	—	<1	<1	1	—	2	4
$CHCl_3$	62	4	<1	2	3	<1	—	<1	1
$CHCl_3$	62	6	—	1	1	<1	<1	2	3
$C_6H_4Me_2$ †	~140	4	—	<1	2	<2	<1	≪1	2
$C_6H_4Me_2$ †	~140	6	—	1	<1	1	—	1	3
Order of elution on silica gel...			1	3	2	5	6	4	7
Order of elution on alumina...			1	2	2	3	4	4	5

* Light petroleum, b. p. 60—80°. † Commercial xylene.

contain only one type of proton environment. The spectra of derivatives (VII, VIII, and IX) have two, three, and three doublets, respectively, and hence this number of different proton environments. Here again, broad absorption regions occur between the doublets, and as these overlap, some of the doublets are superimposed on these broad signals making it difficult to estimate reliably the relative number of protons in each environment. The doublets of compounds (VIII and IX) show signs of further splitting. We consider as an example the spectrum of 2,2,4-trichloro-4,6,6-tris-dimethylaminocyclotriphosphazatriene, $N_3P_3Cl_3(NMe_2)_3$ (VIII) (Scheme 3). This consists



Scheme 3 The three proton environments in 2,2,4-trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene

of three doublets arising from (i) the nongeminal dimethylamino-group in position 4, (ii) and (iii) the geminal dimethylamino-groups at position 2, *cis* and *trans*, respectively, to the nongeminal one at position 4. Proton magnetic resonance studies of simple model compounds show that phosphorus–hydrogen spin–spin coupling decreases with increasing replacement of chlorine atoms by dimethylamino-groups.[5] This further confirms the structures of compounds (VI—IX) and enables us to distinguish between the geminal (V) and the nongeminal (III and IV) bisdimethylamino-compounds. The *cis–trans* assignment of the last two is based on analogy. Only one proton environment is present in each, but the isomer of m. p. 86° is slightly more shielded than the one of m. p. 103°. We tentatively assign a *cis* structure to the former and a *trans* structure to the latter, as in the nongeminal tris-derivatives the *cis* isomer is similarly more shielded than the *trans*. Our assignments for the bis- and tris-isomers are in agreement with parallel studies of Koopman [6] using gas–liquid chromatographic isolation techniques, and dipole moment measurements for structural determinations. Different proton environments could of course arise from conformational effects, but the evidence cited above, together with basicity studies and certain chemical reactions makes the given structural assignments more likely.

Basicity measurements were carried out in nitrobenzene,[7] and pK_a' values, where accessible by our technique, are given in Table 2. We consider geminal aminochlorocyclotriphosphazatrienes to be more basic than their nongeminal isomers,[7] and have used this to assign structures to two pairs of diaminodichloro-2,2-diphenylcyclotriphosphazatrienes, $N_3P_3Ph_2Cl_2Y_2$ (Y = NHMe, piperidino).[8]

TABLE 2

Proton magnetic resonance spectra in carbon tetrachloride, and pK_a' values in nitrobenzene of dimethylaminocyclotriphosphazatrienes

Compound	No. of different proton environments	Structure	pK_a' *
$N_3P_3Cl_5(NMe_2)$ (II)	1	Nongeminal	
$N_3P_3Cl_4(NMe_2)_2$ (III)	1	*cis*-Nongeminal	
$N_3P_3Cl_4(NMe_2)_2$ (IV)	1	*trans*-Nongeminal	
$N_3P_3Cl_4(NMe_2)_2$ (V)	1	Geminal	
$N_3P_3Cl_3(NMe_2)_3$ (VI)	1	*cis*-Nongeminal	−6·0
$N_3P_3Cl_3(NMe_2)_3$ (VII)	2	*trans*-Nongeminal	−6·0
$N_3P_3Cl_3(NMe_2)_3$ (VIII)	3	Geminal	−4·2
$N_3P_3Cl_2(NMe_2)_4$ (IX)	3	*cis*-Nongeminal	−1·4
$N_3P_3(NMe_2)_6$ (XIII)	1	Geminal	7·6

* For a definition of pK_a' see ref. 7.

[5] R. Keat and R. A. Shaw, unpublished results.
[6] H. Koopman, I.U.P.A.C. Conference, London, 1963; Abstracts A, AB4—36, and personal communication.
[7] D. Feakins, W. A. Last, and R. A. Shaw, *Chem. and Ind.*, 1962, 510; *J.*, 1964, 4464; and unpublished results.
[8] K. Hills and R. A. Shaw, *J.*, 1964, 130.

Since the completion of our studies, a Paper[9] dealing with the proton magnetic resonance spectra of the chlorodimethylamino-derivatives (IV, VI, VII, and IX) has appeared, in which the authors assign *cis* and *trans* configurations. The last three of these are in agreement with Koopman's [6] and our own findings, but they differ in assigning a *cis* structure to the bis-derivative of m. p. 103°. Their evidence, based on the *cis* structure of the Friedel–Crafts phenylation product, 2,2-dichloro-4,6-bisdimethylamino-4,6-diphenylcyclotriphosphazatriene, $N_3P_2Ph_3Cl_2(NMe_2)_2$, must be viewed with some caution, as its precursor, $N_3P_3Cl_4(NMe_2)_2$, as well as some other nongeminal aminochlorocyclotriphosphazatrienes, isomerise to a mixture of the *cis* and *trans* forms in the presence of aluminium chloride.[10]

The isolated and characterised individual chlorodimethylamino-derivatives were treated with stoicheiometric quantities of amine in the hope of obtaining chemical evidence for their structures. The approach, intended to be a classical one, depends on the number of isomers obtainable from a given compound. Thus, *e.g.*, the *cis*-bisdimethylamino-compound (III) should give three trisdimethylamino-derivatives, two nongeminal (*cis* and *trans*) (VI and VII), and one geminal (VIII), whilst the *trans*-bisdimethylamino-isomer (IV) should give only two tris-derivatives, one nongeminal (*trans*) (VII), the other geminal (VIII). The above arguments are based on the assumption that the compounds observed are primary reaction products.

The results of our investigations under a variety of conditions are summarised in Table 3. A simple classical approach is clearly not valid. Some experiments in ether or chloroform have a complicating factor or factors, as more products are sometimes obtained than could be accounted for on the above reasoning. We have shown elsewhere that *cis–trans* isomerisation reactions can occur under these conditions.[11] On the other hand, some reactions give fewer products than the classical approach would predict.

TABLE 3

Reactions of chlorodimethylaminocyclotriphosphazatrienes with two equivalents of dimethylamine

Compound	Solvent	Temp.	Approximate product ratios *
(II)	Pet.†	0°	(III) : (IV) : (V) = 1 : 5 : ≪1
,,	Et_2O	,,	(III) : (IV) : (V) = 1 : 2 : ≪1
(III)	Et_2O	,,	(VII) : (VI) : (VIII) = 5 : ≪1 : <1
,,	Pet.	,,	(VII) only
(IV)	Et_2O	,,	(VII) : (VIII) = 4 : 3
,,	Pet.	,,	(VII) : (VIII) = 1 : 1
(V)	Et_2O	,,	(VIII) only
(VI)	$CHCl_3$	,,	(IX) only
,,	Pet.	140 ‡	No reaction
,,	Et_2O	35	(IX) only
,,	Et_2O	20	No reaction
(VII)	$CHCl_3$	0	(IX) only
,,	Pet.	140 ‡	(IX) only
,,	Et_2O	35	(IX) only
(VII)	Et_2O	0	(VII) : (IX) = 5 : 1
(VIII)	$CHCl_3$	,,	(IX) only
,,	Pet.	140 ‡	(IX) only
(IX)	$CHCl_3$	61	(IX) : (XIII) = 3 : 1
,,	Pet.	140	No reaction

* In many cases just detectable traces of starting material, as well as more highly aminolysed derivatives were obtained. † Pet. = light petroleum, b. p. 60—80°. ‡ Reaction carried out in a sealed tube.

Let us consider as an example the reactions of the three bisdimethylamino-isomers with two equivalents of amine. The *trans* compound (IV) gives in light petroleum the *trans* (VII) and geminal (VIII) tris-derivatives. The geminal compound (V) gives solely the geminal tris-derivative (VIII). On the other hand, the *cis*-bis-isomer (III) would be

[9] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.
[10] R. Keat, R. A. Shaw, and C. Stratton, *J.*, 1965, 2223.
[11] R. Keat and R. A. Shaw, *Chem. and Ind.*, 1964, 1232.

expected to yield all the three isomeric tris-compounds, but in light petroleum only the *trans* derivative (VII) is observed, whilst in diethyl ether this is accompanied by small quantities of the geminal (VIII) isomer. In contrast to this, all three tris-isomers (VI—VIII) give only one, the *cis* (IX), tetrakis-derivative. No other tetrakis-derivative could be detected by our most sensitive methods, including thin-layer chromatography, although our experience has shown that with this technique separation becomes more difficult with the increasing replacement of chlorine atoms by dimethylamino-groups. The isolation of only one tetrakisdimethylamino-compound (IX), together with the failure of our attempts to isomerise it with amine hydrochloride [11] or aluminium chloride,[10] suggests that it is the thermodynamically favoured form. Noteworthy also is the absence of reaction of the *cis*-tris-isomer (VI) in light petroleum, even at 140°, whilst its two isomers react under these conditions to give the tetrakis-compound (IX). It is possible that conformational effects may account for the preferred formation of the above compounds.

A similar classical approach to structural problems involving pyrrolidinyl-derivatives of hexachlorocyclotriphosphazatriene was made by Kropacheva and Kashnikova,[12] who assigned *cis*, *trans*, and geminal structures to bis- and tris-pyrrolidinyl derivatives on the basis of their further reactions with pyrrolidine. Whether they encountered difficulties with this approach, similar to those described above, is not clear, as so far no experimental details have been published.

Treatment of the tetrakis-compound (IX) failed to show any evidence for the pentakis-derivative (XII); only starting material and hexakisdimethylaminocyclotriphosphazatriene (XIII) were observed, confirming our earlier findings.[2] Only four monochloropenta-aminocyclotriphosphazatrienes, $N_3P_3ClR_5$, have been reported (R = piperidino,[13] pyrrolidinyl,[14] morpholino,[15] and 1-aziridinyl [16,17]), but only the last has been described in some detail. We have suggested [8] that the absence of some monochloro-derivatives may well be connected with a change in reaction mechanism due to the increasing electron supply of the amino groups to the ring. Such a supply would be much reduced in the case of the aziridine derivatives and may account for the existence of penta-aziridinylchlorocyclotriphosphazatriene. The difference in behaviour between dimethylamine and piperidine,[5] on the one hand, and of aziridine on the other is emphasised by its replacement pattern. Whilst the last-mentioned amine has not been subjected to the same detailed study as the other two, those of its compounds whose structures have been investigated by means of ^{31}P and ^{1}H n.m.r. spectroscopy [17,18] were suggested to be geminal.

The results reported here confirm our earlier observations [2] that the replacement pattern of chlorine atoms in cyclotriphosphazatriene by dimethylamine follows largely a non-geminal pattern. Whilst the geminal tris (VIII) is formed in relatively large amounts, the geminal bis (V) occurs only in traces, and the geminal tetrakis-derivative (XI) has not been detected. We have shown that under suitable conditions *cis–trans* isomerisations can occur.[11] These appear to be largely suppressed in solvents, such as benzene and light petroleum, in which the amine hydrochlorides are not appreciably soluble, and hence the observation of *cis* and *trans* bis-isomers under these conditions suggests that they are formed by direct replacement reactions. These conclusions must however be tentative, as we have no evidence that in these largely heterogeneous systems, added amine hydrochloride exerts the same catalytic effect [11] as that formed *in situ*.

It is highly probable that a dimethylamino-group will increase, relative to a

[12] A. A. Kropacheva and N. M. Kashnikova, *Zhur. obshchei Khim.*, 1963, **33**, 1046.
[13] A. A. Kropacheva, L. E. Mukhina, N. M. Kashnikova, and V. A. Parshina, *Zhur. obshchei Khim.*, 1961, **31**, 1036.
[14] A. A. Kropacheva and N. M. Kashnikova, *Zhur. obshchei Khim.*, 1962, **32**, 652.
[15] A. A. Kropacheva and L. E. Mukhina, *Zhur. obshchei Khim.* 1962, **32**, 521.
[16] A. A. Kropacheva and L. E. Mukhina, *Zhur. obshchei Khim.*, 1961, **31**, 2437.
[17] Y. Kobayashi, L. A. Chasin, and L. B. Clapp, *Inorg. Chem.*, 1963, **2**, 212.
[18] G. Ottmann, H. Agahigian, H. Hooks, G. D. Vickers, E. Kober, and R. Rätz, *Inorg. Chem.*, 1964, **3**, 753.

chlorine atom, the electron density of the phosphorus atom to which it is attached, thus tending to direct the next replacement step, if the reaction is nucleophilic, to a $\equiv PCl_2$ grouping, where furthermore, attack is also somewhat sterically favoured. That these assumptions are substantially correct is borne out by other evidence than that produced by the current work. Hexakisdimethylaminocyclotriphosphazatriene (XIII) is a vastly stronger base than its chloro-analogue (I) [7] (evidence for ring nitrogen protonation is presented elsewhere [7]) and whilst protonation undoubtedly disturbs the electron distribution of the free base, it is highly probable that a considerable transfer of charge from the lone pair of electrons on the exocyclic nitrogen atoms to the adjacent phosphorus atom (and from there partly relayed further) has taken place in the free phosphazene as well. The phosphorus–nitrogen (exocyclic) bond shortening and the flattening and increased bond angles of the dimethylamino-groups in octakisdimethylaminocyclotetraphosphazatetraene [19] are powerful supporting arguments for the above.

We have discussed earlier [8] several possible causes for the absence of certain amino-monochlorophosphazenes. Basicity measurements [7] suggest an increased flow of electrons to the ring as chlorine atoms are replaced by dimethylamino-groups. The possibility of important contributions from a P–Cl bond ionisation mechanism would help to account for the isolation of only one tetrakis-derivative and the absence of a pentakisdimethylamino-compound.

Experimental

Hexachlorocyclotriphosphazatriene was recrystallised to m. p. 114° from light petroleum. Organic solvents were dried by the commercially available " Hi-drite " drying agent. Light petroleum had b. p. 60—80°, except where otherwise stated. Anhydrous dimethylamine was obtained in sealed ampoules from B.D.H. Ltd.

Alumina and silica gel for column chromatography were M.F.C. grade from Messrs. Hopkins and Williams. Alumina was activated for 12 hr. at 110° before use, and silica gel was used as supplied. Alumina and silica gel containing 10% calcium sulphate for thin-layer chromatography were obtained from Merck Ltd. Layers were 270 μ thick and activated for 1 hr. at 110°. Thin-layer chromatograms were developed with a chromic acid spray; for hexachlorocyclotriphosphazatriene exposure to dimethylamine vapour for 5 min. was necessary before spraying. The yields, although formally quoted after chromatographic separation were much reduced owing to losses on adsorbent and to incomplete separation during column chromatography. During all column chromatographic separations 50 ml. fractions were collected, the solvent volume of each reduced to about 2 ml. and a thin-layer chromatogram run to determine the contents of each fraction. Preparative-scale thin-layer chromatography was carried out on 20 × 20 cm. chromaplates with silica gel layers, on to each of which were loaded 150 mg. of the mixture to be separated. After elution with benzene the plates were masked when small sections of the plate could be developed to determine the position of each compound in the form of a band across the plate. The required bands were scraped off and Soxhlet extracted with benzene to obtain the pure compound.

Investigations of isomer ratios (Tables 1 and 3) were carried out on silica gel plates under the conditions stated. It has been shown by Purdy and Truter [20] that a linear relationship applies between the logarithm of the weight of material present and the square-root of the area of the spot. The approximate ratio of the products from a given reaction could be obtained by visual estimation of the size and intensity of the spots produced on development of the chromatogram. Since the relative proportions of each product were of greatest interest, accuracy comparable with that of Purdy and Truter was not essential.

The information from these experiments was then used to achieve reaction conditions under which optimum yields of the new isomers reported below were obtained.

Melting points were determined on a Reichert–Kofler microheating stage fitted with a polarising microscope. Proton magnetic resonance spectra were obtained from a Varian Associates model A60 nuclear magnetic resonance spectrometer equipped with a 60 Mc./sec.

[19] G. J. Bullen, *Proc. Chem. Soc.*, 1960, 425; *J.*, 1962, 3193.
[20] S. J. Purdy and E. V. Truter, *Chem. and Ind.*, 1962, 506.

R.F. source. These spectra were obtained from *ca.* 30% w/w solutions in carbon tetrachloride.

Reactions of Hexachlorocyclotriphosphazatriene (I).—(*a*) *With two equivalents of dimethylamine.* Pentachlorodimethylaminocyclotriphosphazatriene (II), m. p. 16°, b. p. 75°/0·02 mm., was obtained in 63% yield by the method of Ray and Shaw.[2] Thin-layer chromatography showed that this derivative comprised about 80% of the total reaction mixture.

(*b*) *With four equivalents of dimethylamine.* Dimethylamine (9·0 g., 0·2 mole) was added to a solution of hexachlorocyclotriphosphazatriene (I) (17·4 g., 0·05 mole) in ether (300 ml.) cooled to −78°. When the mixture had attained room temperature dimethylamine hydrochloride was filtered off and the filtrate evaporated to give a solid residue. Recrystallisation from light petroleum gave 2,2,4-*trans*-6-tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene (IV), m. p. 103° (lit.,[2] m. p. 103°) (4·9 g., 27%). The mother-liquor from the first recrystallisation was concentrated and chromatographed on silica gel (80 g.) using benzene–light petroleum (1 : 1) as eluant. 25 fractions were collected. Fractions 10—25 were combined and recrystallised from light petroleum (b. p. 40—60°) to give 2,2,4-cis-6-*tetrachloro*-4,6-*bisdimethylaminocyclotriphosphazatriene* (III), m. p. 86° (110 mg., 0·6%) (Found: C, 13·5; H, 3·5; Cl, 38·2; N, 19·2. $C_4H_{12}Cl_4N_5P_3$ requires C, 13·2; H, 3·3; Cl, 38·9; N, 19·2%).

(*c*) *With five equivalents of dimethylamine.* Dimethylamine (22·5 g., 0·5 mole) was distilled *via* a cold-finger kept at −78° into a stirred refluxing solution of hexachlorocyclotriphosphazatriene (I) (34·8 g., 0·1 mole) in chloroform (200 ml.). After cooling, the chloroform was removed under reduced pressure and the residue extracted with hot light petroleum. Crystallisation of a mixture of known bis- and tris-dimethylamino-isomers occurred on standing and these were filtered off. The volume of the mother-liquor was reduced to about 15 ml. and chromatographed on an alumina column (100 g.) using benzene–light petroleum (3 : 18) as eluant. Fractions 1—4, containing a new compound together with bis- and tris-dimethylamino-isomers, were combined for subsequent preparative scale thin-layer chromatography. The extracts from 40 plates, containing the new compound, were bulked and recrystallised from pentane to give 2,2,4,4-*tetrachloro*-6,6-*bisdimethylaminocyclotriphosphazatriene* (V), m. p. 62° (43 mg., 0·12%) (Found: C, 13·6; H, 3·6; Cl, 38·9%).

(*d*) *With six equivalents of dimethylamine.* Dimethylamine (13·5 g., 0·3 mole) was allowed to react with hexachlorocyclotriphosphazatriene (I) (17·4 g., 0·05 mole) in ether (250 ml.) as in (*b*). The product was recrystallised from light petroleum to give 2-*trans*-4,6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene (VII), m. p. 105° (lit.,[2] m. p. 104·5—105·5°) (9·2 g., 49%). The contents of the mother-liquor from the first recrystallisation were subjected to preparative scale thin-layer chromatography as in (*c*). Two new bands were scraped off each plate. Recrystallisation of the extract from the first new (and smaller) band from light petroleum (b. p. 40—60°) gave 2-cis-4-cis-6-*trichloro*-2,4,6-*trisdimethylaminocyclotriphosphazatriene* (VI), m. p. 152° (28 mg., 0·15%) (Found: C, 19·4; H, 4·8; Cl, 28·7; N, 22·1. $C_6H_{18}Cl_3N_6P_3$ requires C, 19·3; H, 4·9; Cl, 28·5; N, 22·5%). The solid obtained from the second new band was recrystallised from pentane to give 2,2,4-*trichloro*-4,6,6-*trisdimethylaminocyclotriphosphazatriene* (VIII), m. p. 71° (45 mg., 0·24%) (Found: C, 19·5; H, 4·8; Cl, 29·2; N, 23·0%).

Improved yields of 2,2,4-trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene (VIII) could be obtained [at the expense of the *cis*-isomer (VI)] by using higher reaction temperatures, and separating the products by column chromatography.

(*e*) *With eight equivalents of dimethylamine.* Dimethylamine (36·0 g., 0·8 mole) was distilled into a stirred, refluxing solution of hexachlorocyclotriphosphazatriene (I) (34·8 g., 0·1 mole) in ether (500 ml.) as in (*c*). Recrystallisation of the product from light petroleum gave 2-*cis*-4-dichloro-2,4,6,6-tetrakisdimethylaminocyclotriphosphazatriene (IX), m. p. 104° (lit.,[2] m. p. 103·5—104°) (27·6 g., 76%). Thin-layer chromatography on alumina using benzene–chloroform (1 : 1) as eluant indicated that traces of tris-, hexakis- and of a new dimethylamino-derivative were also formed.

(*f*) *With ten equivalents of dimethylamine.* Reaction of dimethylamine (22·5 g., 0·5 mole) and hexachlorocyclotriphosphazatriene (I) (17·4 g., 0·05 mole) in refluxing ether as in (*c*) gave mainly 2-*cis*-4-dichloro-2,4,6,6-tetrakisdimethylaminocyclotriphosphazatriene (IX). Thin-layer chromatograms of the mother-liquor showed that the above mentioned (*e*) new compound was again present. The mother-liquor was concentrated and chromatographed on a silica gel column (100 g.) using benzene–ether (9 : 1) as eluant. Hexakisdimethylaminocyclotriphosphazatriene (XIII) and the new compound were eluted together by chloroform. This mixture (0·64 g.)

was chromatographed on an alumina column (15 g.) eluting first with benzene, then from fractions 13 onwards the eluant contained increasing proportions of ether. The new compound was eluted from the column with benzene–ether (19 : 1). It was recrystallised from benzene–light petroleum (1 : 1) to give *hexakisdimethylaminocyclotriphosphazatriene hydrochloride*, m. p. 134—136° (9 mg., 0·045%) (Found: C, 33·4; H, 8·0. $C_{12}H_{37}ClN_9P_3$ requires C, 33·2; H, 8·6%).

(*g*) *With excess of dimethylamine.* An excess of dimethylamine was allowed to react with hexachlorocyclotriphosphazatriene (I) (17·4 g., 0·05 mole) in chloroform (150 ml.) as in (*c*). After cooling, the chloroform was removed and the residue extracted with hot light petroleum (250 ml.). Crystallisation from this solvent gave hexakisdimethylaminocyclotriphosphazatriene (XIII), m. p. 104° (lit.,[2] m. p. 104°) (17·3 g., 87%).

Reactions of Dimethylamino-derivatives with Two Equivalents of Dimethylamine.—Pentachlorodimethylaminocyclotriphosphazatriene (II). Dimethylamine (12·3 mg., 0·273 mmole) in the form of a standard solution in light petroleum was added slowly to an ice-cold solution of pentachlorodimethylaminocyclotriphosphazatriene (II) (50 mg., 0·137 mmole) in light petroleum (25 ml.). The mixture was left overnight, and then examined by thin-layer chromatography on a silica gel plate using benzene as eluant. 2,2,4-*trans*-6-Tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene (IV), m. p. 103°, and 2,2,4-*cis*-6-tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene, m. p. 86°, were obtained in the approximate ratio 5 : 1 with traces of mono- and tris-dimethylamino-derivatives. The authenticity of the products was checked by preparative scale thin-layer chromatography and by comparison of the infrared spectra, m. p.s, and mixed m. p.s of the products isolated with those of authentic specimens. Similar reactions were carried out with other dimethylamino-derivatives in light petroleum, ether, and chloroform, and the results are summarised in Table 3.

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