970. *Phosphorus–Nitrogen Compounds. Part II.*[1] *Non-geminal Phenylchlorocyclophosphazenes from the Reaction of Phenyltetrachlorophosphorane and Ammonium Chloride.*

By R. A. Shaw and C. Stratton.

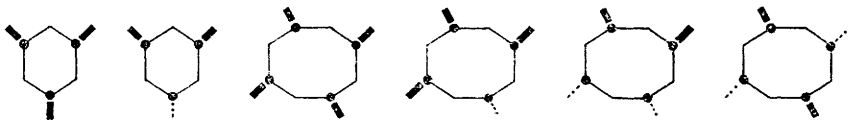
After reaction of phenyltetrachlorophosphorane with ammonium chloride in boiling *s*-tetrachloroethane one 2,4,6-trichloro-2,4,6-triphenylcyclotriphosphazatriene, $N_3P_3Ph_3Cl_3$, and three isomeric 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraenes, $N_4P_4Ph_4Cl_4$, have been isolated. The structural unit NPPhCl was proved by hydrolytic degradation to phenylphosphonic acid. Various derivatives have been prepared by replacing the chlorine atoms with nitrogenous base or alkoxy-residues.

Relatively little is known about alkyl- and aryl-phosphazenes.[2] The ammonolysis of phosphorus pentahalides, the main route to chloro- and bromo-phosphazenes, $(NPX_2)_n$ (X = Cl or Br), has been adapted to afford geminal organophosphorus derivatives, $(NPR_2)_n$

[1] Part I, Ray and Shaw, *J.*, 1961, 872.
[2] Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.

(R = Alkyl or Aryl),[3–5] a modification leading to geminal bisperfluoroalkyl derivatives, $[NP(R_F)_2]_n$.[6] Attempts to make non-geminal derivatives, $(NPRX)_n$, by the ammonolytic route were unsuccessful.[7]

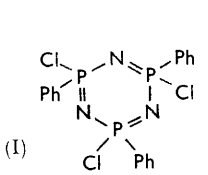
If the possibility of conformational isomerism is neglected, reactions leading to geminal derivatives will give only one compound for any given ring-size, but reactions leading to



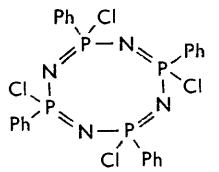
(● indicates phosphorus atom. Only one of the substituents on the phosphorus is denoted.)

non-geminal products will be complicated by *cis–trans*-isomerism. The six-membered ring system could give two, and the eight-membered ring system four, *cis–trans*-isomers as illustrated.

As *cis–trans*-isomers were not known in phosphazene chemistry, we investigated the ammonolysis of phenyltetrachlorophosphorane, $Ph{\cdot}PCl_4 + NH_4Cl \longrightarrow (NPPhCl)_n$ (a preliminary account of some of this work has appeared [8]). Bode and Bach [7] had previously found their glassy reaction mixture intractable and had obtained solely a partial hydrolysis product, $N_3P_3Ph_3ClO_2H_2$. Refluxing phenyltetrachlorophosphorane with an



(I)



(II)

excess of ammonium chloride for 14 hours in s-tetrachloroethane gave crystals admixed with oil, and after extraction with benzene, the sparingly soluble 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (A) (II), m. p. 248°, crystallised as the major component of the reaction mixture. By a combination of solvent extraction, fractional crystallisation, and adsorption chromatography on silica gel, the residue was separated into two isomers, m. p. 202° (B) and 148° (C), of the above compound (II), and a 2,4,6-trichloro-2,4,6-triphenylcyclotriphosphazatriene (I), m. p. 188°. A different cyclotriphosphazatriene derivative (I), m. p. 162°, had been reported recently.[9]

In the identification of six- and eight-membered ring compounds, and in the general process of their separation, use was made of the established differences in the powerful infrared ring vibrations.[4,10] The six-membered ring compound has its strongest absorption band near 1200 cm.$^{-1}$, whereas the eight-membered ring compounds absorb near 1300 cm.$^{-1}$. Isomeric derivatives in the eight-membered ring series show differences in the 700—1100 cm.$^{-1}$ region (see Table 4).

It is apparent from the synthesis that each phosphorus atom carries one phenyl group, and this is confirmed by hydrolytic degradation to give phenylphosphonic acid in good yield. Diphenylphosphinic acid, $Ph_2PO{\cdot}OH$, which would arise from a geminal diphenyl

[3] Searle, *Proc. Chem. Soc.*, 1959, 7.
[4] Bilbo, *Z. Naturforsch.*, 1960, **15b**, 339.
[5] Haber, Herring, and Lawton, *J. Amer. Chem. Soc.*, 1958, **80**, 2116; Bezman and Smalley, *Chem. and Ind.*, 1960, 839; Korshak, Gribova, Artamonova, and Bushmarina, *Vysokomol. Soedineniya*, 1960, **2**, 377.
[6] Tesi and Douglas, *J. Amer. Chem. Soc.*, 1962, **84**, 549; Haber, *Chem. Soc. Special Publ.*, 1961, No. 15, p. 115.
[7] Bode and Bach, *Ber.*, 1942, **75***B*, 215.
[8] Shaw and Stratton, *Chem. and Ind.*, 1959, 52.
[9] Bezman and Humiec, *J. Amer. Chem. Soc.*, 1961, **83**, 2210.
[10] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403; Shaw, *Chem. and Ind.*, 1959, 54.

grouping,[7,11] was shown to be absent by paper chromatography with authentic reference compounds.

As the pure compounds do not change on recrystallisation, polymorphic modifications can be ruled out; conformational isomerism has so far not been established in phosphazene chemistry. The most likely explanation is that the three compounds A—C are three of the four geometrical isomers. These would be the first geometrical isomers in the phosphazene series and one of the first well-identified examples in any purely inorganic ring system.

TABLE 1.

Starting material	Group replacing chlorine	Starting material	Group replacing chlorine
A	NH_2, NHMe, NHEt, $NHPr^n$, $NHPr^i$, $NHBu^t$, NMe_2, NEt_2, NHPh, NH·NHPh, piperidino, cyclohexylamino, OMe, OEt, OPh	B	NHMe, NHEt, $NHPr^i$, NMe_2, piperidino, OEt
		C	NHMe, piperidino
		D	NHMe, piperidino

The chlorine atoms in all these phosphazenes were completely replaced by nitrogenous base or alkoxy-residues, as shown in Table 1; the techniques have already been reported.[1,12]

The isomeric derivatives prepared from compounds A—C exhibit differences in m. p. (and depressed mixed m. p.s) and/or in infrared spectra, thus providing further evidence that the chloro-compounds were not just polymorphs.

Steric effects on the ease of reaction with alkylamines were similar to those for hexachlorocyclotriphosphazatriene,[1] $N_3P_3Cl_6$, and octachlorocyclotetraphosphazatetraene,[13] $N_4P_4Cl_8$. All the chlorine atoms were replaced by methylamine at room temperature, but with t-butylamine sealed tubes at 160° were necessary. The phenylhydrazino-derivative (A), $N_4P_4Ph_4(NH{\cdot}NHPh)_4$, crystallised with solvent of crystallisation from benzene, and solvent-free from chloroform. The tetrachloro-compound (A) was converted by phenylmagnesium bromide into the known octaphenyl derivative, m. p. 230—232°.[5,14]

The methylamino-derivative (A), on being heated, appeared to melt, resolidify, and remelt at a higher temperature. Closer examination showed that this was due to a number of interconvertible solid phases, and similar phenomena, though less striking, were observed with a number of the other compounds prepared. This will be reported in detail elsewhere.[15]

EXPERIMENTAL

Ether, light petroleum (unless otherwise stated, of b. p. 80—100°), and benzene were dried with sodium wire. Phenyldichlorophosphine was prepared by the Michaelis modification of Friedel–Crafts reaction.[16] This product, as well as a gift from the Victor Chemical Company, were purified by distillation under a reduced pressure of nitrogen. Silica gel (M.F.C. grade from Messrs. Hopkin & Williams) was heated to the temperature and for the time stated. Amines were distilled from sodium. Phenylhydrazine was purified by chromatography, followed by recrystallisation from light petroleum (b. p. 60—80°)–benzene.

Typical Synthesis of Non-geminal Phenylchlorocyclophosphazenes.—An excess of dry chlorine was passed into a suspension of ammonium chloride (60 g.) in a solution of phenyldichlorophosphine (86·2 g.) in *s*-tetrachloroethane (500 ml.). After 2 hr. the issue of unchanged chlorine showed the reaction to be complete, and the chlorine flow was cut off. The mixture was refluxed for 14 hr., by which time evolution of hydrogen chloride was negligible. After filtration, the solvent was removed under reduced pressure, yielding a mixture of oil and crystals.

2,4,6,8-*Tetrachloro*-2,4,6,8-*tetraphenylcyclotetraphosphazatetraenes.*—The solid and oil were

[11] Shaw and Wells, *Chem. and Ind.*, 1960, 1189.
[12] Fitzsimmons and Shaw, *Chem. and Ind.*, 1961, 109.
[13] Ray, Shaw, and Smith, unpublished results.
[14] Bode and Thamer, *Ber.*, 1943, **76***B*, 121.
[15] Bullen, Shaw, and Stratton, unpublished results.
[16] *Org. Synth.*, 1951, **31**, 88.

extracted in a Soxhlet apparatus. Successive 24-hr. extractions were made with two lots of light petroleum (b. p. 60—80°), followed by two lots of benzene. The first benzene extract was redissolved in benzene, passed through a short silica gel column (20 g., heated at 400° for 3 hr.), and recrystallised from benzene and then chloroform, to give 2,4,6,8-*tetrachloro*-2,4,6,8-*tetraphenylcyclotetraphosphazatetraene* (*A*), m. p. 248° (10·5 g., 7·0%) (Found: C, 45·3; H, 3·2; Cl, 22·4; N, 8·8; P, 20·0%; *M*, 645, 619. $C_{24}H_{20}Cl_4N_4P_4$ requires C, 45·7; H, 3·2; Cl, 22·5; N, 8·9; P, 19·6%; *M*, 630).

Crystals from the first light petroleum extract were recrystallised from benzene–light petroleum (b. p. 60—80°), then from light petroleum (b. p. 60—80°), to give *isomer* (*C*), m. p. 148° (3·3 g., 2·2%) (Found: C, 45·9; H, 3·7; Cl, 22·3; N, 8·8; P, 19·6%; *M*, 648).

The first light petroleum extract gave a second crystalline compound, more soluble than (C), which likewise recrystallised from light petroleum (b. p. 60—80°), to give *isomer* (B), m. p. 202° (8·0 g., 5·3%) (Found: C, 45·7; H, 3·1; Cl, 22·5; N, 8·9; P, 19·6%; *M*, 619).

The residues from the light petroleum extract were combined, dissolved in light petroleum, and chromatographed on a silica gel column (20 g., heated at 170° for 3 days). In a typical separation, 5 g. of residue were placed on the column and eluted first by light petroleum (b. p. 60—80°; 200 ml.) then by light petroleum (b. p. 60—80°)–benzene (100 ml. lots, the concentration of benzene increasing by 1% steps to 100%). In this way four fractions were separated: (1) A viscous oil from 0—20% benzene; (2) compound (B) from 20—30% benzene; (3) a compound, m. p. 188°, from 30—76% benzene; and (4) a substance, m. p. >245°, from 76% benzene to benzene + 5% chloroform. Fraction (3) recrystallised from light petroleum, to give 2,4,6-*trichloro*-2,4,6-*triphenylcyclotriphosphazatriene*, m. p. 188° (0·44 g., 0·3%) (Found: C, 45·4; H, 3·5; Cl, 22·5; N, 9·0; P, 19·6%; *M*, 461. $C_{18}H_{15}Cl_3N_3P_3$ requires C, 45·7; H, 3·2; Cl, 22·5; N, 8·9; P, 19·6%; *M*, 472·5).

Hydrolytic Degradation of the Phenylchlorocyclophosphazenes.—The tetrachlorotetraphenyl compound (A) (0·1100 g.) was powdered, and hydrolysed with 98% sulphuric acid, alcohol, and water (1 ml., 10 ml., 10 ml.) in a sealed tube at 145° for 24 hr. The mixture was extracted with ether, and the material from the extract weighed (0·866 g., 89%). Comparative paper chromatography against authentic specimens of phenylphosphonic acid and diphenylphosphinic acid showed that the latter was absent, and that the ether extracted was substantially pure phenylphosphonic acid. The remainder of this material was recrystallised and a mixed m. p. with authentic acid was not depressed. Identity of infrared spectra confirmed this. Hydrolyses of the other three condensation products gave similar results.

Replacements.—Isomeric compounds amongst the reactions are designated A—C according to the parent chloro-compound. Seven experimental procedures (*a*—*g*) are described below. The remaining syntheses are summarised in Tables 2 and 3.

(*a*) An excess of dry ammonia was passed into a solution of 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (A) (1·00 g.) in benzene (25 ml.), until there appeared to be no further reaction. Ammonium chloride was filtered off; 2,4,6,8-*tetra-amino*-2,4,6,8-*tetraphenylcyclotetraphosphazatetraene* (*A*) was obtained by evaporation and recrystallised from benzene as needles, m. p. 229° (0·36 g., 45%) (Found: C, 51·8; H, 5·2; N, 20·0. $C_{24}H_{28}N_8P_4$ requires C, 52·1; H, 5·1; N, 20·3%).

(*b*) Dry piperidine (2 ml.) was refluxed with 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (C) (0·150 g.) in benzene (20 ml.) for 3 hr. Piperidine hydrochloride was filtered off and the 2,4,6,8-*tetraphenyl*-2,4,6,8-*tetrapiperidinocyclotetraphosphazatetraene* (*C*) obtained from the solution recrystallised from benzene–light petroleum as prisms, m. p. 240° (0·088 g., 45%) (Found: C, 63·55; H, 7·2; N, 13·5; P, 15·0. $C_{44}H_{60}N_8P_4$ requires C, 64·0; H, 7·3; N, 13·6; P, 15·0%).

(*c*) An excess of phenylhydrazine was added to 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene, (A) (0·24 g.) in benzene (25 ml.) at 80°. After 1 hr. the phenylhydrazine hydrochloride was filtered off. The excess of phenylhydrazine was removed by washing the benzene solution with dilute hydrochloric acid, then with distilled water, this being followed by drying (K_2CO_3) and evaporation. Recrystallisation from chloroform gave 2,4,6,8-*tetraphenyl*-2,4,6,8-*tetrakisphenylhydrazinocyclotetraphosphazatetraene* (*A*), m. p. 176° (0·060 g., 20%) (Found: C, 61·8; H, 5·5; N, 18·0; P, 13·5. $C_{48}H_{48}N_{12}P_4$ requires C, 62·9; H, 5·2; N, 18·3; P, 13·5%). From benzene it crystallised with solvent [m. p. 117° (decomp.), followed by resolidification and m. p. 170—175°] (0·10 g., 34%) (Found: C, 66·0; H, 5·7; N, 17·1; P, 11·5. Calc. for $C_{48}H_{48}N_{12}P_4,2C_6H_6$: C, 65·2; H, 5·4; N, 16·9; P, 12·5%).

(*d*) t-Butylamine (5 ml.) was heated with 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (A) (0·313 g.) in benzene (10 ml.) in a sealed tube for 3 hr. at 160°. t-Butylamine hydrochloride was filtered off, the solvent removed, and the white syrup recrystal-

TABLE 2.

Tetraphenylcyclotetraphosphazatetraene and triphenylcyclotriphosphazatrienes.

No.	Ring size	Parent compound	Groups replacing Cl	Method	Yield (%)	M. p.	Recryst. from *
1	8	A	NHMe	*a*	12	130—154° †	C_6H_6–Pet-2
2	,,	,,	NHEt	*a*	19	101	,,
3	,,	,,	$NHPr^n$	*b*	12	98	,,
4	,,	,,	$NHPr^i$	*b*	68	140	,,
5	,,	,,	NMe_2	*b*	14	180	,,
6	,,	,,	NEt_2	*b*	14	>320	C_6H_6–Pet-1
7	,,	,,	Piperidino	*b*	15	255	,,
8	,,	,,	Cyclohexylamino	*b*	9·5	132	,,
9	,,	,,	NHPh	*c*	5	241	C_6H_6
10	,,	,,	OMe	*e*	12	142	C_6H_6–Pet-1
11	,,	,,	OEt	*e*	15	104	Pet-2
12	,,	B	NHMe	*a*	46	131	,,
13	,,	,,	NHEt	*a*	39	122	C_6H_6–Pet-2
14	,,	,,	$NHPr^i$	*b*	65	133	,,
15	,,	,,	NMe_2	*b*	32	154 ‡	,,
16	,,	,,	Piperidino	*b*	33	224	,,
17	,,	C	NHMe	*a*	35	113	,,
18	6	D	NHMe	*a*	50	167	,,
19	,,	,,	Piperidino	*b*	49	187	,,

* Pet-1 = light petroleum of b. p. 60—80°; Pet-2 = light petroleum of b. p. 80—100°. † M. p. behaviour described in discussion. ‡ Phase change in solid at 139—140°.

TABLE 3.

Analyses of compounds in Table 2.

	Found (%)					Required (%)			
No.	C	H	N	P	Formula	C	H	N	P
1	55·2	5·9	17·3	20·9	$C_{28}H_{36}N_8P_4$	55·3	5·9	18·4	20·4
2	57·6	7·2	16·7	18·4	$C_{32}H_{44}N_8P_4$	57·8	6·6	16·9	18·7
3	60·3	6·8	14·8	17·1	$C_{36}H_{52}N_8P_4$	60·0	7·2	15·6	17·2
4	60·0	7·2	14·8	16·9	$C_{36}H_{52}N_8P_4$	60·0	7·2	15·6	17·2
5	57·9	6·6	—	—	$C_{32}H_{44}N_8P_4$	57·8	6·6	16·9	18·7
6	61·7	7·3	14·8	16·2	$C_{40}H_{60}N_8P_4$	62·0	7·7	14·4	16·0
7	64·1	7·3	13·9	15·05	$C_{44}H_{60}N_8O_4$	64·0	7·3	13·6	15·05
8	65·4	7·8	12·6	14·3	$C_{48}H_{68}N_8P_4$	65·8	7·3	12·8	14·3
9	67·6	5·4	13·0	14·4	$C_{48}H_{44}N_8P_4$	67·3	5·1	13·1	14·5
10	54·9	5·3	9·3	20·5	$C_{28}H_{32}N_4O_4P_4$	54·9	5·2	9·1	20·2
11	57·4	6·0	—	18·7	$C_{32}H_{40}N_4O_4P_4$	57·5	6·0	8·4	18·6
12	54·7	5·9	—	20·9	$C_{28}H_{36}N_8P_4$	55·3	5·9	18·4	20·4
13	58·2	6·8	16·7	18·8	$C_{32}H_{44}N_8P_4$	57·8	7·0	16·9	18·7
14	59·8	7·5	15·6	17·7	$C_{36}H_{52}N_8P_4$	60·0	7·2	15·6	17·2
15	57·8	7·1	16·7	—	$C_{32}H_{44}N_8P_4$	57·8	6·6	16·9	18·7
16	63·7	8·1	13·8	—	$C_{44}H_{60}N_8P_4$	64·0	7·3	13·6	15·05
17	55·2	6·5	18·3	—	$C_{28}H_{36}N_8P_4$	55·3	5·9	18·4	20·4
18	56·1	6·2	18·0	—	$C_{21}H_{27}N_6P_3$	55·3	5·9	18·4	20·4
19	64·3	7·5	13·4	—	$C_{33}H_{45}N_6P_3$	64·0	7·3	13·6	15·05

lised first from acetone–water, then from light petroleum (b. p. 60—80°), to give 2,4,6,8-*tetraphenyl*-2,4,6,8-*tetra-t-butylaminocyclotetraphosphazatetraene* (*A*), m. p. 252° (0·04 g., 9%) (Found: C, 61·8; H, 7·8; N, 14·4. $C_{40}H_{60}N_8P_4$ requires C, 62·0; H, 7·7; N, 14·4%).

(*e*) Sodium (2 g.) was added to ethyl alcohol (5 ml.) in benzene (20 ml.). After the reaction the mixture was cooled and added to 2,4,6,8-*tetrachloro*-2,4,6,8-*tetraphenylcyclotetraphosphazatetraene* (*B*) (0·505 g.) in benzene (20 ml.). After 24 hr. this mixture was washed with water

until neutral to universal indicator paper, and the benzene layer was dried (K_2CO_3). The solvent was removed at room temperature, and the yellowish solid recrystallised by slow evaporation of a cold solution in benzene–light petroleum, giving needles of 2,4,6,8-*tetraethoxy*-2,4,6,8-*tetraphenylcyclotetraphosphazatetraene* (*B*), m. p. 122° (0·070 g., 13%) (Found: C, 57·4; H, 5·5; N, 8·9; P, 18·4. $C_{32}H_{40}N_4O_4P_4$ requires C, 57·5; H, 6·0; N, 8·4; P, 18·4%).

(*f*) Pure dry phenol (10 g.) was dissolved in benzene (20 ml.), and sodium (2 g.) was added. After 2 hours' refluxing, pure dry dioxan (20 ml.) was added and the benzene was distilled off. The dioxan solution was added to a solution of 2,4,6,8-tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (A) (0·5 g.) in dioxan (25 ml.), and the mixture was refluxed for 3 hr. Benzene (50 ml.) was then added and the whole shaken repeatedly with water until the aqueous layer was neutral. The benzene layer was dried (K_2CO_3) and evaporated. Recrystallisation of the residue from benzene–light petroleum gave 2,4,6,8-*tetraphenoxy*-2,4,6,8-*tetraphenylcyclotetraphosphazatetraene* (*A*), m. p. 133·5° (0·100 g., 16%) (Found: C, 66·6; H, 5·3; N, 7·5; P, 14·6. $C_{48}H_{40}N_4O_4P_4$ requires C, 67·0; H, 4·7; N, 7·5; P, 14·4%).

TABLE 4.

Infrared absorption bands for some isomers within the eight-membered ring series.

Compound	P–N ring vibrations ($cm.^{-1}$)	Bands which appear to be dependent on the symmetry of the molecule ($cm.^{-1}$)
A	1260sh, s, 1290s, 1305s	800m, 785sh, m, 748sh, s, 745s, 712s, 703s, 688s
B	1270sh, s, 1295s, 1310s	788w, 752m, 746m, 719m, 705s, 690s
C	1270sh, s, 1290s, 1305s	785w, 760sh, m, 750m, 710m, 692s
$(NHMe_4)$ (A) ...	1215s, 1245s	1118s, 1080s, 860s, 850sh, s, 760m, 745m
$(NHMe)_4$ (B) ...	1220—1260s	1118s, 1090s, 1075s, 904s, 860w, 800w, 756m, 738s
$(NHMe)_4$ (C) ...	1240s	1120s, 1100s, 1080s, 904s, 747s

(*g*) 2,4,6,8-Tetrachloro-2,4,6,8-tetraphenylcyclotetraphosphazatetraene (A) (1·0 g.) in pure dry anisole (50 ml.) was refluxed with phenylmagnesium bromide (2 mol.) in anisole (20 ml.) for 6 hr. After filtration, the excess of the Grignard reagent was destroyed by water, and the anisole was removed under reduced pressure. The brown solid residue was taken up in benzene and dried (K_2CO_3). The benzene solution was decolorised by passage through silica gel (20 g., heated at 170° for 3 days) and, on concentration, octaphenylcyclotetraphosphazatetraene crystallised as white needles, m. p. and mixed m. p. 319—320° [5,14] (0·12 g., 10%) (authentic infrared spectrum).

The three piperidino-derivatives reported have infrared spectra with only minor differences from each other and were proved to be distinct only by depression of their mixed m. p.s.

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