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PHOSPHORUS-NITROGEN COMPOUNDS. PART 72.¹ THE REACTIONS OF OCTACHLOROCYCLOTETRA-PHOSHAZATETRAENE WITH SPERMIDINE AND SPERMINE

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 72.¹ THE REACTIONS OF OCTACHLOROCYCLOTETRA- PHOSPHAZATETRAENE WITH SPERMIDINE AND SPERMINE

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The reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, with spermidine and spermine in a mixture of $Et_2O/MeCN$ (1:2) have been studied. Spermidine gave two products. Both consisted of two tetramer units; in one they were linked by one spermidine residue, in the other by two. Spermine gave one product, two tetramer units linked by a spermine residue. All three products contained six-membered spiro moieties. Their ^{31}P and ^{13}C n.m.r. spectra are reported and compared with the products of the same two amines with hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$.

Key words: Octachlorocyclotetraphosphazatetraene; spermidine; spermine; spiro compounds; bridge structures; n.m.r. studies.

INTRODUCTION

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (1), and of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (2), with difunctional and polyfunctional reagents have been recently reviewed.² Whilst a considerable body of work with difunctional reagents has been published, especially with the hexachloride, (1), studies with reagents of higher functionality are few. The reactions of compound (1) with spermidine (a tri-amine) and spermine (a tetra-amine) have been reported by the Toulouse group.^{3,4} One compound (3), respectively (4), from each reaction system was isolated and characterized. The reactions of compounds (1) and (2) with glycerol^{5,6} (a tri-ol) and pentaerythritol⁷ (a tetra-ol) have also been reported. The poly-ols gave more complex mixtures than the poly-amines. No studies of the octachloride, (2), with a poly-amine have been published.

RESULTS AND DISCUSSION

We have reinvestigated the reactions of the hexachloride, (1), with spermidine and spermine and confirm the isolation of the compounds (3) and (4) reported earlier.^{3,4} The reactions of its homologue, (2), with these two poly-amines yielded two, respectively one, compounds. ^{31}P and ^{13}C (and to a lesser extent 1H) n.m.r. spec-

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troscopic studies on the products of these four reaction systems were carried out and are reported here.

³¹P n.m.r. Studies

The data for compounds (3) to (7) are in Table I. All five compounds contain two phosphazene units. For the trimer system these were confirmed crystallographically, for the tetramer system by mass spectrometry. Compound (5) is the analogue of (3) in the spermidine reaction, compound (7) that of (4) in the spermine system. The former, (5), gives an A₂BC spectrum, the latter, (7), two superimposed A₂BC spectra. Compound (6) consists of two tetramer linked by two spermine residues. Two structures must be considered with the two bridges in 2,6- and 2,4-positions. The fact that the spectrum is of the ABCD type clearly points to the latter.

¹³C n.m.r. Studies

The data are given in Table II. Compound (7) was insufficiently soluble for this study. As in earlier studies^{8,9} carbon nuclei alpha to nitrogen resonate at lower field, if the nitrogen atom is tertiary rather than if it is secondary.

We have also shown that three-bond coupling constants are not only a function of the dihedral angle PNCC, but also of the stereochemistry of the nitrogen atom and of the carbon-nitrogen bond length.¹⁰ We note that ³J(PNCC) values decrease in the order C₆ > C₅ > C₂. C₂ is constrained in a ring, whilst C₅ and C₆ are freely rotating. Coupling to the former takes place across a tertiary nitrogen atom, to the latter across a secondary one. In keeping with our earlier observations,¹⁰ coupling constants to C₆ are larger than those for C₅.

TABLE I
³¹P n.m.r. data of compounds (1-7)

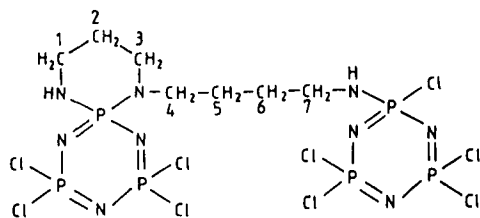
Compound	δPCL ₂ ^a	δPspiro ^a	δPCL (NHR) ^a	² J[PCL ₂ -Pspiro] ^b	² J[PCL ₂ -PCL ₂] ^b	² J[PCL ₂ -Cl(NHR)] ^b	² J[Pspiro-PCL(NHR)] ^b
(1)	19.9						
(3)	22.4	11.1		40.35			
	22.15					47.3	
(4)	21.4	9.7		40.65			
(2)	-6.5						
(5)	-2.8(2) ^c	-0.35		27.6	38.8		
	-6.9(1)						
	-4.4(2)		-5.2		33.3	27.3	
	-7.1(1)						
(6)	-1.6(1)	6.1	-0.1	25.5	21.9		39.15
	-3.8(1)						
(7)	-5.3(2)	-0.6		28.0 ^d	26.85		
	-7.3(1)						

^aIn p.p.m.

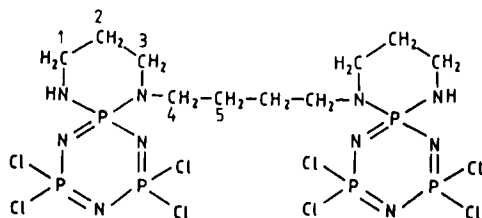
^bIn Hz.

^cRelative number of nuclei in brackets.

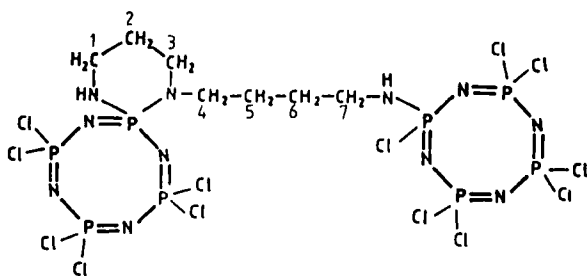
^d¹J(Pspiro-PCL₂) = 3.7 Hz.



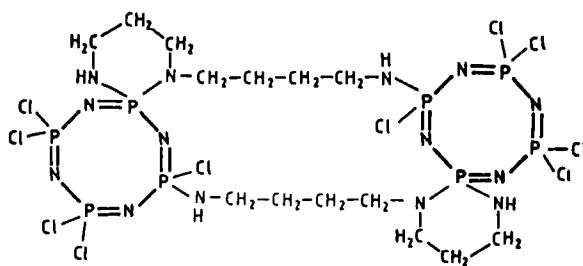
(3)



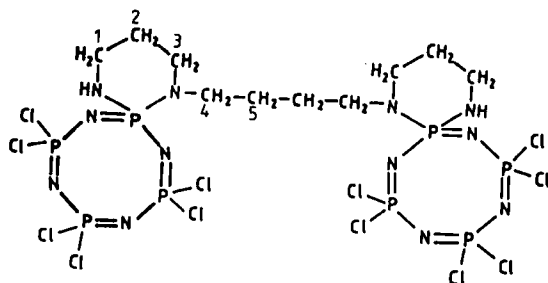
(4)



(5)



(6)



(7)

TABLE II
 ^{13}C n.m.r. data for compounds (3) to (6)

Com- pound	δ/ppm							Coupling Constant (Hz.)	
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	$^2J(\text{PnC})$	$^3J(\text{PNCC})$
(3)	41.20	26.95	47.13	47.48	24.67	28.62	41.14	3.80(PC ₁)	9.15(PC ₆) 5.50(PC ₅) 4.85(PC ₂)
(4)	40.53	26.63	46.65	47.42	24.62	—	—	3.76(PC ₁) 1.60(PC ₃)	5.38(PC ₅) 4.84(PC ₂)
(5)	41.54	27.29	47.22	47.67	24.75	27.83	41.22	3.76(PC ₁)	9.13(PC ₆) 6.98(PC ₅) 4.83(PC ₂)
(6)	40.79	27.53	47.53	49.16	27.65	27.60	43.41	4.83(PC ₁) 2.68(PC ₇)	8.59(PC ₆) 4.83(PC ₅)

^1H n.m.r. Studies

All the compounds (3–7) gave very complex spectra, which were not analyzed in any detail. In the double-bridged derivative (6) NCH_2 (spiro) [δ 3.84 p.p.m., $^3J(\text{PH})$ 14.2 Hz.], can be distinguished from NCH_2 (bridge) [δ 3.45 p.p.m., $^3J(\text{PH})$ 13.9 Hz.]. Two NH signals were also observed in this compound at δ 3.62 p.p.m. and δ 2.72 p.p.m.

SUMMARY

All compounds (3–7) are based on two phosphazene units. Compound (5) is the tetramer analogue of the trimer derivative (3), compound (7) that of (4). Compound (6) is, so far, a unique structural type, being the first doubly-bridged tetramer derivative. Some examples of doubly-bridged trimer derivatives have been reported.^{1,11,12}

EXPERIMENTAL

Chemicals were obtained as follows: acetonitrile (anhydrous, 99%), spermidine, spermine, (Aldrich Chem. Co. Ltd.), triethylamine (B.D.H. Chemical Co. Ltd.), dichloromethane, benzene, tetrahydrofuran (Fluka Ltd.), deuteriated solvents for n.m.r. spectroscopy (Aldrich Chem. Co. Ltd.), hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazetetrane (Shin Nisso Kako Co. Ltd.). Solvents were dried by conventional methods. The experimental techniques and spectroscopic methods were described in an earlier paper.¹³

The reactions of (1) (a) with N-(3-aminopropyl)-1,4-diaminobutane (spermidine) in ether-acetonitrile (1:2). Triethylamine (6.58 g, 65 mmol), $\text{N}_3\text{P}_3\text{Cl}_6$, (1), (7.52 g, 21.6 mmol) and spermidine (2.28 g, 15.7 mmol) were allowed to react and worked up as in (b). Na_2SO_4 and amine hydrochlorides were filtered off and the solvents removed in vacuo. The resulting colourless, oily product was subjected to column chromatography (silica gel, 100 g for a 3 g mixture, column length 65 cm, diameter 4 cm) using $\text{THF}/\text{CH}_2\text{Cl}_2$ (1:1) as eluent to eliminate the remaining traces of hydrochlorides. After that the oily, crude product showed one t.l.c. spot at $R_f = 0.45$ with CH_2Cl_2 as eluent. It was dissolved in boiling *n*-heptane and set aside for crystallization of compound (3).

(b) With N,N'-bis(3-aminopropyl)-1,4-diaminobutane (spermine) in ether-acetonitrile mixture (1:2). Triethylamine (8.75 g, 86.5 mmol) was added to a stirred solution of $\text{N}_3\text{P}_3\text{Cl}_6$, (1), (7.12 g, 20.4 mmol)

TABLE III
Experimental Details

n	Starting Compound		Reactant		triethylamine g (mmol)	Chromatographic eluent ratios	Recrystal- lization Solvent	Product Number	Yield g
	g (mmol)	in Et ₂ O- MeCN (1:2) (cm ³)	g (mmol)	in Et ₂ O- MeCN (1:2) (cm ³)					
	7.52 (21.6) [N ₃ P ₃ Cl ₆ (1)]	300	2.28 (15.7)	75	6.58 (65.0) (Spermidine)	CH ₂ Cl ₂ /THF (1:1)	<i>n</i> -heptane	(3)	5.14
	7.12 (20.4) [N ₃ P ₃ Cl ₆ (1)]	300	2.02 (10.0)	75	8.75 (86.5) (Spermine)	CH ₂ Cl ₂ /THF (2:1)	Et ₂ O	(4)	3.52
	9.57 (21.0) [N ₄ P ₄ Cl ₈ (2)]	200	2.00 (13.8)	100	6.96 (68.8) (Spermidine)	CH ₂ Cl ₂ /benzene (5:3)	CH ₂ Cl ₂ /benzene (3:1)	(5) (6)	0.56 1.40
	4.73 (10.2) [N ₄ P ₄ Cl ₈ (2)]	300	1.00 (4.5)	75	5.00 (49.5) (Spermine)	CH ₂ Cl ₂ /THF (1:2)	<i>n</i> -hexane/ CH ₂ Cl ₂ (1:1)	(7)	2.00

TABLE IV
Analytical Data

Com- pound	Formula	M.p. (°C)	Elemental Analysis (%) Found (Calculated)					Mass <u>M</u> ^a (<u>M</u>) ^a
			C	H	N	P	Cl	
(3)	C ₇ H ₁₆ N ₉ P ₆ Cl ₉	103	11.58 (11.50)	2.22 (2.21)	17.12 (17.24)	25.36 (25.42)	43.70 (43.64)	727 (727)
(4)	C ₁₀ H ₃₂ N ₁₀ P ₆ Cl ₈	227	16.02 (15.98)	2.98 (2.95)	18.56 (18.63)	24.48 (24.72)	37.67 (37.72)	748 (748)
(5)	C ₇ H ₁₆ N ₁₁ P ₈ Cl ₁₃	59	8.98 (8.80)	1.97 (1.68)	15.83 (16.00)	25.45 (25.73)	47.65 (47.86)	922 ^b (957)
(6)	C ₁₄ H ₃₂ N ₁₄ P ₈ Cl ₁₀	151	16.79 (16.84)	3.09 (3.23)	19.34 (19.63)	24.58 (24.81)	35.76 (35.49)	959 ^b (994)
(7)	C ₁₀ H ₂₂ N ₁₂ P ₈ Cl ₁₂	121	12.28 (12.21)	2.35 (2.26)	16.97 (17.09)	25.12 (25.19)	43.16 (43.25)	978 (978)

^aBased on mass of most abundant isotopes.

^b(M - Cl)⁺.

in ether-acetonitrile mixture (1:2) (300 cm³). Anhydrous Na₂SO₄ (10 g) was also added to this mixture. The flask was then placed in an ice-bath and spermine (2.02 g, 10 mmol), dissolved in the above mixture (75 cm³), was added dropwise (0.5 h). The mixture was stirred gently at room temperature for four days. Triethylammoniumchloride, Et₃NHCl, and sodium sulfate, Na₂SO₄, were then filtered off and the solvent removed in vacuo. The residue was washed with *n*-hexane. Thin-layer chromatography revealed one spot at R_f = 0.24 with CH₂Cl₂/THF (2:1) mixture as eluent. The crude product was subjected to column chromatography (silica gel, 100 g) using THF/CH₂Cl₂ (2:1) as eluent to remove traces of salts and polymeric products. The resulting white product was crystallized from Et₂O to give compound (4).

(c) With *N*-(3-aminopropyl)-1,4-diaminobutane (spermidine) in ether-acetonitrile mixture (1:2). N₃P₄Cl₈ (2), (9.57 g, 21 mmol) dissolved in Et₂O/MeCN mixture (1:2) (200 cm³), anhydrous Na₂SO₄ (10 g) and triethylamine (6.96 g, 68.8 mmol) were put in a round-bottom flask. The mixture was cooled with solid CO₂. Spermidine (2.00 g, 13.8 mmol) dissolved in the above mixture (100 cm³) was added dropwise (1 h) to the reaction mixture. The mixture was stirred gently at room temperature for four days. It was filtered to remove Et₃NHCl and Na₂SO₄, and the solvent removed on a rotary evaporator.

Traces of solvent and amine were removed under high vacuum. The residue was examined by t.l.c. using dichloromethane/benzene (5:3) as mobile phase, and four compounds were detected. The crude product was subjected to column chromatography (column length 65 cm, diameter 4 cm, 100 g silica gel for a 3 g mixture) using dichloromethane/benzene (5:3) as eluent. They were separated and compounds (6 and 7) were characterized by using spectroscopic techniques, mass spectrometry and elemental analyses. The others gave very complex ¹H, ³¹P and ¹³C n.m.r. spectra and were not characterized.

When the quantities of reagents were changed [N₃P₄Cl₈ (2), (12.77 g, 27.5 mmol), spermidine (2.0 g, 13.8 mmol), triethylamine (5.57 g, 55.1 mmol)]; five compounds were detected and separated by column chromatography as above. Only two compounds (6 and 7) were characterized.

Compounds (6 and 7) were crystallized from dichloromethane/benzene (3:1). The yields from the first experiment for compounds (6) and (7) were 0.56 g (5.5%) and 1.40 g (13.4%), respectively. The second experiment gave 0.47 g (4.7%) of compound (6) and 1.20 g (11.4%) of compound (7).

(d) with *N,N'*-bis(3-aminopropyl)-1,4-diaminobutane (spermine) in etheracetonitrile (1:2). Triethylamine (5.00 g, 49.50 mmol), N₃P₄Cl₈ (2), (4.73 g, 10.2 mmol) and spermine (1.00 g, 4.49 mmol) were allowed to react and worked-up as in (b). Hydrochlorides and Na₂SO₄ were filtered off and the solvent removed in vacuo. The colourless product was subjected to column chromatography (silica gel, 75 g) using THF/CH₂Cl₂ (1:2) as eluent to remove the remaining traces of hydrochlorides. T.l.c. showed only one spot at R_f = 0.15 with CH₂Cl₂ as eluent. It was dissolved in boiling *n*-hexane-CH₂Cl₂ (1:1) and set aside for crystallization of compound (5). Reaction conditions are given in Table III, analytical data in Table IV.

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