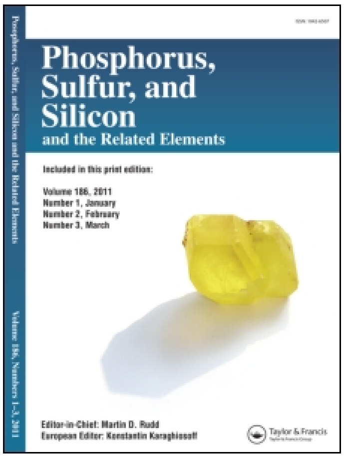

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 71[1]. THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE WITH BIS(2-HYDROXYETHYL)ETHER. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC STUDIES OF THE PRODUCTS

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The reactions of hexachlorocyclotriphosphazatriene with bis(2-hydroxyethyl)ether yield eight products: three spiro-derivatives, $N_3P_3Cl_4[(OCH_2CH_2)_2O]$, $N_3P_3Cl_2[(OCH_2CH_2)_2O]_2$, $N_3P_3[(OCH_2CH_2)_2O]_3$, an ansa, $N_3P_3Cl_4[(OCH_2CH_2)_2O]$, and a spiro-ansa product $N_3P_3Cl_2[(OCH_2CH_2)_2O]_2$, as well as single $(N_3P_3Cl_5)_2[(OCH_2CH_2)_2O]$ and double-bridged derivatives, $(N_3P_3Cl_4)_2[(OCH_2CH_2)_2O]_2$. A hydrolysis product, $N_3P_3Cl_4[O(CH_2)_2O(CH_2)_2OH]ON_3P_3Cl_5$, was also isolated. The ^1H, ^{31}P and ^{13}C n.m.r. spectra are reported.

Key words: Hexachlorocyclotriphosphazatriene; bis(2-hydroxyethyl)ether; spiro compounds; ansa structures; bridge structures; n.m.r. studies.

INTRODUCTION

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**1**) with ethane-diol, propane-1,3-diol and butane-1,4-diol led to examples of all four product types: spiro, ansa, bridging and monofunctional, with the first predominating.[2] When the central CH_2 group in propane-1,3-diol was exchanged for a CMe_2 group in 2,2-dimethylpropane-1,3-diol[3] ansa moieties were increased relative to spiro units when compared to the former diol. By contrast replacement of the CH_2 grouping of the former diol by a $C(CO_2Et)_2$ moiety gave exclusively spiro products.[4] Reports by the Toulouse group[5] that bis(2-aminoethyl)ether gave overwhelmingly a mono-ansa derivative, $N_3P_3Cl_4[(NHCH_2CH_2)_2O]$ (traces of its monospiro isomer were reported, but not isolated), whose structure was subsequently proven by X-ray crystallography[6] and a di-ansa compound,[5] later identified as a spiro-ansa derivative,[7] $N_3P_3Cl_2[(NHCH_2CH_2)_2O]_2$, prompted us to investigate the effect of an ether oxygen on the reactions of a diol. It has been known for some time[8] that amines being more powerful nucleophiles than alcohols gave a smaller number of derivatives for a given stoichiometry.

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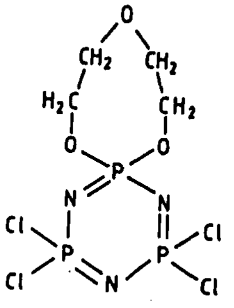
RESULTS AND DISCUSSIONS

We therefore chose to investigate the reactions of the diol analogue, bis(2-hydroxyethyl)ether, $(HOCH_2CH_2)_2O$, **(2)**, with the hexachloride, **(1)**. We isolated eight products from this system: $N_3P_3Cl_4[(OCH_2CH_2)_2O]$ (two isomers), **(3, 4)** $N_3P_3Cl_2[(OCH_2CH_2)_2O]_2$ (two isomers), **(5, 6)**, $N_3P_3[(OCH_2CH_2)_2O]_3$, **(7)**, $(N_3P_3Cl_5)_2[(OCH_2CH_2)_2O]$, **(8)** and $(N_3P_3Cl_4)_2[(OCH_2(H_2)_2O]_2$, **(9)**. A hydrolysis product, $N_3P_3Cl_4[O(CH_2)_2O(CH_2)_2OH]ON_3P_3Cl_5$, **(10)** was also isolated and characterised. We now discuss the structures of these derivatives based on n.m.r. spectroscopic and mass spectrometric studies.



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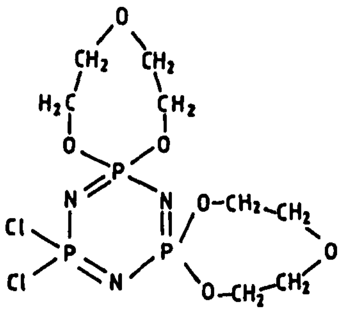

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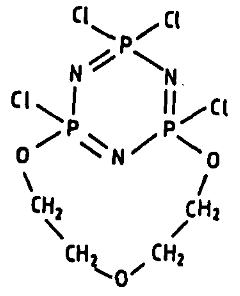

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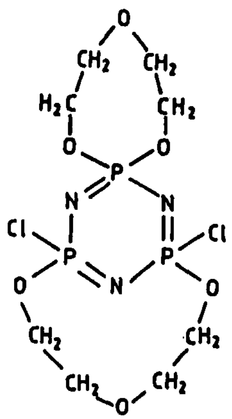

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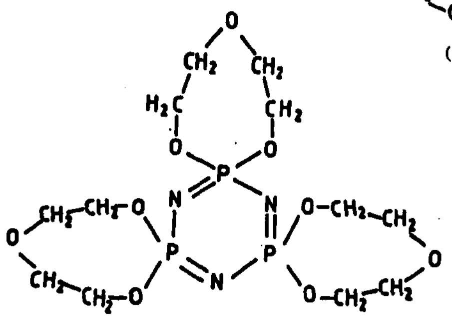

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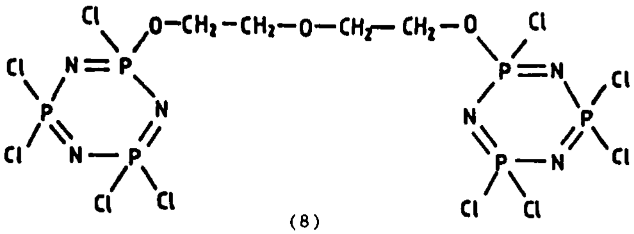
^{31}P *n.m.r. studies*

Compounds (**3**) and (**4**), whose analyses and mass spectra showed these to be $N_3P_3Cl_4[(OCH_2CH_2)_2O]$ could have in principle two structures: spiro (**3**) or ansa (**4**). Both types are known for 2,2-dimethylpropane-1,3-diol. Experience with these two isomers shows that the ansa compound has an AB_2 spectrum, whilst that of the spiro isomer is of the A_2X type. Proton coupling affects the B_2 part of the former and the X part of the latter. The spectrum of compound (**3**) is of the A_2X type, with the X part showing further splitting on proton coupling. Thus this compound can be assigned with confidence the spiro structure (**3**). Its isomer has an AB_2 spectrum and its B_2 part is affected by proton coupling. It is thus assigned the ansa structure (**4**). In the present system, as in that with 2,2-dimethylpropane-1,3-diol, the yield of the ansa compound (**4**) is somewhat larger than that of its spiro isomer (**3**).

The isomeric compounds (**5**) and (**6**) exhibit A_2X and AB_2 spectra respectively. Proton coupling experiments as well as comparison with the analogous propane-diol and 2,2-dimethylpropane-diol derivatives, allow unambiguous assignments of structures. Compound (**5**) is the dispiro derivative, compound (**6**) its spiro-ansa asomer. The yields of these two isomers were comparable in the 2,2-dimethylpropane-diol system, in contrast to that of the unmethylated diol and the present one, where the dispiro compound (**5**) is in larger yield. The sharp singlet observed for $N_3P_3[(OCH_2CH_2)_2O]_3$ demonstrates it to be the tris spiro derivative (**7**). The compound of composition $(N_3P_3Cl_4)_2[(OCH_2CH_2)_2O]$ has an A_2B spectrum, the B part giving fine structure on proton coupling. We therefore assign a singly-bridged structure (**8**) to this. We also obtained another product (**9**), which was purified with difficulty and whose inadvertent loss prevented complete characterisation. Its ^{31}P spectrum at 25.8 p.p.m. presented as a singlet suggesting either a triply-bridged or



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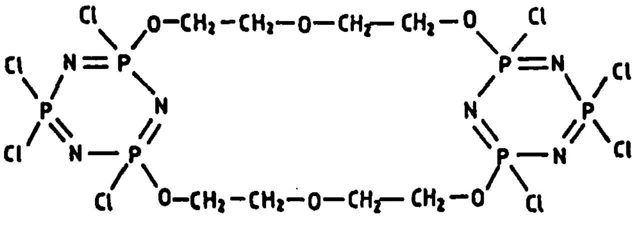

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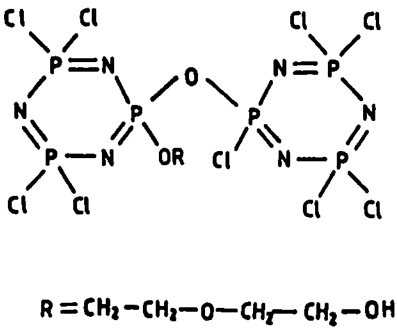

(10)

a doubly-bridged structure, with the PCl_2 and PCl(OR) chemical shifts in the latter very, very close. Our own and other groups' experience with the chemical shifts of bridged species suggest the latter to be feasible and that in conjunction with the ^1H and ^{13}C data (see below) makes us put forward a doubly-bridged structure **(9)** for this compound.

The spectrum of compound **(10)** consists of two similar A_2X spectra, the X portions of these two being coupled to each other (18.3 Hz). This together with the ^1H and ^{13}C spectra (see below) of this compound, shows that it contains two N_3P_3 units linked by an oxygen bridge and also has a diol moiety as an open-chain substituent. The structure based on the n.m.r. data is $N_3P_3Cl_4[O(CH_2)_2$-$O(CH_2)_2OH]ON_3P_3Cl_5$.

The ^{31}P data are summarised in Table I.

TABLE I

^{31}P n.m.r. data of derivatives **(1)**, **(3)**–**(10)**[a]

Compound	δ Pspiro[b]	δ PCl_2[b]	δ P(OR)Cl[b]
(1)		19.9	
(3)[c]	4.9	23.2	
(5)[d]	10.2	25.9	
(7)	15.3		
(4)[e]		27.6	22.3
(6)[f]	14.4		27.1
(8)[g]		23.5	25.8
(9)[h]		25.8	−7.8[i,j]
(10) $N_3P_3Cl_4(OR)O$ moiety		22.2	1.4[k]
$N_3P_3Cl_5O$ moiety		20.7	

[a] In $CDCl_3$ (85% phosphoric acid external reference) at 80.95 and 162.0 MHz. (room temperature).

[b] In p.p.m.

[c] $J(\underline{P}spiro\text{-}\underline{P}Cl_2)$ 70.8 Hz.

[d] $^2J(\underline{P}spiro\text{-}\underline{P}Cl_2)$ 75.3 Hz.

[e] $^2J[\underline{P}(OR)Cl\text{-}\underline{P}Cl_2]$ 59.3 Hz.

[f] $^2J[\underline{P}spiro\text{-}\underline{P}(OR)Cl]$ 75.3 Hz.

[g] $^2J[\underline{P}(OR)Cl\text{-}\underline{P}Cl_2]$ 49.3 Hz.

[h] $^2J[\underline{P}(OR)Cl\text{-}\underline{P}Cl_2]$ Hz.

[i] $^2J[\underline{P}(OR)O\text{-}\underline{P}Cl_2]$ 77.0 Hz.

[j] $^2J(\underline{P}O\underline{P})$ 18.3 Hz.

[k] $^2J(\underline{P}ClO\text{-}\underline{P}Cl_2)$ 71.5 Hz.

^{1}H n.m.r. data

These spectra were exceedingly complex and no analysis was attempted. The approximate chemical shifts of the α- and β-$C\underline{H}_2$ protons are given in Table II.

^{13}C n.m.r. data

In contrast to earlier studies,[2,3] in the present one the chemical shifts of the α- and β-carbon nuclei are close together, as both are adjacent to oxygen atoms. The

TABLE II

^{1}H n.m.r. data for compounds **(2–10)**[a]

Compound	δ $POC\underline{H}_2$[b]	δ $CH_2C\underline{H}_2O$[b]
(2)[d]	3.3	3.2
(3)	4.3	3.9
(5)	4.2	3.8
(7)	4.2	3.9
(4)	4.3	3.7
(6) spiro	4.3	3.9
ansa	4.3	3.7
(8)	4.0	3.7
(9)	4.2	3.7
(10)[e]	4.2	3.8

[a] $CDCl_3$ (TMS internal reference) at 199.5 MHz. (room temperature).

[b] In p.p.m.

[c] In Hz.

[d] Assignment uncertain; signals pertain to $HOC\underline{H}_2$ and $HOCH_2C\underline{H}_2$ groupings; $\underline{H}O$ observed at ~4.6 p.p.m.

[e] Two further signals at 3.8 and 3.6 p.p.m.

TABLE III

^{13}n.m.r. data of derivatives **(2)–(10)**[a]

Compound	δ $PO\underline{C}$[b]	δ $POC\underline{C}$[b]	$^{2}J(\underline{P}\underline{C})$[c]	$^{3}J(\underline{P}\underline{C})$[c]
(2)[d]	71.4	60.3		
(3)	71.0d	69.0d	0.9	7.1
(5)	70.9s	68.0t	0.0	7.3
(7)	71.0s	67.4q	0.0	4.8
(4)	70.4s	69.8t	0.0	10.2
(6) spiro	70.9s	68.1	0.0	7.0
	70.8s	67.5	0.0	6.7
ansa	70.7s	69.0t	0.0	9.6
(8)	71.0s	69.0d	0.0	7.3
(9)	70.5s	69.5q[e]	0.0	9.6[e]
(10)[f]	69.2d	68.1d	8.0	6.4

[a] In $CDCl_3$ (TMS internal reference) at 50.1 MHz. (room temperature).

[b] In p.p.m.

[c] In Hz.

[d] Assignment uncertain; signals pertain to $HO\underline{C}H_2$ and $HOCH_2\underline{C}H_2$ groupings.

[e] Complicated second order spectrum; quartet structure and *J*-value could be misleading.

[f] Also singlets at 71.6 and 42.6 p.p.m.

three bond coupling constants $^3J(\underline{PC})$ are very much larger than the two bond ones and hence the expected multiplicities can be readily seen in the former, but only rarely in the latter. In compound (**9**) the multiplicity and $^3J(\underline{PC})$ could be misleading, because of a complicated second order spectrum. The three bond coupling constants in the ansa moieties are significantly larger than in the spiro or bridging groups. The data are collected in Table III.

SUMMARY

In contrast to the findings reported for bis(2-aminoethyl)ether,[5] its di-ol analogue (**2**) gave a complex series of products containing spiro, ansa, bridging and open-chain moieties. It thus resembles the behaviour of propane-1,3-diol[2] and 2,2-dimethylpropane-1,3-diol.[3] The greater specificity of the amino reagent[5] is in keeping with earlier observations on monofunctional amino and hydroxy compounds.[8]

EXPERIMENTAL

Chemicals were obtained as follows: benzene, light petroleum (b.p. 40–60°C), dichloromethane (May & Baker Ltd), deuteriated solvents for n.m.r. spectroscopy, bis(2-hydroxyethyl)ether, (Aldrich Chem. Co., Ltd) pyridine, *n*-hexane (BDH Chemical Co., Ltd), hexachlorocyclotriphosphazatriene (Shin Nisso Kako Co., Ltd). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60 254 (silica gel) precoated T.L.C. plates and sprayed with Ninhydrin (0.5 w/v%) in butanol solution, and developed at approximately 130°C. Separations of products were carried out by flash column chromatography[9] using Kieselgel 60. Melting points were determined on a Reichert-Kofler micro heating stage and a Mettler FB 82 hot stage connected to a FP800 central processor both fitted with a polarising microscope.

^1H n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 199.5 MHz.), and a varian XL400 spectrometer (operating at 399.5 MHz.—University College, London). Samples were dissolved in $CDCl_3$ and placed in 5mm n.m.r. tubes. Measurements were carried out using a $CDCl_3$ lock, TMS as internal reference and sample concentrations of 15–20 mg/cm.^{3} ^{31}P n.m.r. spectra were recorded using a JEOL JNM FX-60 spectrometer (operating at 24.15 MHz.), a Varian XL-200 spectrometer (operating at 80.98 MHz.—University College, London), a Varian VXR 400 (operating at 162.0 MHz.—University College, London), 85% H_3PO_4 was used as an external reference. ^{13}C n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 50.10 MHz.) and a Varian VXR 400 spectrometer (operating at 100.577 MHz.—University College, London), TMS was used as an internal reference.

The mass spectra were recorded using a VG 7070H Mass Spectrometer with Finnigan INCOS Data System at University College, London and a VG ZAB IF mass spectrometer at the School of Pharmacy.

Microanalyses were carried out by University College, London microanalytic service.

The reactions of compound (1) with diol (**2**).

(a) one equivalent of (**2**). The hexachloride, $N_3P_3Cl_6$, (**1**), (4g, 11.49 mmol) was dissolved in dichloromethane (150 cm^3). To this solution pyridine (1.8 g, 22.75 mmol) was added dropwise. Liquid bis(2-hydroxyethyl)ether (1.21 g, 11.41 mmol) was then added to this mixture whilst stirring at room temperature. Pyridine hydrochloride precipitated from the reaction mixture approximately 10 hours after the start of the reaction. The reaction mixture was filtered. T.l.c. using CH_2Cl_2 as eluent reveals the formation of two major products. An intense spot is observed on the base line of the t.l.c. plate due to a mixture of pyridine hydrochloride and polymeric products. Column chromatography was used [dichloromethane/benzene (7:1) as eluent] to remove polymeric products and pyridine hydrochloride.

(i) The phosphazene derivative was identified as the mono spiro compound, (**3**), m.p. 160°C, yield 1.1 g (27.5%) [Found: C, 12.78; H, 2.06; N, 10.86%; $\underline{M}^+$, 399 $C_4H_8O_3N_3P_3Cl_4$ requires C, 12.67; H, 2.12; N, 11.00%; $\underline{M}$, 379]

(ii) the singly-bridged compound, (**8**), an oil, yield; 1.73 g, (43.5%) [Found: C, 6.76; H, 1.26; N, 12.03%; $\underline{M}^+$, 724. $C_4H_8O_3N_6P_6Cl_{10}$ requires, C, 6.63; H, 1.10; N, 11.61%, M, 724].

(b) Two equivalents of (**2**). The same procedure as for (**a**): Three major compounds were separated by column chromatography using dichloromethane/benzene (4.5:1) as eluent.

(i) The spiro ansa compound (**6**), m.p. 111–113°C, yield 0.67 g, (16.75%) [Found: C, 22.96; H, 3.72; N, 9.87%; $\underline{M}^+$, 413 $C_8H_{16}O_6N_3P_3Cl_2$ requires C, 23.24; H, 3.87; N, 10.00%, $\underline{M}$, 413].

(c) Three equivalents of (**2**). The reaction was carried out as in (**a**). The stirring time was 12 hours. Three phosphazene derivatives were separated by column chromatography using a mixture of dichloromethane/hexane, (6:3) as eluent.

(i) The mono ansa compound (**4**), m.p. 97°C, yield 1.39 g, (34.5%) [Found: C, 13.30; H, 2.19; N, 10.83%; $\underline{M}^+$, 379. $C_4H_8O_3N_3P_3Cl_4$ requires C, 12.67; H, 2.12; N, 11.00%, $\underline{M}$, 379.]

(ii) The dispiro isomer (**5**), m.p. 122–123°C, yield 0.60 g (15%) [Found: C, 23.59, H, 3.72; N, 9.95; $\underline{M}^+$, 413. $C_8H_{16}O_6N_3P_3Cl_2$ requires C, 23.10; H, 3.00; N, 10.00%; $\underline{M}$, 413]

(iii) The tris-spiro compound (**7**), an oil, yield 0.83 g (20.7%) [Found: C, 34.30; H, 5.52; N, 8.51; $\underline{M}^+$, 447. $C_{12}H_{24}O_9N_3P_3$ requires C. 33.70; H, 5.28; N, 9.20%; M, 447].

(iv) The hydrolysis product (**10**), an oil, yield 1.29 g (32.25%) [Found: C, 6.03; H, 0.93; N, 11.62%; $\underline{M}^+$, 689 $(M - H_2O + H)^+$, $C_4H_9O_4N_6P_6Cl_9$ requires C, 6.80; H, 1.27; N, 11.89; $\underline{M}^+$, 706].

Note: Products were recrystallized from the minimum quantity of benzene by adding few drops of light petroleum (b.p. 40–60°C).

ACKNOWLEDGEMENTS

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