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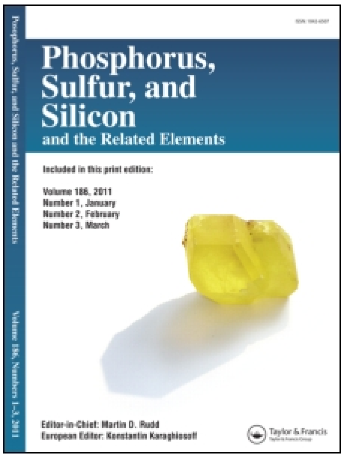

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 66.[1] THE REACTIONS OF OCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH 2,2-DIMETHYLPROPANE-1,3-DIOL. SYNTHETIC AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC INVESTIGATIONS.

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The reactions of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, with 2,2-dimethylpropane-1,3-diol gave the following isolated and characterised derivatives; $N_4P_4Cl_6[(OCH_2)_2CMe_2]$, $N_4P_4Cl_4[(OCH_2)_2CMe_2]_2$ (2 isomers) and $N_4P_4Cl_2[(OCH_2)_2CMe_2]_3$. ^{31}P, ^1H and ^{13}C n.m.r. spectroscopic investigations showed all derivatives to have spiro structures. The isomeric bis derivatives have 2,2,4,4- and 2,2,6,6-structures.

Key words: Octachlorocyclotetraphosphazatetraene, 2,2-dimethylpropane-1,3-diol, spiro compounds, n.m.r. studies.

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INTRODUCTION

We have recently reported the reactions of octachlorocyclotetraphosphazatetraene, (**1**) with ethanediol, propane-1,3-diol and butane-1,4-diol.[2] Spiro derivatives were the only products observed. The great complexity of their ^1H n.m.r. spectra required heteronuclear and homonuclear decoupling techniques to extract the relevant parameters. We have therefore studied the reactions of compound (**1**) with 2,2-dimethylpropane-1,3-diol. Not only are the $OC\underline{H}_2$ proton signals much less complicated than those with propane-1,3-diol derivatives, but in addition the $C\underline{H}_3$ groups give rise to singlets, and hence different environments are more readily detected.

RESULTS AND DISCUSSION

We isolated four products from the above reaction system: $N_4P_4Cl_6[(OCH_2)CMe_2]$, (**2**), $N_4P_4Cl_4[(OCH_2)CMe_2]_2$ (two isomers) (**3** and **4**) and $N_4P_4Cl_2[(OCH_2)CMe_2]_3$, (**5**). We now discuss their structures based on n.m.r. spectroscopic studies.

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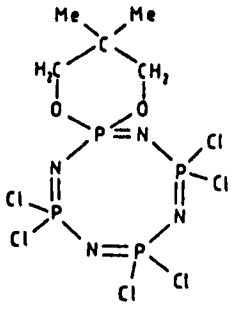
^{31}P *n.m.r. Studies*

In this study, as in our earlier one with propane-1,3-diol,[2] we observed spectra of three types: $A_2MX(A_2BX)$, $AA'XX'$ $(AA'BB')$ and A_2X_2 (A_2B_2). Compounds (**2** and **5**) show spectra of the A_2MX type establishing that these mono- and tris-derivatives are both spiro compounds. Proton coupled spectra allow unambiguous assignments to ≡Pspiro and ≡PCl_2 moieties. A spectrum of the A_2MX type has been published in an earlier report.[2] The spectrum of compound (**3**) exhibits two triplets; (A_2X_2) this derivative is thus shown to have a 2,2,6,6-bis-spiro structure. The spectrum of compound (**4**) is of the $AA'XX'$ type. This establishes this compound to be clearly a 2,2,4,4-bis spiro derivative.



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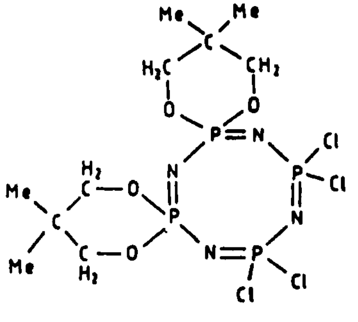

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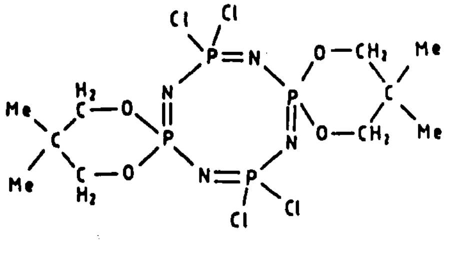

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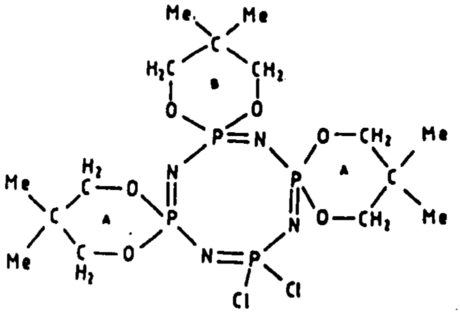

(5)

From the data provided in Table I it can be seen that: i) increasing substitution by the spiro group in the molecule leads to overall downfield shifts for both ≡$\underline{P}Cl_2$ and ≡$\underline{P}$spiro groups (**1**) < (**2**) < (**3**) < (**4**) < (**5**).

Proton and Carbon Spectroscopy

The ^1H and ^{13}C n.m.r. spectra of the tris-spiro derivative (**5**) will be taken as an example for this series of the compounds and these are described below.

TABLE I

The ^{31}P n.m.r. data of the octachloride derivatives

Compound	δ $\underline{P}$spiro[a]	δ $\underline{P}Cl_2$[a]	$^2\underline{J}(\underline{P}spiro\text{-}\underline{P}Cl_2)$[b]	$^2\underline{J}(\underline{P}X_2\text{-}\underline{P}X_2)$[b]
$N_4P_4Cl_8$ (**1**)		−6.5		
$N_4P_4Cl_6[(OCH_2)_2CMe_2]$ (**2**)	−10.8	−5.4(1)[c] −4.0(2)	58.1	29.6 (X_2═Cl_2)
$N_4P_4Cl_4[(OCH_2)_2CMe_2]_2$ (**3**)	−9.7	−1.6	57.2	
$N_4P_4Cl_4[(OCH_2)_2CMe_2]_2$ (**4**)	−6.7	−4.6	55.9	82.8 (X_2═spiro) 34.5 (X_2═Cl_2)
$N_4P_4Cl_2[(OCH_2)_2CMe_2]_3$ (**5**)	−2.1(1) −5.7(2)	−2.6	52.7	80.6 (X_2═spiro)

[a] In p.p.m., [b] in Hz, [c] relative number of nuclei in brackets.

^1H n.m.r. Studies

The ^1H n.m.r. absorption for the $OC\underline{H}_2$ methylene protons is observed as a doublet and a multiplet (Figure 1). Those of ring (**B**) give a doublet. The $C\underline{H}_2$ protons of the two spiro rings (**A**) directly adjacent to the ≡PCl_2 group are observed as non-equivalent, since the protons within each methylene group are in a different environment, (one of the methylene protons observes the ≡PCl_2 group and the other faces the ≡Pspiro ring). The ^1H data are given in Table II.

Thus the multiplicity of the signals at δ 4.13 and δ 3.89 can clearly be assigned to the protons of the two spiro groups (**A**), whilst the doublet at δ 4.04 is assigned to the —$OC\underline{H}_2$ protons of the spiro ring (**B**).

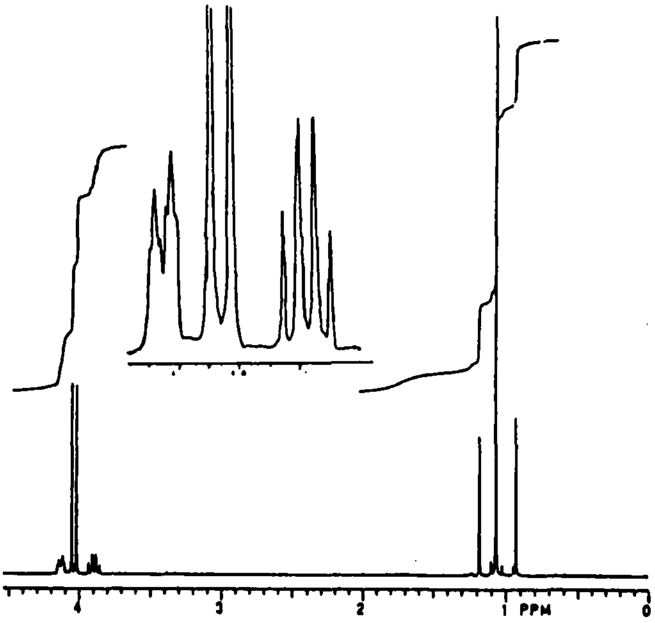

FIGURE 1 The ^1H n.m.r. spectrum of compound (**5**) at room temperature in $CDCl_3$ at 399.95 MHz.

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TABLE II

The ^1H n.m.r. data of the octachloride derivatives

Compound	δ POC$\underline{H}_2$[a]	δ CC$\underline{H}_3$[a]	$^2J(\underline{P}\text{-}\underline{H})$[b]
(2)	4.06	1.10	13.4
(3)	4.05	1.08	13.4
(4)	4.02	1.09	11.4
	3.91	0.95	10.7
(5)	4.13[c], 3.89[c]	1.18[c], 0.93[c]	11.1[c], 11.1[c]
	4.04[d]	1.08[d]	13.5[d]

[a] In p.p.m., [b]in Hz, [c] data for spiro ring (**A**), [d] data for spiro ring (**B**).

The methyl protons of the dimethyl groups of the two spiro rings (**A**) directly adjacent to the $\equiv PCl_2$ group have two environments; thus two singlets were observed at 1.18 and 0.93 p.p.m. On the other hand the $—C\underline{H}_3$ protons in the case of the spiro ring directly opposite to the $\equiv PCl_2$ group have only one environment; hence one (more intense) signal was observed at 1.08 p.p.m.

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^{13}C *n.m.r. Studies*

Aspects of the carbon-13 n.m.r. spectrum for compound (**5**) are shown in Figure 2. Compound (**5**) possesses two different types of spiro rings [two opposite each other (**A**) and one opposite to the $\equiv PCl_2$ group (**B**)]. The differentiation between these two rings can be made on the basis of the presence or absence of long range virtual coupling in the ^{13}C n.m.r. spectrum. [All the carbon nuclei are in identical

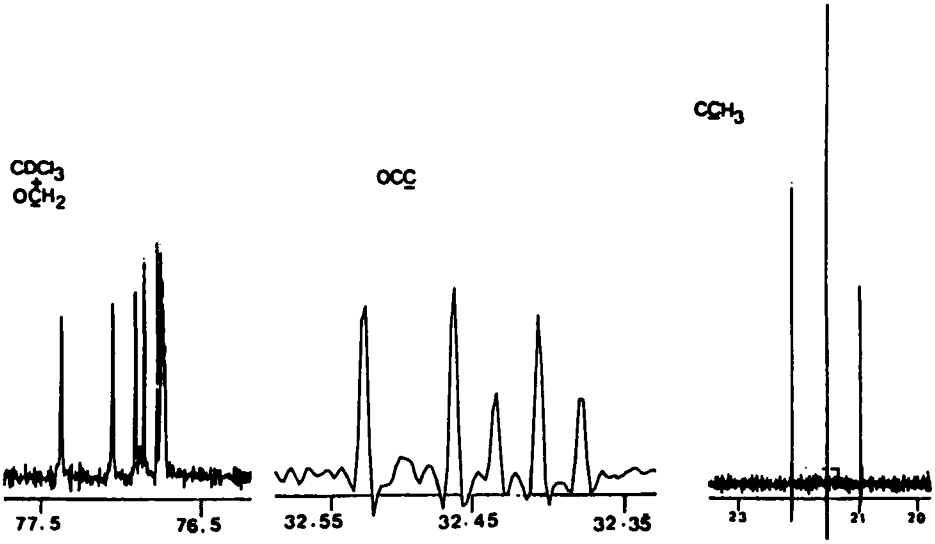

FIGURE 2 Sections of the ^{13}C n.m.r. spectrum of compound (**5**) at room temperature in $CDCl_3$ at 99.95 MHz.

TABLE III

The ^{13}C n.m.r. data of the octachloride derivatives

Compound	δ PO$\underline{\text{C}}$[a]	δ POC$\underline{\text{C}}$[a]	δ C$\underline{\text{C}}$H$_3$[a]	$^2\underline{\text{J}}(\underline{\text{P}}\text{O}\underline{\text{C}})$[b]	$^3\underline{\text{J}}(\underline{\text{P}}\text{OC}\underline{\text{C}})$[b]
(**2**)	77.10	32.56	21.44	5.9	5.7
(**3**)	76.84	32.43	21.50	5.9	5.6
(**4**)	76.83	32.44	22.01	5.6	5.6
			21.90		
(**5**)	76.81[c]	32.49[c]	22.01[c], 20.98[c]	5.6[c]	5.7[c]
	76.90[d]	32.41[d]	21.53[d]	5.6[d]	5.7[d]

[a] In p.p.m., [b] in Hz, [c] data for spiro ring (**A**), [d] data for spiro ring (**B**).,

environments within each spiro ring, although the substituent methyl carbons of rings (**A**) will show two different environments.]

Since the two phosphorus nuclei of the (**A**) rings are in identical chemical environments and linked to similar groups, virtual coupling might be expected. Thus triplet signals were observed for the methylene carbon nuclei, POC$\underline{H}_2$, as well as for the central carbon nuclei (POC$\underline{C}$). In the case of the (**B**) ring the ^{13}C n.m.r. absorptions of the corresponding nuclei were different; only doublets were observed due to the absence of the virtual coupling effect. The ^{13}C n.m.r. absorptions for the methyl carbons were observed as follows:

(i) Two singlets at δ 22.01 and δ 20.98 for the —C$\underline{H}_3$ nuclei of the dimethyl groups of the two spiro rings (**A**) directly opposite each other; and

(ii) One (more intense) singlet at δ 21.53 for the third spiro ring (**B**) due to the identity of the environment. The ^{13}C data are given in Table III.

SUMMARY

In contrast to its lower homologue, $N_3P_3Cl_6$, where the change from propane-1,3-diol[3] to 2,2-dimethylpropane-1,3-diol[4] led to significant changes in product distribution and type, the reactions of the octachloride, $N_4P_4Cl_8$, (**1**) with the same two diols gave essentially similar products. All the products were spiro-derivatives and in both cases mono-, 2,2,4,4- and 2,2,6,6-bis-, and tris-spiro derivatives were isolated and characterised. No tetrakis-spiro compounds were isolated for these two diols.[2] There is tentative mass spectrometric evidence of a trace of a tetrakis-derivative in the present study.

The absence, or near absence, of tetrakis-spiro derivatives with these two diols, contrasts with the ready isolation of such derivatives with butane-1,4-diol[2] and with diethyl bis(hydroxymethyl) malonate.[5]

The ^{1}H and ^{13}C n.m.r. spectra of the compounds reported in the present study allow easier interpretation than those of the propane-1,3-diol derivatives.[2]

EXPERIMENTAL

Chemicals were obtained as follows: acetonitrile, light petroleum (b.p. 40–60°C), dichloromethane (May & Baker Ltd.), tetrahydrofuran (Fluka-Garantie 99.5%), deuteriated solvents for n.m.r. spec-

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troscopy, 2,2-dimethylpropane-1,3-diol, (Aldrich Chem. Co. Ltd.), pyridine, (B.D.H. Chemical Co. Ltd.), octachlorocyclotetraphosphazatetraene (Shin Nisso Kako Co. Ltd.). Solvents were dried by conventional methods.

The experimental techniques and spectroscopic methods were described in an earlier paper.[4] The reaction of the octachloride, $N_4P_4Cl_8$, (8 g, 17.24 mmol) with an excess of 2,2-dimethylpropane-1,3-diol (14.3 g, 137.50 mmol) and pyridine (10.4 g, 138.00 mmol) was carried out in boiling acetonitrile (300 cm^3) for approximately 20 h. Four products were isolated by column chromatography using THF/CH_2Cl_2 (1:1) as eluent. The following products were isolated in the order given:

a) mono spiro derivative $N_4P_4Cl_6[(OCH_2)_2CMe_2]$ as major product, m.p. 69°C, yield 0.72 g (9%). (Found: C, 12.2; H, 2.1; N, 11.0%; $\underline{M}^+$, 492. $C_5H_{10}O_2N_4P_4Cl_6$ requires C, 12.1; H, 2.1; N, 11.05; $\underline{M}$, 492)

b) 2,2,6,6-bis-spiro derivative, m.p. 193°C, yield 0.56 g (7%). (Found: C, 22.9; H, 4.0; N, 10.6%; $\underline{M}^+$, 524. $C_{10}H_{20}O_4N_4P_4Cl_4$ requires C, 22.8; H, 3.8; N, 10.65%; $\underline{M}$, 524.

c) 2,2,4,4-bis-spiro derivative, m.p. 162°C, yield 0.48 g (6%). (Found: C, 22.9; H, 4.0; N, 10.7%; $\underline{M}^+$, 524.

d) tris-spiro derivative $N_4P_4Cl_2[(OCH_2)_2CMe_2]_3$, m.p. 150°C, yield 0.2 g (3%). (Found: C, 32.3; H, 5.5; N, 10.1%; $\underline{M}^+$, 556. $C_{15}H_{30}O_6N_4P_4Cl_2$ requires C, 32.3; H, 5.4; N, 10.1%; $\underline{M}$, 556).

A mixture of light petroleum (b.p. 40–60°C) and dichloromethane was used for the recrystallisation of the above compounds.

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