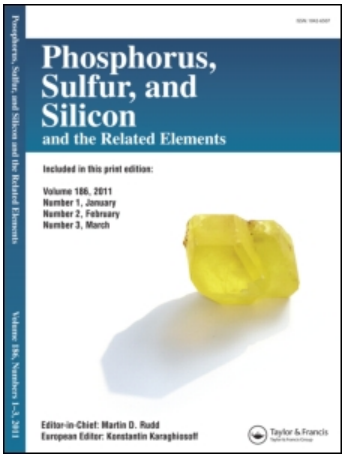


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# PHOSPHORUS-NITROGEN COMPOUNDS. PART 64.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE WITH 2, 2-DIMETHYLPROPANE-1, 3-DIOL. NUCLEAR MAGNETIC RESONANCE STUDIES OF THE PRODUCTS

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# PHOSPHORUS–NITROGEN COMPOUNDS. PART 64.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE WITH 2,2-DIMETHYLPROPANE-1,3-DIOL. NUCLEAR MAGNETIC RESONANCE STUDIES OF THE PRODUCTS

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The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with 2,2-dimethylpropane-1,3-diol yield monospiro-, $N_3P_3Cl_4[(OCH_2)_2CMe_2]$, dispiro-, $N_3P_3Cl_2[(OCH_2)_2CMe_2]_2$, and trispiro-derivatives, $N_3P_3[(OCH_2)_2CMe_2]_3$. An ansa, $N_3P_3Cl_4[(OCH_2)_2CMe_2]$, and a spiro-ansa, $N_3P_3Cl_2[(OCH_2)_2CMe_2]_2$ and a doubly-bridged compound, $(N_3P_3Cl_4)_2[(OCH_2)_2CMe_2]_2$ were also isolated. Product types and relative yields were compared with those arising from propane-1,3-diol. The yields of ansa products from the reactions of the dimethyl diol seem to be considerably enhanced relative to those of its unmethylated analogue. $^{31}P$ and $^1H$ n.m.r. spectra are reported.

*Key words:* Hexachlorocyclotriphosphazatriene; 2,2-dimethylpropane-1,3-diol; ansa compounds; spiro compounds; doubly-bridged compound; n.m.r. studies.

## INTRODUCTION

We have recently reported the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (**1**) with ethanediol, propane-1,3-diol and butane-1,4-diol.[2] Spiro derivatives were the most prevalent products. These contained, with the above reagents, 5-, 6-, and 7-membered phosphate rings. In a number of these the $OCH_2$ protons, and, where appropriate, the $CCH_2$ protons were in different chemical environments. Differences in chemical shifts of these methylene protons were only pronounced in the 6-membered phosphate rings, and these proved most useful for structural assignments. The very complexity of their $^1H$ n.m.r. spectra required heteronuclear and homonuclear decoupling techniques to extract the relevant parameters. The widths of these signals were, however, in some cases too large for satisfactory homonuclear decoupling, and this applied particularly to the decoupling of the $CCH_2$ protons.

We have therefore studied the reactions of compound (**1**) with 2,2-dimethylpropane-1,3-diol. Not only are the $OCH_2$ proton signals much less complicated than those with propane-1,3-diol derivatives, but in addition the

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$CCH_3$ groups give rise to singlets, and hence different environments are more readily detected.

Through the inductive effects of the methyl groups the methylated diol should be a somewhat stronger nucleophile than its unmethylated analogue. As a corollary, the presence of the methylated spiro ring should be somewhat more deactivating than its unmethylated counterpart, towards further $S_N2$ type of attack. Additionally the effects of the gem-dimethyl groups are well known, viz. the Thorpe–Ingold effect.[3] We therefore wished to examine the effects, if any, of the above structural changes of the diol on the type and the quantity of products produced, such as spiro (6-membered ring), ansa (8-membered ring), bridging and monodenate derivatives.

## RESULTS AND DISCUSSION

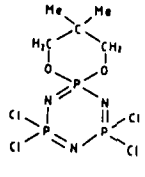
We isolated six products from the above reaction system: $N_3P_3Cl_4(OCH_2CMe_2CH_2O)$ (two isomers), $N_3P_3Cl_2(OCH_2CMe_2CH_2O)_2$ (two isomers), $N_3P_3(OCH_2CMe_2CH_2O)_3$, and $(N_3P_3Cl_4)_2(OCH_2CMe_2CH_2O)_2$. We now discuss their structure based on n.m.r. spectroscopic studies.



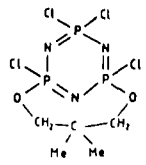
## $^{31}P$ N.M.R. STUDIES

Compounds (**2**) and (**3**), whose analyses and mass spectra showed these to be $N_3P_3Cl_4(OCH_2CMe_2CH_2O)$ could have in principle two structures: spiro (**2**) or ansa (**3**). Both types are known for propane-1,3-diol, although the ansa compound occurs only in very low yield. Experience with these two isomers shows that the ansa compound has an $A_2B$ spectrum, whilst that of the spiro isomer is of the $A_2X$ type. Proton coupling affects the $A_2$ part of the former and the X part of the latter. The spectrum of compound (**2**) 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 (**2**). Its isomer has its $A_2$ part affected by proton coupling. It is thus assigned the ansa structure (**3**). In contrast to the propane diol system, where the yield of the ansa compound is minute and only a fraction of that of its spiro isomer,[2] in the present system the yield of the ansa compound (**3**) is somewhat larger than that of its spiro isomer (**2**).

The isomeric compounds (**4**) and (**5**) both exhibit $A_2X$ spectra. Proton coupling experiments as well as comparison with the analogous propane-diol derivatives, allow unambiguous assignments of structures. Compound (**4**) is the dispiro derivative, compound (**5**) its spiro-ansa isomer. The yields of these two isomers (**4**) and (**5**) are comparable in this system, in contrast to that of the unmethylated diol, where the dispiro compound is in larger yield.[2] The sharp singlet observed for $N_3P_3(OCH_2CMe_2CH_2O)_3$ demonstrates it to be the tris spiro derivative (**6**). The compound of composition $(N_3P_3Cl_4)_2(OCH_2CMe_2CH_2O)_2$ has an $A_2B$ spectrum, the $A_2$ part giving fine structure on proton coupling. We therefore assign a doubly-bridged structure (**7**) to this. This contains an inner 16-membered ring. The $^{31}P$ data are summarised in Table I.



(2)



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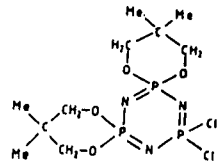

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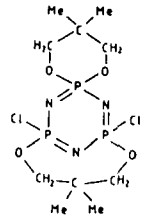

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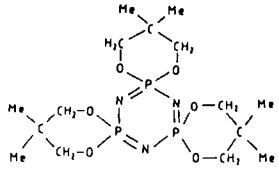

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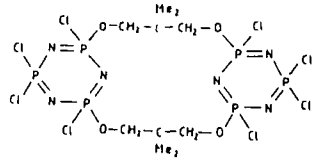

(7)



TABLE I

$^{31}$P n.m.r. data of derivatives (**2**)–(**7**)[a]

| Compound | δPspiro[b] | δ $PCl_2$[b] | δP(OR)Cl[b] |
|---|---|---|---|
| (**1**) | | 19.9 | |
| (**2**)[c] | 2.2 | 23.3 | |
| (**4**)[d] | 8.7 | 26.1 | |
| (**6**) | 13.9 | | |
| (**3**)[e] | | 23.5 | 25.0 |
| (**5**)[f] | 9.8 | | 31.8 |
| (**7**)[g] | | 26.4 | 27.4 |

[a] In $CDCl_3$ (85% phosphoric acid external reference) at 80.95 and 162.0 MHz (room temperature).
[b] In p.p.m.
[c] $^2J$(*P* spiro–$PCl_2$) 69.3 Hz.
[d] $^2J$(*P* spiro–$PCl_2$) 70.4 Hz.
[e] $^2J$[*P*(OR)Cl–$PCl_2$]64.2 Hz.
[f] $^2J$[*P* spiro–*P*(OR)Cl] 70.9 Hz.
[g] $^2J$[*P*(OR)Cl–$PCl_2$] 57.6 Hz.

## $^1$H N.M.R. DATA

These spectra are greatly simplified compared to those of the propane-1,3-diol derivatives. Those of the two spiro derivatives, $N_3P_3Cl_2[O(CH_2)_3O]_2$ and $N_3P_3Cl_2[(OCH_2)_2CMe_2]_2$ are compared in Figure 1.

The $OCH_2$ protons are about 0.5 p.p.m. more shielded than those of the corresponding propanediol derivatives. The expected small shielding on passing from mono- to tris- derivative is observed for $OCH_2$ and to a lesser extent for the $CH_3$ protons. The ansa (**3**), the dispiro (**4**), the ansa portion of the spiro–ansa (**5**) and the doubly-bridged derivative (**7**) show remarkable similarity in $OCH_2$ and $CH_3$ in chemical shifts. $^3J(PH)$ values fall into three distinct groups: (i) mono-spiro (**2**), tris-spiro (**6**) and the spiro section of the spiro-ansa derivative (**5**); (ii) ansa (**3**), ansa section of compound (**5**) and doubly-bridged derivative (**7**); (iii) dispiro compound (**4**). The data are in Table II.

## SUMMARY

If we consider the present findings pertaining to the reactions of 2,2-dimethylpropane-1,3-diol with the hexachloride (**1**) and compare these with our



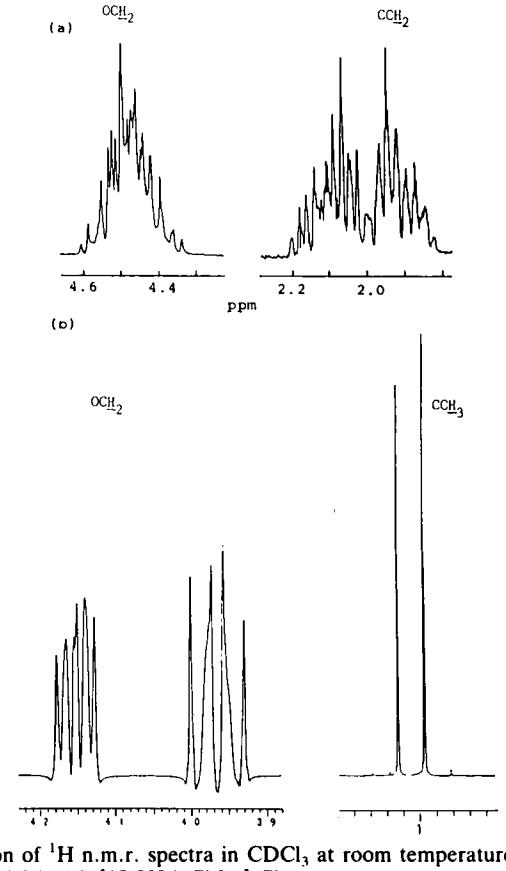


FIGURE 1 Comparison of $^1$H n.m.r. spectra in $CDCl_3$ at room temperature at 399.95 MHz. of (a) $N_3P_3[O(CH_2)_3O]_2Cl_2$ and (b) $N_3P_3[(OCH_2)_2CMe_2]_2Cl_2$.

TABLE II

$^1$H n.m.r. data for compounds (**2–7**)[a]

| Compound | $\delta$ $OCH_2$[b] | $\delta$ $CCH_3$[b] | $^3J(PH)$[c] | $^2J(H_A-H_B)$ |
|---|---|---|---|---|
| (**2**) | 4.14 | 1.10 | 13.2 | |
| (**4**) | 4.20 | 1.15 | 5.05 | 11.9 |
| | 3.88 | 0.99 | 17.3 | |
| (**6**) | 4.00 | 1.06 | 13.1 | |
| (**3**) | 4.22 | 1.10 | 7.9 | |
| | 3.86 | 0.98 | 8.2 | 11.4 |
| (**5**) spiro | 4.13 | 1.05 | 13.1 | |
| | 4.07 | | 13.1 | |
| ansa | 4.20 | 1.09 | 7.9 | 11.8 |
| | 3.80 | 0.95 | 8.2 | |
| (**7**) | 4.28 | 1.07 | 7.75 | |
| | 3.88 | 0.98 | 8.8 | |

[a] In $CDCl_3$ (TMS internal reference) at 199.5 and 399.95 MHz. (room temperature).
[b] In p.p.m.
[c] In Hz.

earlier ones on propane-1,3-diol,[2] we note resemblances as well as contrasts. Whilst the latter gave predominantly spiro derivatives (mono, bis, and tris), the C-methylated diol gave yields of mono ansa and spiro ansa derivatives comparable to those of its spiro isomers. Unlike in our earlier study[2] we did not observe any monodentates or singly bridged compounds. On the other hand we isolated the first example of a double bridge diol derivative with a central 16-membered ring. Doubly-bridged di(primary amino) derivatives have been reported by Labarre and co-workers.[4] In their examples the chains linking the two phosphazene rings were considerably larger (8 or 10 atoms) than ours (5 atoms).



## EXPERIMENTAL

Chemicals were obtained as follows:
benzene, light petroleum (b.p. 40–60°C), anhydrous diethyl ether (May & Baker Ltd.), 1,4-dioxane (Fisons Scientific Apparatus), deuteriated solvents for n.m.r. spectroscopy, 2,2-dimethylpropane-1,3-diol (Aldrich Chem. Co. Ltd.), pyridine, dichloromethane (B.D.H. Chemical Co. Ltd.), hexachlorocyclotriphosphazatriene (Shin Nisso Kako Co. Ltd.). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60F 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. Separation of products were carried out by flash column chromatography[5] using Kieselgel 60. Melting points were determined on a Reichart-Kofler micro heating stage and a Mettler FB 82 hot stage connected to a FP 800 central processor both fitted with a polarising microscope. $^1$H n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 199.5 MHz), a Bruker WH 250 spectrometer (operating at 250.48 MHz.—King's College, London) and a Varian XL-400 spectrometer (operating at 399.95 MHz.—University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm 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 Varian XL-200 spectrometer (operating at 80.96 MHz.—University College, London), a Varian VXR 400 spectrometer (operating at 162.0 MHz.—University College, London); 85% $H_3PO_4$ was used as an external 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.

Reactions with 2,2-dimethylpropane-1,3-diol:

(*a*) One equivalent. To $N_3P_3Cl_6$ (9 g, 25.86 mmol) in dioxane (150 $cm^3$) was added anhydrous pyridine (4.1 g, 51.83 mmol) dropwise as hydrogen chloride acceptor. The 2,2-dimethylpropane-1,3-diol (2.7 g, 25.92 mmol) solution in dioxane (50 $cm^3$) was added to the trimer solution. After 20 h, the bulk of the pyridine hydrochloride was filtered off, the remainder being removed by column chromatography using a mixture of benzene/dichloromethane (1:6) as eluent. Three main phosphazene fractions were obtained: (i) $N_3P_3Cl_6$, (ii) the mono spiro derivative (**2**) [this and other derivatives, except (**6**) were recrystallised from benzene containing a few drops of light petroleum (b.p. 40–60°C)], m.p. 157–158°C, yield 2.6 g (29%). (Found: C, 15.9; H, 2.7, N, 11.1%; $M^+$, 377. $C_5H_{10}O_2N_3P_3Cl_4$ requires C, 15.85; H, 2.7; N, 11.1%; *M*, 377); (iii) the doubly-bridged derivative (**7**), m.p. 178–179°C, yield 0.9 g (10%). [Found: C, 15.85; H, 2.8; N, 11.1%; $(M+1)^+$, 755, C.I. in $NH_3$. $C_{10}H_{20}O_4N_6P_6^{35}Cl_8$ requires C, 15.85; H, 2.7; N, 11.1%; *M*, 754].

(*b*) Two equivalents. The reaction was carried out as in (*a*) with reflux for 3h. Two phosphazene derivatives were separated by column chromatography using a mixture of $C_6H_6/CH_2Cl_2$ (1:6) as eluent. (i) The bis spiro compound (**4**), m.p. 194–196°C, yield 2.2 g (25%). (Found: C, 29.3; H, 4.9; N, 10.3%; $M^+$, 409. $C_{10}H_{20}O_4N_3P_3Cl_2$ requires C, 29.3; H, 4.9; N, 10.2%; *M*, 409); (ii) the spiro-ansa isomer (**5**), m.p. 114–116°C yield 0.7g (8%). (Found: C, 29.3; H, 5.0; N, 10.3%; $M^+$, 409).

(*c*) Three equivalents. The same procedure as for (*a*); the reflux time was 8 h. One major compound was separated by column chromatography using diethyl ether/dichloromethane (1:1) as eluent. The tris spiro derivative (**6**) was recrystallised from $CH_2Cl_2$, m.p. 277–279°C, yield 1.8 g (20%). (Found: C, 43.5; H, 6.9; N, 10.2%; $M^+$, 441. $C_{15}H_{30}O_6N_3P_3$ requires C, 43,5; H, 6.9; N, 10.2% *M*, 441).

(*d*) Three equivalents in dichloromethane. To (**1**) (4g, 11.49 mmol) in dichloromethane (100 $cm^3$) was added dropwise anhydrous pyridine (5.44 g, 68.86 mmol). 2,2-Dimethylpropane-1,3-diol (3.51 g, 34.41 mmol) in dichloromethane (50 $cm^3$) was then added dropwise. The solution was allowed to stand for 12 h; the bulk of the pyridine hydrochloride was filtered off and the remainder removed by column chromatography. Elution with $PhH/CH_2Cl_2$ (1:5) gave four known and one new phosphazene derivative. All were recrystallised from PhH containing a few drops of light petroleum (b.p. 40–60°C). Order of elution and yields were as follows: (**2**) (24.5%), (**3**) (36.2%) m.p. 187°C. (Found: C, 15.9; H, 2.6, N, 11.2%; $M^+$, 377. $C_5H_{10}O_2N_3P_3Cl_4$ requires C, 15.85; H, 2.7; N, 11.1%; *M*, 377), (**5**) (17.1%), (**4**) (14.1%) and (**7**) (6.3%).



## ACKNOWLEDGEMENTS

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