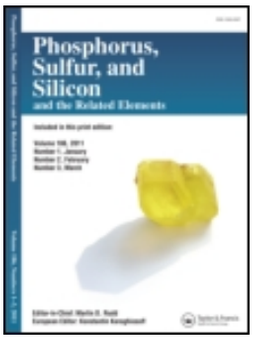

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Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: www.tandfonline.com/journals/gpss20

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To cite this article: Sedat Ture (2016) Phosphorus-nitrogen compounds: Reinvestigation of the reactions of hexachlorocyclotriphosphazene with 1,4-butane- and 1,6-hexane-diols—NMR studies of the products, Phosphorus, Sulfur, and Silicon and the Related Elements, 191:8, 1174-1182, DOI: 10.1080/10426507.2016.1160238

To link to this article: https://doi.org/10.1080/10426507.2016.1160238

PHOSPHORUS, SULFUR, AND SILICON
2016, VOL. 191, NO. 8, 1174–1182
http://dx.doi.org/10.1080/10426507.2016.1160238

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Phosphorus-nitrogen compounds: Reinvestigation of the reactions of hexachlorocyclotriphosphazene with 1,4-butane- and 1,6-hexane-diols—NMR studies of the products

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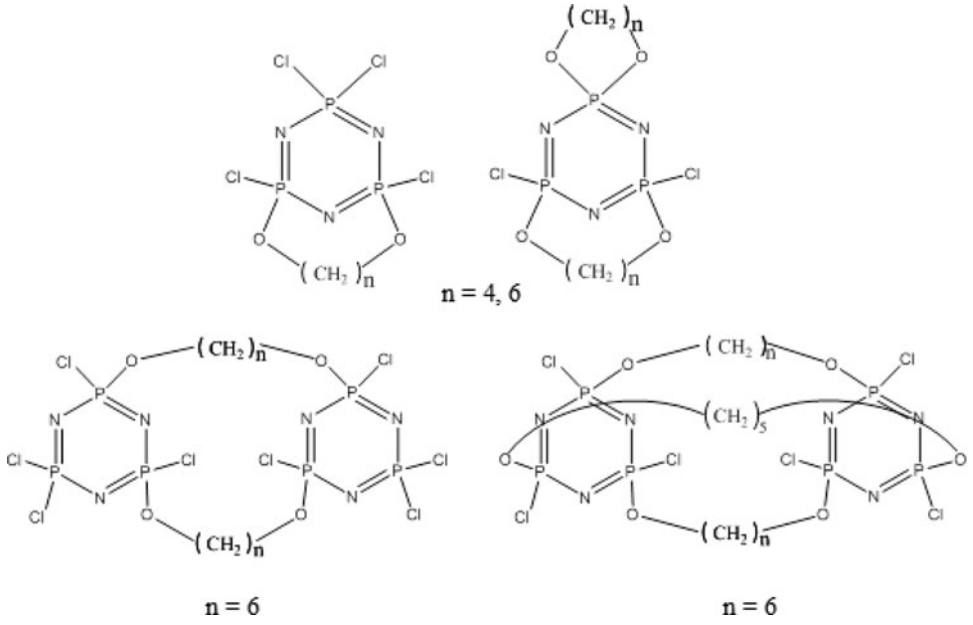
ABSTRACT

Reactions of hexachlorocyclotriphosphazene $N_3P_3Cl_6$ (1) with 1,4-butane-(2) and 1,6-hexane-diols (3) in (1:1:2, 1:2:4, and 1:3:6) stoichiometries in THF solution at room temperature (r.t.) and under refluxing conditions yield a total of 15 products: two open chain, $N_3P_3Cl_5[O(CH_2)_nOH]$ (n = 4, 6) (4, 5), two mono-spiro, $N_3P_3Cl_4[O(CH_2)_nO]$ (n = 4, 6) (6, 7), two mono-ansa, $N_3P_3Cl_4[O(CH_2)_nO]$ (n = 4,6) (8, 9), two dispiro, $N_3P_3Cl_2[O(CH_2)_nO]_2$ (n = 4, 6) (10, 11), two spiro-ansa, $N_3P_3Cl_2[O(CH_2)_nO]_2$ (n = 4, 6) (12, 13), one tri-spiro, $N_3P_3[O(CH_2)_4O]_3$ (14), two single-bridged, $N_3P_3Cl_5[O(CH_2)_nO]N_3P_3Cl_5$ (n = 4, 6) (15, 16), one double-bridged, $N_3P_3Cl_4[O(CH_2)_6O]_2N_3P_3Cl_4$ (17), and one tri-bridged, $N_3P_3Cl_3[O(CH_2)_6O]_3N_3P_3Cl_3$ (18) derivatives. Their structures have been elucidated by MS, ^{31}P, and ^{1}H NMR spectroscopy. The results obtained, based on the synthesis, characterization, product types, and the relative yields, are compared with those of previous studies on the reactions of **1** with 1,2-ethane-, 1,3-propane-, 1,4-butane-, 1,5-pentane-, and 1,6-hexane-diols.

ARTICLE HISTORY
Received 17 September 2015
Accepted 18 February 2016

KEYWORDS
Hexachlorocyclotriphosphazene; 1,4-butane-diol; 1,6-hexane-diol; spiro compounds; ansa compounds; bridged derivatives; dangler derivatives

GRAPHICAL ABSTRACT



Introduction

The reactions of hexachlorocyclophosphazene (1) with monofunctional and difunctional reagents have received a great deal of attention.[1–29,42–51] Diols have probably received the most detailed attention than all of the systems reported so far.[7,30–41] We have reinvestigated the reactions of hexachlorocyclotriphosphazene (1) with 1,4-butane- and 1,6-hexane-diols and isolated a total of 15 compounds. Preliminary reports of these work have appeared.[7,37,42–43] The results have been compared with those previously reported[7,37] and show that compounds **4, 6, 10, 14**, and **15**[7] as well as compounds **9, 16**, and **17**[37] have already been described in the literature. Compounds **7** and **18**[37] have only been detected by ^{31}P NMR spectroscopic analysis in the reaction mixture. The remaining compounds **5, 8, 11, 12, 13**, as well as the analytical characterization of **7** and **18** are reported here for the first time.

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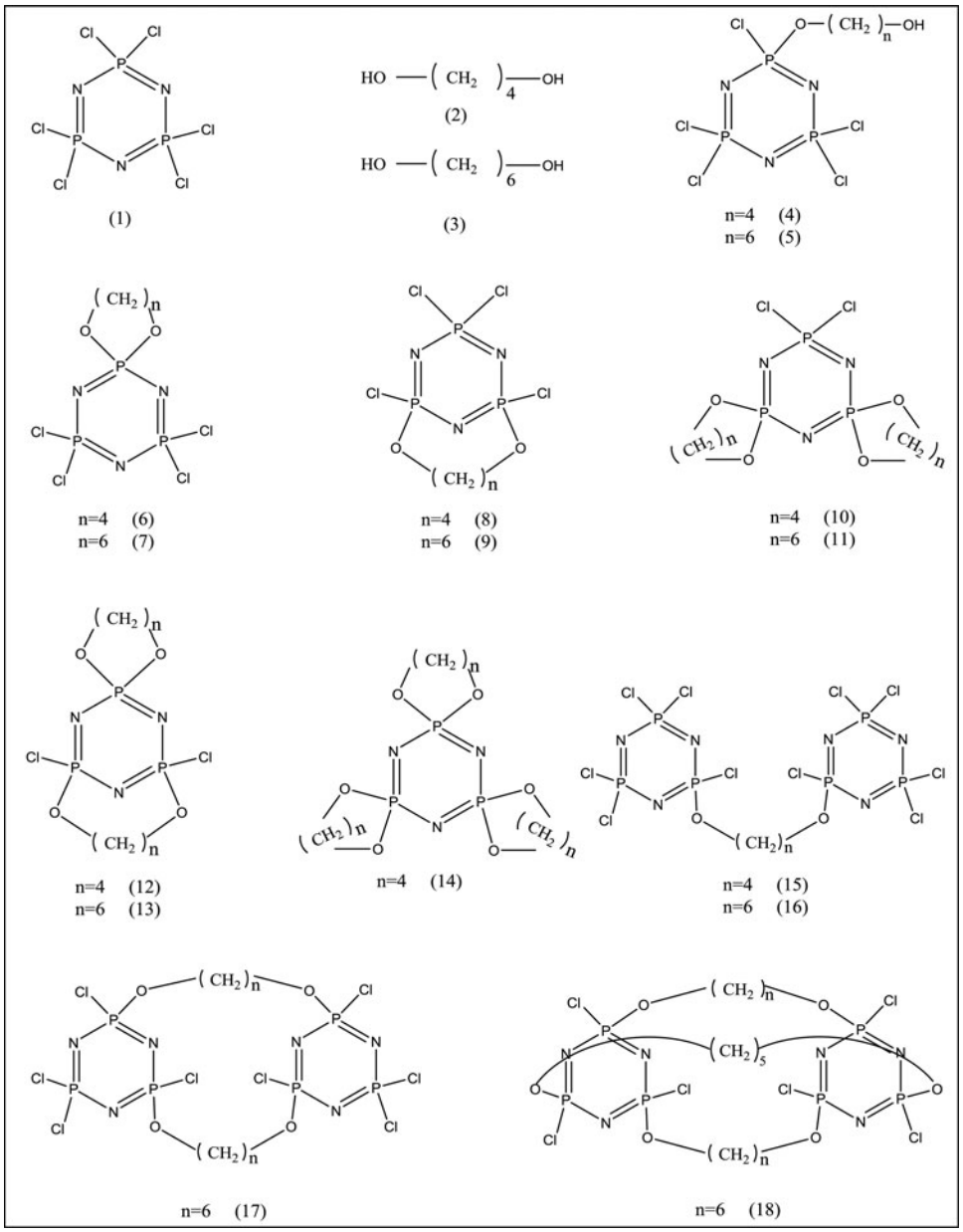

Figure 1. Structures of the compounds **1–18**.

Results and discussion

The reactions of $N_3P_3Cl_6$ (1) with butane-1,4- and hexane-1,6-diols in 1:1:2, 1:2:4, and 1:3:6 stoichiometries gave the following isolated and characterized derivatives: two open chain (4, 5), two mono spiro (6, 7), two mono ansa (8, 9), two di-spiro (10, 11), two spiro-ansa (12, 13), one tri-spiro (14), two single-bridged (15, 16), one double-bridged (17), and one tripply bridged compound (18). The structures of the compounds are shown in Figure 1.

The synthesized compounds **4–18** were characterized by elemental analysis, MS, ^{1}H, and ^{31}P NMR spectroscopy (Tables 1–3). The yields of the compounds **4–18** are presented in Table 4.

The reactions of **1** with 1,4-butane- and 1,6-hexane-diols are complicated due to the high reactivity, the large number of possible isomers, as well as the difficulties of separation and purification. However, we were able to separate a large number of products (4–18). The spiro derivatives are by far the major products in the case of 1,2-ethylene-1,3-propane- and 1,4-butane-diols[7], while the ansa and the bridged derivatives are the major products in the case of 1,6-hexane-diol. The spiro-ansa compounds **12** and **13** are formed in considerably smaller amounts as compared to the di-spiro isomers **10** and **11**. The ansa derivative **9** is isolated in larger amount than its spiro isomer **7** and the bridged compounds **15** and **16** are obtained in better yields than the open chain derivatives **4** and **5**.

^{31}P NMR spectra

First indication for the number of compounds formed is given by the ^{31}P and ^{31}P{^{1}H} NMR spectra. ^{1}H NMR and MS data have also proved to be useful auxiliaries for the structural assignment of the compounds formed.

The existence of all the isomers formed was confirmed by the observed fine splitting in the proton coupled spectra for

Table 1. Selected ^{31}P NMR parameters of compounds **4–18**[a].

Compound	δPCl_2[b]	$\delta P(OR)_2$[b]	$\delta P(OR)Cl$[b]	$^2J[\underline{P}(OR)_2\text{-}\underline{P}Cl_2]$[c]	$^2J[\underline{P}(OR)Cl\text{–}\underline{P}Cl_2]$[c]
1	19.9				
4	23.6		16.0		62.3
5	23.9		15.5		61.8
6	24.2	10.3		70.4	
7	23.3	4.9		65.0	
8	29.7		25.3		58.2
9	27.1		20.2		67.5
10	27.7	16.2		77.0	
11	24.5	14.9		77.6	
12		12.3	28.6		77.7
13		13.6	26.5		82.0
14			21.9		
15	23.5		15.9		61.9
16	23.2		15.6		62.3
17	25.9		19.4		67.1
18			22.2		

[a]In $CDCl_3$ (65% phosphoric acid external reference) at 162.00 MHz (room temperature). [b]In ppm. [c]In Hz.

the $P(OR)_2$ and P(OR)Cl parts, while the signals of the PCl_2 moieties remained unchanged. A comparison of selected ^{31}P NMR parameters of spiro, ansa, and bridged derivatives of hexachlorocyclotriphosphazene (1) with relative diols are summarized in Table 2. The tri-spiro and tri-bridged cyclophosphazene derivatives (14 and 18) consist of only $P(OR)_2$ and P(OR)Cl groups and the ^{31}P NMR spectra are single lines, whereas all the other cyclophosphazene derivatives comprise $P(OR)_2$, PCl_2, and P(OR)Cl groups and the ^{31}P NMR give rise to A_2B (or A_2X) type spin systems, which can be readily assigned by consideration of signal intensities, chemical shifts, and coupling patterns. Geometrical isomers can be differentiated in this way, since the spin system would remain the same and possible differences in ring conformation would be too small to affect the ^{31}P NMR spectra significantly.

The isomeric compounds $N_3P_3Cl_4[O(CH_2)_4)O]$ (6 and 8) and $N_3P_3Cl_4[O(CH_2)_6)O]$ (7 and 9) could have, in principle, two types of structures: spiro or ansa. As indicated above, the spiro isomer shows an A_2X spectrum, while that of the ansa isomer is of AB_2 type. Also splitting patterns are different for the two isomers. Proton coupling affects the X part of the spectrum of the former and the B part of the later. Thus these isomeric compounds can be assigned with confidence, as the spiro (6 and 7) and the ansa (8 and 9) derivatives. The ^{31}P NMR proton-coupled and decoupled spectra of compound **8** are presented in Figure 2.

Compounds $N_3P_3Cl_2[O(CH_2)_4)O]_2$ (10 and 12) and $N_3P_3Cl_2[O(CH_2)_6)O]_2$ (11 and 13) exhibit AB_2 (di-spiro) and A_2X (spiro-ansa) type spectra, respectively. Proton coupling experiments as well as comparison with the spectra of the former diol derivatives[7,37–41] allows unambiguous assignment of the structures. Yields of the isomers are comparable in case of the 1,4-butane- and 1,6-hexane-diol derivatives, while the di-spiro derivatives in both systems are formed in larger yields. The ^{31}P NMR proton-coupled and decoupled spectra of compounds **12** and **13** are shown in Figure 3.

Compounds **4, 5, 15**, and **16** show ^{31}P NMR spectra of A_2B type similar in appearance. The spectra of the single-bridged derivatives **15** and **16** consist of two distinct signals representing the PCl_2 and the P(OR)Cl moieties, respectively, and show that the phosphazene rings are chemically equivalent. The proton coupled ^{31}P NMR spectrum suggests that the A part of the spectrum arises from the PCl_2 groups, since it remains unaffected, whereas the B part, which splits into further lines, is assigned to the alcohol substituted phosphorus atom in these compounds. The proton-coupled ^{31}P NMR spectra of compounds **5** and **15** are illustrated in Figure 4.

The ^{31}P NMR spectrum of the double-bridged compound **17** exhibits an A_2B spin system with very close PCl_2 and P(OR)Cl chemical shifts. For diamino- and diol-substituted cyclophosphazenes, it is known that there are two configurational isomers in the case of double-bridged derivatives.[28,37] Of the two different meso forms, which appear with equal probability as diastereoisomers, one has a center of symmetry and the other has a plane of symmetry. However, the ^{31}P NMR spectrum of the isolated product **17** does not show two sets of closely spaced signals of equal intensity. We also observed a very sharp melting point for this compound (163–164°C).

The ^{31}P NMR spectra of compounds **14** and **18** at low or medium field strengths give rise to A_3 spin systems, tending to a single line due to chemical and magnetic equivalence of the phosphorus nuclei. Therefore, they can be clearly assigned to the tri-spiro **14** and tri-bridged **18** compound. Selected ^{31}P NMR chemical shifts and $^2J(\underline{PP})$ values of the compounds are given in Table 1.

^{1}H NMR spectra

Proton NMR spectra of difunctional cyclophosphazene derivatives can give valuable information regarding the position and the geometrical disposition of the substituents. For example, the isomeric derivatives of the mono-spiro (6, 7) and mono-ansa (8, 9), the di-spiro (10, 11) and spiro-ansa (12, 13) cylophosphazenes can be readily distinguished by the appearance in the ^{1}H NMR spectra of $POC\underline{H}_2$ and $POCC\underline{H}_2$ protons, respectively. In general, the shielding of $POCH_2$ protons increases with increasing degree of chlorine substitution. Furthermore, the shielding of the $POC\underline{H}_2$ protons for the bridged derivatives is greater than for the corresponding spiro or ansa derivatives. Selected chemical shifts as well as $^3J_{PH}$ and $^4J_{PH}$ values are presented in Table 3.

The single-(16), double-(17), and tripple-bridged derivatives (18) show remarkable similarity in the chemical shifts of the $OC\underline{H}_2$ and $POCC\underline{H}_2$ protons. The NMR parameters of the α-, β-, and γ-protons of the spiro, ansa, and bridged derivatives are similar to those of our earlier investigations based on trimeric and tetrameric alkanedioxycyclophosphazene derivatives.[7,39,40]

Summary

In this study, reaction of **1** with 1,4-butane-diol (in the presence of pyridine to neutralize the HCl formed) has been shown to yield predominantly spiro substituted derivatives, in particular forming a mono-spiro compound (intramolecular reaction). On the other hand, reaction of **1** with 1,6-hexane-diol yields bridged derivatives (intermolecular reaction) as the most prevalent products. It was also found

Table 2. Comparison of selected ^{31}P NMR parameters of spiro, ansa, and bridged derivatives of hexachlorocyclotriphosphazene **1** with relative diols [7,33,37,39] and derivatives **4–18**.

Compound	δPCl_2 [b]	$\delta P(OR)_2$ [b]	$\delta P(OR)Cl$ [b]	$^2J[\underline{P}(OR)_2\text{-}\underline{P}Cl_2]$ [c]	$^2J[\underline{P}(OR)Cl\text{–}\underline{P}Cl_2]$ [c]
Mono-spiro					
$N_3P_3Cl_4[O(CH_2)_2O]$ [a]	26.0	24.5		68.0[7]	
$N_3P_3Cl_4[O(CH_2)_3O]$ [a]	24.1	3.4		69.2[7]	
$N_3P_3Cl_4[O(CH_2)_4O]$ [a]	24.1	10.3		70.5[7]	
$N_3P_3Cl_4[O(CH_2)_4O]$ [a]	24.2	10.3		70.4[6]	
$N_3P_4Cl_4[O(CH_2)_5O]$ [a]	23.1	5.3		71.4[39]	
$N_3P_3Cl_4[O(CH_2)_5O]$ [d]	23.2	4.8		69.2[37]	
$N_3P_3Cl_4[O(CH_2)_6O]$ [a]	23.3	4.9		65.0[7]	
$N_3P_3Cl_4[O(CH_2)_6O]$ [d]	23.2	4.8		64.9[37]	
$N_3P_3Cl_4[O(CH_2)_8O]$ [d]	23.1	4.8		63.9[37]	
$N_3P_3Cl_4[O(CH_2)_{10}O]$ [d]	23.1	4.8		63.4[37]	
$N_3P_3Cl_4[O(CH_2)_2\ (CF_2)_2O]$ [e]	25.2	8.6		75.0[33]	
Di-spiro					
$N_3P_3Cl_2[O(CH_2)_2O]_2$ [a]	31.3	31.0		76.8[7]	
$N_3P_3Cl_2[O(CH_2)_3O]_2$ [a]	26.5	9.1		70.8[7]	
$N_3P_3Cl_2[O(CH_2)_4O]_2$ [a]	27.8	16.0		76.9[7]	
$N_3P_3Cl_2[O(CH_2)_4O]_2$ [a]	27.7	16.2		77.0[10]	
$N_3P_3Cl_2[O(CH_2)_5O]_2$ [a]	25.4	10.3		74.3[39]	
$N_3P_3Cl_2[O(CH_2)_6O]_2$ [a]	24.5	14.9		77.6[11]	
$N_3P_3Cl_2[O(CH_2)_2\ (CF_2)_2O]_2$ [e]	29.5	14.4		81.5[33]	
Tri-spiro					
$N_3P_3[O(CH_2)_2O]_3$ [a]		37.4[7]			
$N_3P_3[O(CH_2)_3O]_3$ [a]		14.1[7]			
$N_3P_3[O(CH_2)_4O]_3$ [a]		21.7[7]			
$N_3P_3[O(CH_2)_4O]_3$ [a]		21.9[14]			
$N_3P_3[O(CH_2)_2\ (CF_2)_2O]_3$ [e]		19.9[33]			
Mono-ansa					
$N_3P_3Cl_4[O(CH_2)_3O]$ [a]	29.5		30.1		56.9[7]
$N_3P_3Cl_4[O(CH_2)_4O]$ [a]	29.7		25.3		58.2[8]
$N_3P_3Cl_4[O(CH_2)_5O]$ [a]	26.8		18.7		67.4[39]
$N_3P_3Cl_4[O(CH_2)_5O]$ [d]	25.0		17.6		67.0[37]
$N_3P_3Cl_4[O(CH_2)_6O]$ [a]	27.1		20.2		67.5[9]
$N_3P_3Cl_4[O(CH_2)_6O]$ [d]	26.9		19.9		67.3[37]
$N_3P_3Cl_4[O(CH_2)_8O]$ [d]	26.8		18.3		72.8[37]
$N_3P_3Cl_4[O(CH_2)_{10}O]$ [d]	24.7		17.6		68.2[37]
$N_3P_3Cl_4[O(CH_2)_2\ (CF_2)_2O]$ [e]	25.2		23.6		65.0[33]
Single-bridged					
$(N_3P_3Cl_5)_2[O(CH_2)_3O]$ [a]	23.4		16.0		63.0[7]
$(N_3P_3Cl_5)_2[O(CH_2)_4O]$ [a]	23.5		15.9		61.9[7]
$(N_3P_3Cl_5)_2[O(CH_2)_4O]$ [a]	23.5		15.9		61.9[15]
$(N_3P_3Cl_5)_2[O(CH_2)_5O]$ [a]	23.8		16.1		62.3[39]
$(N_3P_3Cl_5)_2[O(CH_2)_5O]$ [d]	22.6		15.0		62.2[37]
$(N_3P_3Cl_5)_2[O(CH_2)_6O]$ [a]	23.2		15.6		62.3[16]
$(N_3P_3Cl_5)_2[O(CH_2)_6O]$ [d]	23.7		16.1		62.1[37]
$(N_3P_3Cl_5)_2[O(CH_2)_8O]$ [d]	23.6		16.2		62.1[37]
$(N_3P_3Cl_5)_2[O(CH_2)_{10}O]$ [d]	22.3		14.8		62.2[37]
Double-bridged					
$(N_3P_3Cl_4)_2[O(CH_2)_5O]_2$ [d]	24.4		18.3		65.5 *anti*[37]
$(N_3P_3Cl_4)_2[O(CH_2)_5O]_2$ [d]	24.5		18.3		65.9 *syn*[37]
$(N_4P_3Cl_4)_2[O(CH_2)_6O]_2$ [a]	25.9		19.4		67.1[17]
$(N_4P_3Cl_4)_2[O(CH_2)_6O]_2$ [d]	25.9		19.4		67.0 *anti*[37]
$(N_4P_3Cl_4)_2[O(CH_2)_6O]_2$ [d]	26.0		19.3		67.5 *syn*[37]
$(N_3P_3Cl_4)_2[O(CH_2)_8O]_2$ [d]	25.9		19.3		66.9 *anti*[37]
$(N_3P_3Cl_4)_2[O(CH_2)_8O]_2$ [d]	25.9		19.3		67.3 *syn*[37]
$(N_3P_3Cl_4)_2[O(CH_2)_{10}O]_2$ [d]	24.8		18.2		67.1 *anti*[37]
$(N_3P_3Cl_4)_2[O(CH_2)_{10}O]_2$ [d]	24.8		18.2		67.2 *syn*[37]
Tri-bridged					
$(N_3P_3Cl_3)_2[O(CH_2)_5O]_3$ [a]			21.7[39]		
$(N_3P_3Cl_3)_2[O(CH_2)_5O]_3$ [d]			21.1[37]		
$(N_4P_3Cl_3)_2[O(CH_2)_6O]_3$ [a]			22.2[18]		
$(N_4P_3Cl_3)_2[O(CH_2)_6O]_3$ [d]			22.1[37]		
$(N_3P_3Cl_3)_2[O(CH_2)_8O]_3$ [d]			22.3[37]		
$(N_3P_3Cl_3)_2[O(CH_2)_{10}O]_3$ [d]			21.3[37]		
Spiro-ansa		$\delta P(OR)_2$ [b]	$\delta P(OR)Cl$ [b]		$^2J[\underline{P}(OR)Cl\text{–}P(OR)_2]$ [c]
$N_3P_3Cl_2[O(CH_2)_3O]_2$ [a]		10.1	31.2		73.0[7]
$N_3P_3Cl_2[O(CH_2)_4O]_2$ [a]		12.3	28.6		77.7[12]

(*Continued*)

Table 2. Continued

$N_3P_3Cl_2[O(CH_2)_5O]_2$[a]	14.6	27.0	80.6[39]
$N_3P_3Cl_2[O(CH_2)_6O]_2$[a]	13.6	26.5	82.0[13]
$N_3P_3Cl_2[O(CH_2)_2(CF_2)_2O]_2$[e]	13.9	28.5	86.5[33]

[a]In $CDCl_3$ (65% phosphoric acid external reference) at 162.00 MHz (room temperature). [b]In ppm. [c]In Hz. [d]At 202.38 MHz, ^{31}P NMR chemical shifts (ppm) in $CDCl_3$ with respect to external 85% H_3PO_4. [e]At 200.00 MHz, ^{31}P NMR chemical shifts (ppm) in $CDCl_3$ with respect to external 85% H_3PO_4.

Table 3. Comparison of selected ^1H NMR parameters of compounds **4–18** [a] with those of other diol derivatives from the literature.

Compound	$\delta POCH_2$[b]	δCCH_2[b]	$\delta CCCH_2$[b]	δOH[b]	$^3J_{PH}$[c]	$^4J_{PH}$[c]
Open chain						
$N_3P_3Cl_4[O(CH_2)_3OH]$[a]	4.38	2.22		4.30	9.1	1.5[7]
$N_3P_3Cl_4[O(CH_2)_4OH]$[a]	4.25	1.94		4.30	9.2	<0.3[7]
4	4.25	1.94		4.30	9.2	<0.3
5	4.31	1.77		4.32	13.7	
Mono-spiro						
$N_3P_3Cl_4[O(CH_2)_2O]$[a]	4.48	–			11.2	–[7]
$N_3P_3Cl_4[O(CH_2)_3O]$[a]	4.53	2.07			12.9	1.6[7]
$N_3P_3Cl_4[O(CH_2)_4O]$[a]	4.24	1.96			18.5	<0.3[7]
6	4.24	1.95			18.5	<0.3
7	4.37	1.78	1.44		13.5	
Mono-ansa						
$N_3P_3Cl_4[O(CH_2)_3O]$[a]	4.54	2.28			20.1	<0.3[7]
	4.31	2.10			21.2	<0.3
8	4.33	1.85			20.8	
	4.27	1.77			22.2	
9	4.32	1.70	1.57		21.0	
	4.15		1.38		22.7	
Di-spiro						
$N_3P_3Cl_2[O(CH_2)_2O]_2$[a]	4.44	–			10.8	–[7]
$N_3P_3Cl_2[O(CH_2)_3O]_2$[a]	4.51	2.09			10.7	<0.3[7]
$N_3P_3Cl_2[O(CH_2)_4O]_2$[a]	4.19	1.91			18.4	<0.3[7]
10	4.24	1.96			18.5	<0.3
11	4.31	1.75	1.43		13.4	
Spiro-ansa						
$N_3P_3Cl_2[O(CH_2)_3O]_2$[a]						
Spiro	4.49	2.01			12.8	1.5[7]
	4.48				12.8	
Ansa	4.50	2.21			20.0	<0.3
	4.21	2.02			21.0	<0.3
12 Spiro	4.37	1.97			14.9	1.66
	4.31	1.89			14.9	
Ansa	4.23	1.76			17.8	<0.3
	4.16	1.71			18.0	
13 Spiro	4.42	1.81	1.45		13.6	
	4.33	1.79			13.6	
Ansa	4.49	1.73	1.47		22.0	
	4.28	1.69			22.4	
Tri-spiro						
$(N_3P_3)_2[O(CH_2)_2O]_3$[a]	4.40	–			11.6	–[7]
$(N_3P_3)_2[O(CH_2)_3O]_3$[a]	4.45	1.96			12.7	<0.3[7]
$(N_3P_3)_2[O(CH_2)_4O]_3$[a]	4.14	1.87			17.7	<0.3[7]
14	4.15	1.87			17.7	<0.3
Single-bridged						
$(N_3P_3Cl_5)_2[O(CH_2)_3O]_2$[a]	4.35	2.20			9.1	1.5[7]
$(N_3P_3Cl_5)_2[O(CH_2)_4O]$[a]	4.26	1.94			9.0	<0.3[7]
15	4.26	1.94			9.1	<0.3
16	4.24	1.81	1.50		13.9	
Double-bridged						
17	4.23	1.80	1.52		12.8	
Tri-bridged						
18	4.20	1.75	1.44		12.6	

[a]In $CDCl_3$ (TMS internal reference) at 199.5 and 399.95 MHz (room temperature). [b]In ppm. [c]In Hz. [d]In $CDCl_3$ (referenced to internal TMS) at 250.13 MHz (room temperature).

Table 4. Yields of compounds **4–18** depending on the molar ratio of the reactants; reaction in THF solution at room temperature and under reflux conditions.

Compound (%)	1:1	1:2	1:3
4	14.20		
5	13.60		
6	38.80		27.50
7	22.30	8.20	
8			19.30
9		22.40	
10	26.70		22.20
11	18.40		
12			17.20
13		12.70	
14			15.30
15	18.60		
16	45.70	24.50	
17		18.10	
18		14.20	

that the spiro-ansa compound **13** resulting from the reaction with 1,6-hexane-diol is obtained in a larger amount as compared with the analogous reactions with 1,3-propane- and 1,4-butane-diols. Open-chain and single-bridged derivatives were observed as minor products in the reaction of **1** with 1,4-butane-diol, indicating that chain length is a contributing factor in determining the type of product formed.[7,37] It is observed that with increasing chain length of the diol there is a decrease in the product formed by intramolecular reactions (spiro or ansa compounds) and an increase in the amount of products formed by intermolecular reactions (single-, double-, and tri-bridged compounds).

Experimental

Materials

Reagent grade solvents were used throughout the work: benzene, light petroleum (bp 40–60°C), anhydrous diethyl ether, dichloromethane, chloroform and THF (May and Baker Ltd., London), deuterated solvents for NMR spectroscopy, butane-1,4-diol and hexane-1,6-diol (Aldrich Chem. Co. Ltd., Gillingham, England), pyridine, *n*-hexane (B.D.H. Chemical Co. Ltd.,

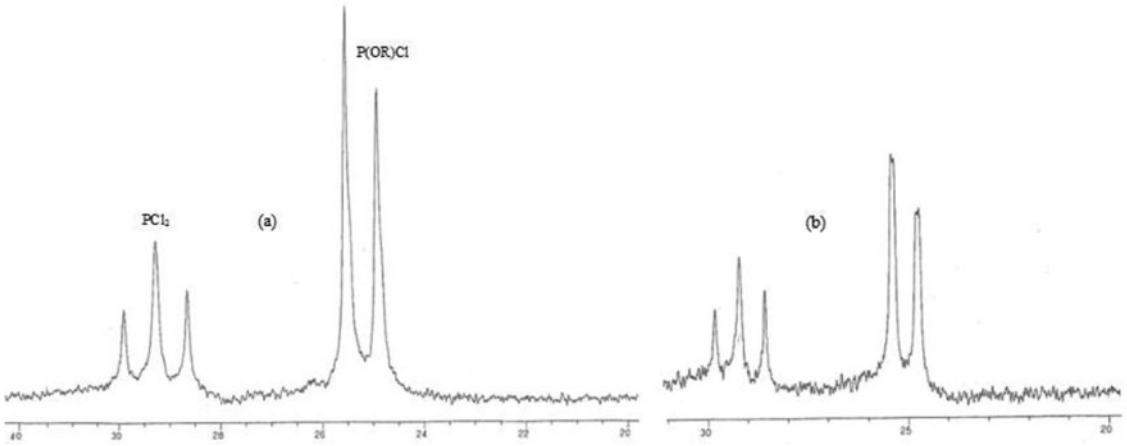

Figure 2. ^{31}P NMR spectra of compound **8**: (a) proton decoupled, and (b) proton coupled, in $CDCl_3$ at 162.00 MHz (room temperature), referenced to external 85% H_3PO_4.

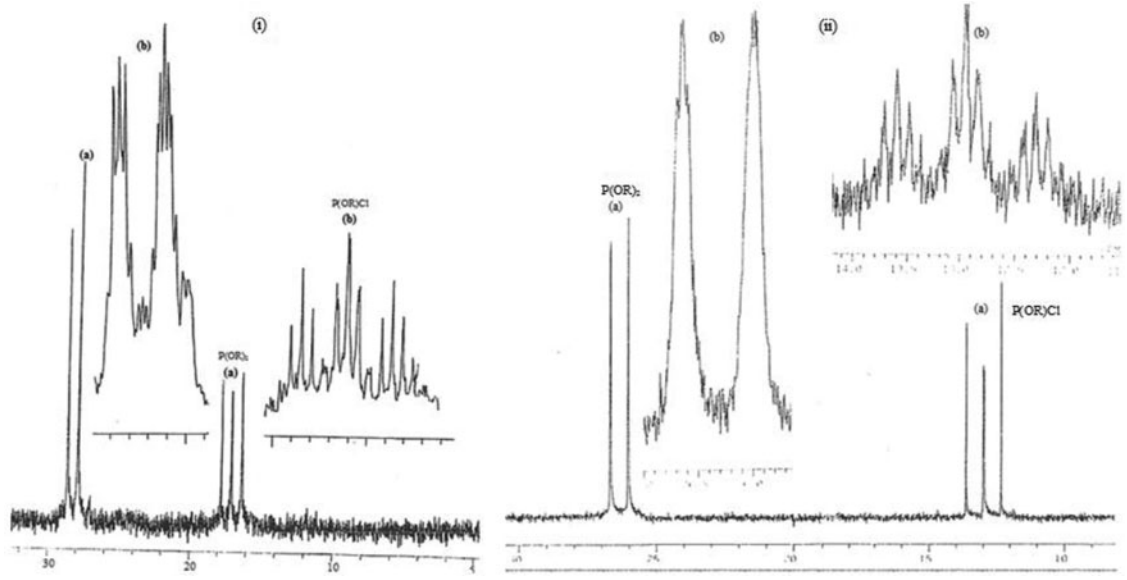

Figure 3. ^{31}P NMR spectra of compounds **12** (i) and **13 (**ii): (a) proton decoupled, and (b) proton coupled, in $CDCl_3$ at 162.00 MHz (room temperature), referenced to external 85% H_3PO_4.

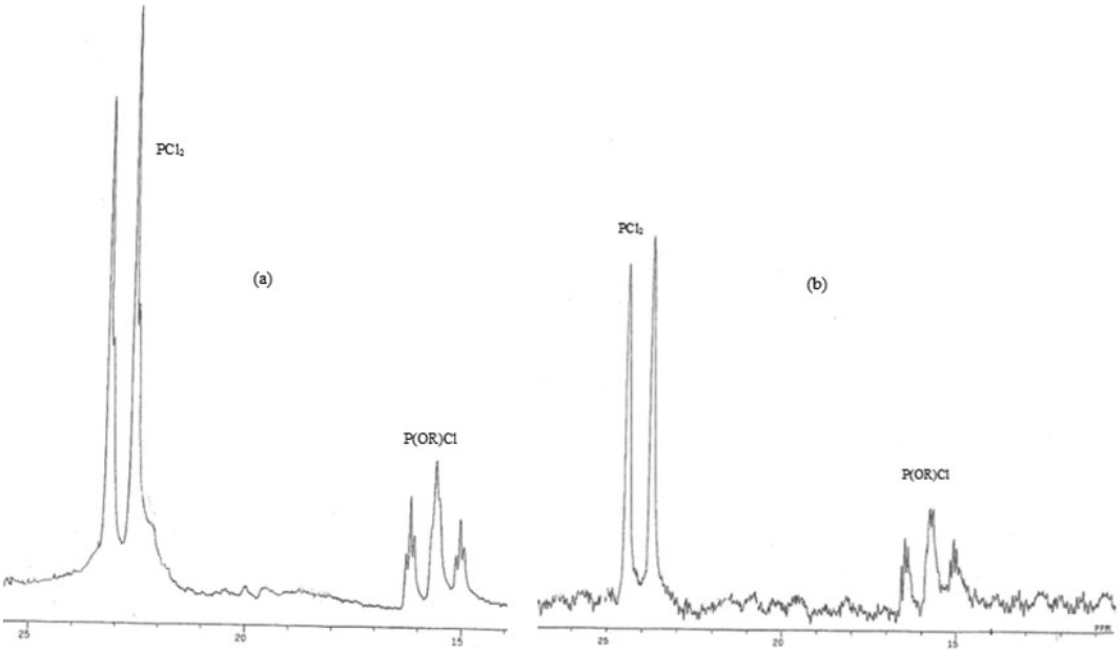

Figure 4. Proton coupled ^{31}P NMR spectra of compounds **15** (a) and **5** (b) in $CDCl_3$ at 162.00 MHz, room temperature, referenced to external 85% H_3PO_4.

East Yorkshire, England), and hexachlorocyclotriphosphazene (Shin Nisso Kako Co. Ltd., Tokyo, Japan). Solvents were dried by conventional methods. Hexachlorocyclotriphosphazene was purified by fractional crystallization from hexane. THF was distilled over sodium–potassium alloy under an atmosphere of dry argon. Thin layer chromatography (TLC)/silica gel (Merck 60, 0.063–0.200 mm) was used for column chromatography.

Methods

All reactions were monitored using silica gel (Kieselgel 60° 254) precoated TLC plates and sprayed with Ninhydridine (0.5% w/v) in butanol solution, and developed at approximately 130°C. Separation of the products was carried out by flash column chromatography using Kieselgel 60 (Merck 60, 0.063–0.200 mm; for 2 g crude mixture, 100 g of silica gel was used in a column of 2.5 cm in diameter and 90 cm in length). Melting points were determined with a Reichart-Kofler micro heating stage and a Mettler FB 82 hot stage connected to a FP 800 central processor both fitted with a polarizing microscope. ^1H NMR spectra were recorded with a JEOL FX-200 spectrometer (operating at 199.5 MHz), a Bruker WH 250 spectrometer (operating at 250.48 MHz at King's College, London), and a Varian XL-400 spectrometer (operating at 399.5 MHz, at University College, London). Samples were dissolved in $CDCl_3$ and placed in 5 mm NMR 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 NMR spectra were recorded using a Varian XL-200 spectrometer (operating at 80.96 MHz at University College, London) and a Varian 400 spectrometer (operating at 162.0 MHz at University College, London); 85% H_3PO_4 was used as external reference. ^{13}C NMR 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 at University College, London); TMS was used as internal reference. The mass spectra were recorded using a VG 7070H Mass Spectrometer with Finingan INCOS Data System at University College, London, and a VG 2AB IF mass spectrometer at the School of Pharmacy. Microanalyses were carried out by University College, London, micro analytical service. The yields of the reported products are found in Table 4 and the NMR data may be found in Tables 1–3.

Reactions of hexachlorocyclotriphosphazene (1) with 1,4-butane-diol (2)

One equivalent of 2

Hexachlorocyclotriphosphazene (**1**, 4.0 g, 11.59 mmol) was dissolved in THF (150 mL) and placed in a 250 mL three-necked round-bottomed flask. This mixture was stirred for 10 min at r.t. and four equivalents of pyridine (1.83 g, 23.18 mmol) in THF (10 mL) was added dropwise to this solution and left stirring for approximately 30 min. To this solution two equivalents of 1,4-butane-diol (1.04 g, 11.59 mmol) in THF (10 mL) was added dropwise with stirring. Then the reaction mixture was boiled under reflux approximately for 16 h and TLC analysis using benzene:diethyl ether (4:1) revealed essentially the formation of four products. Then the reaction mixture was filtered to remove the pyridine hydrochloride and the other insoluble materials. The solvent was removed at reduced pressure and the resulting colorless oil was subjected to column chromatography, using benzene:diethyl ether (4:1) as the eluent.

$N_3P_3[(OCH_2)_4O]Cl_4$ (6): Mp 160–161°C, yield (1.11 g, 38.80%). Elemental analysis: For $C_4H_8O_2N_3P_3Cl_4$: Calcd.: C, 13.22; H, 2.20; N, 11.57. Found: C, 13.20; H, 2.29; N, 11.57%. MS: M^+ 363.

$N_3P_3Cl_2[O(CH_2)_4O]_2$ (10): Mp 215°C, yield (0.77 g, 26.70%,). For $C_8H_{16}O_4N_3P_3Cl_2$: Calcd.: C, 25.20; H, 4.20; N, 11.00. Found: C, 25.10; H, 4.20; N, 11.10%. MS: M^+ 381.

$N_3P_3Cl_5[O(CH_2)_4OH]$ (4): Oil, yield (0.31 g, 14.20%). For $C_4H_9O_2N_3P_3Cl_5$: Calcd.: C, 12.00; H, 2.25; N, 10.53. Found: C, 12.10; H, 2.30; N, 10.53% MS: M^+ 399.

$N_3P_3Cl_5[O(CH_2)_4O]N_3P_3Cl_5$ (15): Mp 82–83°C, yield (0.36 g, 18.60%). For $C_8H_{16}O_4N_3P_3Cl_2$: Calcd.: C, 6.70; H, 1.1; N, 11.80. Found: C, 6.71; H, 1.13; N, 11.80%.

Three equivalents of 2

Hexachlorocyclotriphosphazene (**1**, 4.0 g, 11.59 mmol) and three equivalents of 1,4-butane-diol (3.13 g, 34.77 mmol) were dissolved in 150 mL of dry THF in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and pyridine (5.49 g, 69.54 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The stirring was continued for 1 h and then the mixture was boiled under reflux for further 16 h. The progress of the reaction was followed by TLC using silica gel plates and dichloromethane:diethyl ether (5:1) as the mobile phase. Five products were observed together with a very little amount of starting compound. The reaction mixture was filtered to remove the pyridine hydrochloride and any other insoluble material. The solvent was removed at reduced pressure and the resulting colorless oil was subjected to column chromatography using dichloromethane:diethyl ether (5:1, for the first two spots and 3:1 for the last three spots) as the eluent. Two known (**6**, 0.92 g, 27.50%; **10**, 0.76 g, 22.20%;) and three new products were isolated:

$N_3P_3[(OCH_2)_4O]Cl_4$ (8): Mp 148–151°C, yield 0.63 g (19.30%). For $C_4H_8O_2N_3P_3Cl_4$: Calcd.: C, 13.22; H, 2.20; N, 11.57. Found: C, 13.17; H, 2.23; N, 11.57%. MS: M^+ 363.

$N_3P_3[(OCH_2)_4O]_2Cl_2$ (12): Mp 184–185°C, yield 0.41 g (17.20%). For $C_8H_{16}O_4N_3P_3Cl_2$: Calcd.: C, 25.20; H, 4.20; N, 11.00. Found: C, 23.13; H, 4.24; N, 11.03%.

$N_3P_3[O(CH_2)_4O]_3$ (14): Mp 246–247°C, yield 0.36 g (15.30%). For $C_{12}H_{24}O_6N_3P_3$: Calcd.: C, 36.00; H, 6.00; N, 10.53. Found: C, 36.10; H, 6.13; N, 10.53%. MS: M^+ 399.

Reaction of hexachlorocyclotriphosphazene (1) with hexane-1,6-diol (3)

One equivalent of 2

Hexachlorocyclotriphosphazene (**1**, 4.0 g, 11.59 mmol) was dissolved in dichloromethane (160 mL). To this solution pyridine (1.83 g, 23.18 mmol) was added dropwise. Solid 1,6-hexanediol (1.37 g, 11.59 mmol) was then added to this mixture while stirring at r.t. The mixture was stirred (16 h) until TLC indicated the completion of the reaction. The reaction mixture was also monitored by ^{31}P NMR spectroscopy. The reaction mixture was filtered to remove the pyridine hydrochloride and any other insoluble materials. To separate the individual cyclophosphazene derivatives, the mixture was subjected to column chromatography using benzene:diethyl ether (3:1) as the eluent. Four main fractions were obtained:

$N_3P_3Cl_4[O(CH_2)_6O]$ (7): Mp 177–179°C, yield 0.46 g (22.30%). For $C_6H_{12}O_3N_3P_3Cl_4$: Calcd.: C, 18.32: H, 3.05; N, 10.68. Found: C, 18.38; H, 3.10; N, 10.66%. MS: M^+ 392.9.

$N_3P_3Cl_5[O(CH_2)_6OH]$ (5): Oil, yield 0.28 g (13.60%). For $C_6H_{13}O_2N_3P_3Cl_5$: Calcd.: C, 16.76; H, 3.03; N, 9.79. Found: C, 16.79; H, 3.18; N, 9.81%. MS: M^+ 429.

$N_3P_3Cl_2[O(CH_2)_6O]_2$ (11): Mp 226–228°C, yield 0.43 g (18.40%). For $C_{12}H_{24}O_4N_3P_3Cl_2$: C, 32.88; H, 5.48; N, 9.59. Found: C, 32.77; H, 5.56; N, 9.60%. MS: M^+ 438.

$N_3P_3Cl_5[O(CH_2)_4O]N_3P_3Cl_5$ (16): Mp 117–119°C, yield 1.2 g (45.70%). For $C_6H_{12}O_2N_6P_6Cl_{10}$: Calcd.: C, 9.72; H, 1.62; N, 11.34. Found: C, 9.70; H, 1.66; N, 11.34%. MS: M^+ 741.

Two equivalents of 2

Hexachlorocyclotriphosphazene (**1**, 4.0 g, 11.49 mmol) was dissolved in THF (150 mL) and placed in a 500 mL three-necked round-bottomed flask. To this solution pyridine (1.8 g, 22.75 mmol) in THF (10 mL) was added dropwise. Solid 1,6-hexane-diol (1.35 g, 11.44 mmol) in THF (10 mL) was then added to this mixture while stirring at r.t. (1 h). Then the reaction mixture was boiled under reflux for a further 15 h and the reaction was followed by TLC using silica gel plates and benzene:diethyl ether (5:2). The reaction mixture was allowed to reach r.t.; the pyridine hydrochloride and the other insoluble materials were filtered off and the filtrate was concentrated (15 mL). TLC revealed the formation of four major and two minor products. Separation of these compounds was achieved by column chromatography (120 g silica gel) using benzene:diethyl ether (4:1) as the eluent. Fractions containing the major compounds were collected, the solvent was evaporated to dryness, and the residue recrystallized from light petroleum (bp 40–60°C) containing a few drops of benzene. In addition to **7** (yield 0.25 g, 8.20%) and **15** (yield 0.66 g. 24.50%), the following compounds were obtained:

$N_3P_3Cl_4[O(CH_2)_6O]$ (7): Oil, yield 0.62 g (22.40%). For $C_6H_{12}O_3N_3P_3Cl_4$: Calcd.: C, 18.32: H, 3.05; N, 10.68. Found: C, 18.38; H, 3.13; N, 10.68%: MS: M^+, 393.

$N_3P_3Cl_2[O(CH_2)_6O]_2$ (13): Mp 191–193°C, yield 0.37 g (12.70%). For $C_{12}H_{24}O_4N_3P_3Cl_2$: Calcd.: C, 32.88; H, 5.48 N, 9.59. Found: C, 32.90; H, 5.55; N, 9.59%. MS: M^+ 438.

$N_3P_3Cl_4[O(CH_2)_4O]_2N_3P_3Cl_4$ (17): Mp 163–164°C, yield 0.52 g (18.10%). For $C_{12}H_{24}O_4N_6P_6Cl_8$: Calcd.: C, 18.32; H, 3.05; N, 10.69. Found: C, 18.36; H, 3.30; N, 10.69%. MS: M^+ 786.

$N_3P_3Cl_3[O(CH_2)_4O]_3N_3P_3Cl_3$ (18): Mp 213–215°C, yield 0.41 g (14.20%). For $C_{18}H_{36}O_6N_6P_6Cl_8$: Calcd.: C, 25.99; H, 4.33; N, 10.11. Found: C, 26.05; H, 4.42; N, 10.11%. MS: M^+ 831.

Acknowledgments

We are grateful to Shin Nisso Co. Ltd. for gifts of hexachlorocyclotriphosphazene (1). We are indebted to the School of Pharmacy for mass spectrometric data obtained under the auspices of the University of London intercollegiate research services. The author would also like to thank Mr. Don Ship and Dr. H. G. Parkes for obtaining the NMR data. Finally, the author wishes to express gratitude to Prof. Dr. D. B. Davies for his financial support, helpful suggestions, and insight during his postdoctoral studies.

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