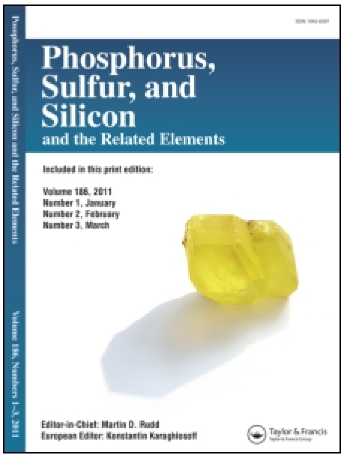

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 65.[1] THE REACTIONS OF HEXACHLOROCYCLOTRI-PHOSPHAZATRIENE WITH DIETHYL BIS- (HYDROXYMETHYL)MALONATE. COMPARISON OF PRODUCT TYPE AND OF THE ^{31}P, ^{1}H AND ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA WITH THE SPIRO DERIVATIVES OF PROPANE- 1,3-DIOL AND 2,2-DIMETHYL-PROPANE-1,3-DIOL

Abdulla H. Alkubaisi[a]; Robert A. Shawt[a]
[a] Department of Chemistry, Birkbeck College (University of London), Gordon Square, London, UK

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 65.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE WITH DIETHYL BIS(HYDROXYMETHYL)MALONATE. COMPARISON OF PRODUCT TYPE AND OF THE ^{31}P, ^{1}H AND ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA WITH THE SPIRO DERIVATIVES OF PROPANE-1,3-DIOL AND 2,2-DIMETHYLPROPANE-1,3-DIOL

ABDULLA H. ALKUBAISI and ROBERT A. SHAW†
Department of Chemistry, Birkbeck College (University of London), Gordon House, 29 Gordon Square, London WC1H OPP, UK

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The reactions of hexachlorocyclotriphosphazatriene with diethyl bis(hydroxymethyl)malonate give the following spiro derivatives: mono, $N_3P_3Cl_4[(OCH_2)_2C(CO_2Et)_2]$, bis, $N_3P_3Cl_2[(OCH_2)_2C(CO_2Et)_2]_2$ and tris, $N_3P_3[(OCH_2)_2C(CO_2Et)_2]_3$. A comparison is made of the products obtained by the above diol with those from propane-1,3-diol and 2,2-dimethylpropane-1,3-diol. The ^{31}P, ^{1}H and ^{13}C n.m.r. spectra of the spiro derivatives of the above three diols are compared.

Key words: Hexachlorocyclotriphosphazatriene; diethyl bis(hydroxymethyl)malonate; spiro compounds; N.M.R. studies.

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$; (**1**), with the difunctional reagents, propane-1,3-diol, $(HOCH_2)_2CH_2$, (**2**)[2] and 2,2-dimethylpropane-1,3-diol, $(HOCH_2)_2CMe_2$, (**3**), have been investigated.[1] We now report our findings with diethyl bis(hydroxymethyl)malonate, $(HOCH_2)_2C(CO_2Et)_2$, (**4**).

Difunctional reagents can, in principle, give rise to four types of products: (i) spiro (both ends attached to same phosphorus atom), ansa (the two ends of the reagent attached to different phosphorus atoms in the same molecule), bridging (the two ends bonded to phosphorus atoms in different molecules) and dangling (only one functional group attached to phosphorus, the other free). With propane-1,3-diol, (**2**), all four types were observed (**5B**, **6B**, **7B**, **8**, **9B**, **10**, **11**), although spiro products predominated.[2]

We then investigated the reaction products of the hexachloride, (**1**), with 2,2-dimethylpropane-1,3-diol, (**3**), for spectroscopic reasons (see below) and also whether the geminal dimethyl group gave rise to a Thorpe-Ingold,[3] and possibly other effects. We noted that relative to the diol (**2**), a somewhat larger proportion of the spiro-ansa isomer, (**9B**), was obtained. Danglers or singly-bridged compounds were not observed, but a good yield of a doubly-bridged derivative, (**12**), was isolated.

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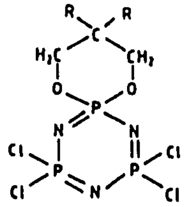
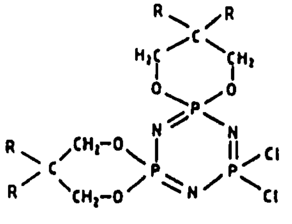
† Author to whom correspondence should be addressed.



(5A, R = CO_2Et
B, R = H
C, R = Me)



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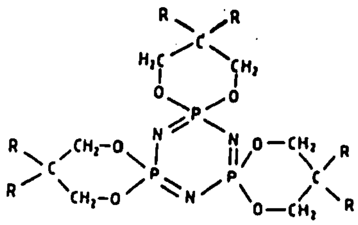

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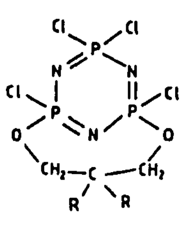

(8B, R = H
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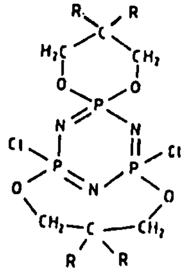
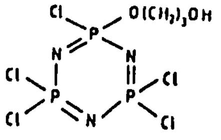


(9B, R = H
C, R = Me)



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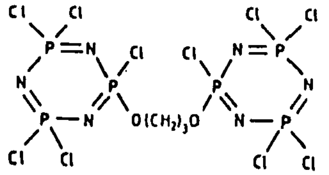

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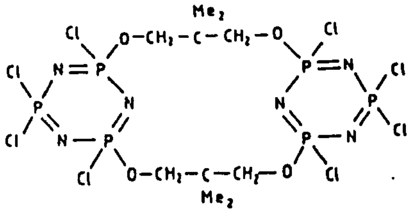

(12)

Having compared the unsubstituted diol, (**2**), with its electron releasing dimethyl analogue, (**3**), we now extend our studies to a diol with electron-withdrawing carboxy-ethyl groups, (**4**).

The diol, (**4**), itself is somewhat unstable to hydrolysis and hence difficult to purify and to keep pure. The same pertains also probably to its phosphazene derivatives. This was borne out in the present study, as we obtained more uncharacterised, probably polymeric, material, than with the other two diols (**2** and **3**). The only products we isolated were the mono-, $N_3P_3Cl_4[(OCH_2)_2C(CO_2Et)_2]$, bis-, $N_3P_3Cl_2[(OCH_2)_2C(CO_2Et)_2]_2$ and tris-derivatives, $N_3P_3[(OCH_2)_2C(CO_2Et)_2]_3$. All three were shown (see below) to have the spiro structures (**5A**, **6A** and **7A**).

Nuclear magnetic resonance spectroscopy (^{31}P, ^{1}H and ^{13}C) proved to be a most useful tool. The ^{31}P spectra of the mono malonate (**5A**) and bis malonate (**6A**) derivatives were of the A_2X and AX_2, type respectively. Proton coupling revealed further splitting of the X part in the former (**5A**) and of the A_2 part of the latter, thus proving the spiro structures (**5A** and **6A**), respectively. The tris-spiro derivative gave the expected single line of an A_3 system.

We now compare the ^{31}P n.m.r. spectra of the mono-, (**5**), bis-, (**6**) and tris-derivatives, (**7**), of the three di-ols (**2**, **3** and **4**) with that of the hexachloride starting material, (**1**). We similarly compare the ^1H and ^{13}C spectra of the derivatives (**5**–**7**) with those of their precursor di-ols (**2**–**4**).

^{31}P *N.m.r. Spectra*

The effects of changing R (CO_2Et, H, Me) in the spiro substituent on the ^{31}P spectra are minor and apparently not systematic. Perhaps an exception to this is the increased deshielding observed ($R = CO_2Et \rightarrow R = Me$) in the tris-derivatives (**7**). Considerably more marked are the chemical shift changes of the ≡Pspiro absorptions, which are progressively deshielded on passing from mono- to bis-(5–6.5 p.p.m.) and tris-derivatives (5–6 p.p.m.). A similar deshielding is observed in the $\equiv PCl_2$ groups, though the effect is only about half of that of the ≡Pspiro moiety. Two-bond coupling constants are uniformly large (~70 Hz) as is generally observed, when the substituents are alkoxy groups. The data are found in Table I.

^1H *N.m.r. Spectra*

$POCH_2$: These protons are shielded (~0.7 p.p.m.) in the expected order $CO_2Et < H < Me$. Within each group shielding on passing from mono- to tris-derivatives is much less marked (~0.1 p.p.m.). ^{3}**J(PH)** marginaly decreases in the same manner. These absorptions are much simpler than those of the analogous (**B**) series

TABLE I

^{31}P N.m.r. data for six-membered spiro derivatives[a]

Compound	δ Pspiro[b]	δ PCl_2[b]	$^2J(Pspiro\text{-}PCl_2)$[c]
$N_3P_3Cl_6$		19.9	
$N_3P_3Cl_4[(OCH_2)_2C(CO_2Et)_2]$	3.1	23.9	70.8
$N_3P_3Cl_4[(OCH_2)_2CH_2]$[d]	3.1	23.8	69.4
$N_3P_3Cl_4[(OCH_2)_2CMe_2]$[e]	2.2	23.3	69.8
$N_3P_3Cl_2[(OCH_2)_2C(CO_2Et)_2]_2$	9.0	26.7	71.4
$N_3P_3Cl_2[(OCH_2)_2CH_2]_2$[d]	8.1	25.8	71.2
$N_3P_3Cl_2[(OCH_2)_2CMe_2]_2$[e]	8.7	26.2	67.5
$N_3P_3[(OCH_2)_2C(CO_2Et)_2]_3$	14.4		
$N_3P_3[(OCH_2)_2CH_2]_3$[d]	14.1		
$N_3P_3[(OCH_2)_2CMe_2]_3$[e]	13.9		

[a] In $CDCl_3$ (85% phosphoric acid as external reference) at 80.1 MHz (room temperature).

[b] In p.p.m.

[c] In Hz.

[d] Data from ref. 2.

[e] Data from ref. 1.

due to the absence of CCH_2 protons in the adjacent position. Thus the mono-derivative (**5A**) gives a simple doublet, whilst the tris-derivative (**7A**) shows a quartet due to virtual coupling with three equivalent ^{31}P nuclei. In the bis-derivative (**6A**), the two protons within each methylene group are non-equivalent (AB quartet) and 10 out of 12 possible lines (virtual coupling with two equivalent ^{31}P nuclei) are observed. CCH_2: Shielding of the same order (~0.1 p.p.m.) is noted for the **B** series. CCH_3: In the **C** series this effect is lessened to ~0.05 p.p.m., and to the same order for $COCH_2$ in the **A** series. At 400 MHz the CCH_2 and CCH_2CH_3 protons of the bis-derivative (**6A**) showed the expected two environments, which had previously been observed for the CCH_3 protons of its analogue, (**6C**). Finally, a very small effect (.02 p.p.m.) is still noticeable in the **A** series for CH_2CH_3. All this is indicative that the electron-withdrawing power decreases $N_3P_3Cl_4 > N_3P_3Cl_2[(OCH_2)_2CR_2] > N_3P_3[(OCH_2)_2CR_2]_2$. The data are collected in Table II.

^{13}C N.m.r. Spectra

We note the following: in all three derivatives (**5A**, **6A** and **7A**) coupling to phosphorus is observed for the POC and the POCC nuclei. In the mono-derivative (**5A**) this gives the expected doublets. In the bis-derivative (**6A**) long range virtual coupling with the two equivalent P spiro nuclei gives the same signals as triplets.

For the tris-derivative virtual coupling with the three equivalent ^{31}P nuclei gives rise to quartet structures for the POC and POCC nuclei.

We now compare here the ^{13}C n.m.r. spectra of the spiro derivatives [**5**,**6**,**7** (A,B,C)] amongst themselves, as well as with those of the starting di-ols (**2**–**4**) (Table III).

$POCH_2$: The chemical shifts, within each series (e.g. **5A**–**7A**) decrease by ~1 p.p.m. The values of the **A** and **B** series are very close; those of the **C** series are about 10 p.p.m. more deshielded. $^2J(PC)$ values decrease by ~1 Hz on passing from mono- (**5**) to tris-derivatives (**7**). CCR_2: These values differ considerably between the three series (**A**–**C**). The shielding decreases R = H > CO_2Et > Me. $^3J(PC)$ values decrease by 0.2–0.5 Hz on passing from mono-(**5**) to tris-derivatives (**7**). We have shown earlier for the PNCC[4], as well as the POCC, system[5] that changes in three-bond coupling constants, $^3J(PNCC)$ and $^3J(POCC)$ are not only attributable to dihedral angle changes. In a number of cases those changes in three bond coupling constants are largely functions of the stereochemistry of the hetero-atom (N or O), as well as of the P—N or the P—O bond length.[4,5] As lone-pair back-donation is more pronounced with N than with O atoms, coupling constant changes are larger in the PNCC than in the POCC system. The decreases in the $^3J(POCC)$ values in the present study are almost certainly due, at least in part, to P—O bond lengthening as electron-withdrawing $\equiv PCl_2$ groups are replaced by the more electron-supplying ≡Pspiro moieties. The observation that the changes in the malonate derivatives (0.2 Hz) are smaller than for the other two diol derivatives, is in keeping with the strongly electron-withdrawing nature of the R = CO_2Et, compared to those where group R = H or Me. $COCH_2$: Again deshielding is observed from mono- (**5A**) to tris-derivative (**7A**). The effect is, however, reduced to 0.45 p.p.m. C = O: It is even smaller here, 0.2 p.p.m.

TABLE II

^{1}H N.m.r. data for six-membered spiro derivatives[a]

Compound	δ $POCH_2$[b]	δ CCH_2[b]	δ $COCH_2$[b]	δ CCH_3[b]	δ CH_2CH_3[b]	$^3J(PH)$[c]	$^3J(HH)$[c]
$(HOCH_2)_2C(CO_2Et)_2$	4.11[d]		4.25		1.28		
$(HOCH_2)_2CH_2$	3.85[d]	1.82					
$(HOCH_2)_2CMe_2$	3.47[d]			0.89			
$N_3P_3Cl_4[(OCH_2)_2C(CO_2Et)_2]$	4.86		4.29		1.30	13.8	7.2[e]
$N_3P_3Cl_4[(OCH_2)_2CH_2]$[g]	4.53	2.07				12.9	5.46[f]
$N_3P_3Cl_4[(OCH_2)_2CMe_2]$[h]	4.14			1.10		13.2	
$N_3P_3Cl_2[(OCH_2)_2C(CO_2Et)_2]_2$	4.83		4.26		1.29	13.7	7.2[e]
$N_3P_3Cl_2[(OCH_2)_2CH_2]_2$[g]	4.51	2.09				10.7	
$N_3P_3Cl_2[(OCH_2)_2CMe_2]_2$[h]	4.20			0.99		5.05	
	3.88					17.3	
$N_3P_3[(OCH_2)_2C(CO_2Et)_2]_3$	4.75		4.24		1.28	13.3	7.2[e]
$N_3P_3[(OCH_2)_2CH_2]_3$[g]	4.45	1.96				12.7	
$N_3P_3[(OCH_2)_2CMe_2]_3$[h]	4.00			1.06		13.1	

[a] In $CDCl_3$ (TMS internal reference) at 199.95 MHz (room temperature).

[b] In p.p.m.

[c] In Hz.

[d] Refers to $HOCH_2$.

[e] Refers to CH_2CH_3.

[f] Refers to CH_2CH_2.

[g] Data from ref. 2.

[h] Data from ref. 1.

TABLE III

^{13}C N.m.r. data for six-membered spiro derivatives[a]

Compound	δ $POCH_2$[b]	δ CCR_2[b,c]	δ $COCH_2$[b]	δ CH_2CH_3[b]	δ C=O[b]	$^2J(PC)$[d]	$^3J(PC)$[d]
$(HOCH_2)_2C(CO_2Et)_2$	61.9[e,f]	61.2	63.1[f]				
$(HOCH_2)_2CH_2$	61.8[e]	34.9					
$(HOCH_2)_2CMe_2$	70.5[e]	36.5					
$N_3P_3Cl_4[(OCH_2)_2C(CO_2Et)_2]$	68.7	54.4	63.05	13.95	166.2	7.0	4.8
$N_3P_3Cl_4[(OCH_2)_2CH_2]$[g]	68.05	25.9				6.45	7.5
$N_3P_3Cl_4[(OCH_2)_2CMe_2]$[h]	77.0	32.2				6.45	5.9
$N_3P_3Cl_2[(OCH_2)_2C(CO_2Et)_2]_2$	68.3	54.5	62.8	13.95	166.1	5.4	4.8
$N_3P_3Cl_2[(OCH_2)_2CH_2]_2$[g]	67.4	25.9				5.9	7.5
$N_3P_3Cl_2[(OCH_2)_2CMe_2]_2$[h]	76.6	32.1				4.8	5.9
$N_3P_3[(OCH_2)_2C(CO_2Et)_2]_3$	67.9	54.5	62.6	13.95	166.0	6.05	4.6
$N_3P_3[(OCH_2)_2CH_2]_3$[g]	66.9	26.1				5.5	7.0
$N_3P_3[(OCH_2)_2CMe_2]_3$[h]	76.1	32.0				5.1	5.4

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

[b] In p.p.m.

[c] R = CO_2Et, H, Me respectively.

[d] In Hz.

[e] Refers to HOCH.

[f] Assignment made on assumption that the ^{13}C deshielding follows a similar pattern as the ^1H deshielding (unambiguous assignment) in Table 2.

[g] Data from ref. 2.

[h] Data from ref. 1.

Mass Spectra

When determining the mass spectra by electron impact of the three spiro malonate derivatives (**5A**, **6A**, **7A**), no molecular ions, M^+, were observed. Instead for compounds (**5A**) and (**6A**), $(M + 1)^+$, and for compound (**7A**), $(M + 3)^+$ were found. A very recent paper[6] reported that for a very small number of compounds (10 out of 1400 examined), the molecular ion M^+ was generally absent, but the mono-protonated species $(M + H)^+$ was present in excess of 10% of the base peak. The common structural feature in these 14 compounds was the presence of a carbonyl group and the phenomenon was described as self-induced chemical ionisation under electron ionisation conditions. Compounds (**5A–7A**) contain 2,4 and 6 such groups respectively. We can therefore add two more compounds (**5A** and **6A**) to the list of those showing $(M + H)^+$ peaks and report, what we believe to be the first example, of a derivative (**7A**) showing an $(M + 3H)^+$ peak. This phenomenon will be subjected to more detailed investigations, which will be reported later on.

Summary

All three diols (**2–4**) have a preference for spiro derivative formation. The diols (**2** and **3**) give singly and doubly bridged derivatives respectively. The same two diols (**2** and **3**) give ansa derivatives, the latter apparently giving a somewhat higher proportion of the spiro-ansa isomer. With the simplest diol (**2**) danglers were also isolated. Diethyl bis(hydroxymethyl)malonate is prone to base and acid catalysed hydrolysis. The same is very probably true of its phosphazene derivatives. This instability may contribute to the smaller number of derivatives isolated. It is tempting, however, to relate the presence of ansa moieties to the electron-supplying/withdrawing capacity of the substituents R. For R = Me ansa products were considerable, for R = H, they were only minor, for R = CO_2Et, none were observed. The greater similarity between the reaction products of $N_3P_3Cl_6$, (**1**) with the diols (**2**)[2] and (**3**),[1] compared to those observed with the malonate (**4**), is also mirrored in the reaction of its homologue, $N_4P_4Cl_8$. In this system the diols (**2**)[7] and (**3**)[8] did not yield tetrakis spiro derivatives, whilst in the malonate system such a compound was isolated.[9] The malonate derivatives of the phosphazenes may, because of the functionality of their organic substituents prove useful intermediates, especially for incorporating into polymer systems. The comparison of n.m.r. parameters amongst the spiro derivatives of these three diols (**2–4**) is, however, not affected by instability considerations. ^{31}P N.m.r. chemical shifts are notoriously difficult to interpret in terms of electron supply. The same is, however, not true for ^1H and ^{13}C chemical shifts. The shielding of the $POCH_2$ protons is affected by the R substituents and the order is the predicted one: Me > H > CO_2Et. As expected all protons are more shielded (to a varying degree) when electron-withdrawing chlorine atoms are replaced by the more electron-supplying spirodioxy groups. It is, however, possible that the magnetic anisotropy of the carbonyl group may cause some apparent anomalies, such as the closeness of the $POCH_2$ chemical shifts for R = H and CO_2Et, and hence comparisons within the same series, e.g. **A** are less prone to such effects. Overall the ^1H and ^{13}C spectra demonstrate that the electron-withdrawing power of the phosphazene moiety decreases in the order $N_3P_3Cl_4 > N_3P_3Cl_2[(OCH_2)_2CR_2] > N_3P_3[(OCH_2)CR_2]_2$.

EXPERIMENTAL

Chemicals were obtained as follows: benzene, light petroleum (b.p. 40–60°C), anhydrous diethyl ether (May and Baker Ltd.), tetrahydrofuran (Fluka-Garantie 99.5%), deuteriated solvents for n.m.r. spectroscopy (Aldrich Chem. Co. Ltd.), pyridine, dichloromethane (B.D.H. Chemical Ltd.), hexachlorocyclotriphosphazatriene (Shin Nisso Kako Co. Ltd.). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60 F 524 (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[10] using Kieselgel 60. Melting points were determined on a Reichert-Kofler microheating stage and a Mettler FB 82 hot stage connected to a FP 800 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 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 JEOL JNM FX-60 spectrometer (operating at 24.15 MHz.), a Varian XL-200 spectrometer (operating at 80.98 MHz.—University College, London), and a Varian VXR 400 (operating at 162.0 MHz.—University College, London), 85% H_3PO_4 was used as an external reference.

The mass spectra were recorded by electron impact using a VG 7070 H mass spectrometer with Finnigan INCOS Data System at University College, London.

(**a**) 1 Equivalent diethyl bis)hydroxymethylmalonate. To $N_3P_3Cl_6$ (3 g, 8.6 mmol) in THF (100 cm^3 was added diethyl bis(hydroxymethyl)malonate (1.9 g, 8.6 mmol) in 10 cm^3 THF and pyridine (1.37 g, 17.3 mmol) in THF (5 cm^3). Addition was dropwise over a period of 30 min. The reaction mixture was stirred for 5 h and heated under reflux for a further 1.5 h and then allowed to attain room temperature. The reaction was monitored by t.l.c. and ^{31}P spectroscopy. T.l.c. examination revealed the completion of the reaction and the formation of one major compound. Small spots of polymeric products and trimer were also observed. The bulk of pyridine hydrochloride was filtered off and the filtrate concentrated to 15 cm^3 and column chromotographed using 30 g of silica gel and eluted with anhydrous diethyl ether/light petroleum (b.p. 40–60°C) (1:2). The major product was isolated and a recrystallised from a light petroleum (b.p. 40–60°C)/CH_2Cl_2 mixture (5:1) and found to be the mono derivative (**5**), m.p. 76–78°C, yield 1.55 g (52%).

(**b**) 2 Equivalents. To $N_3P_3Cl_6$ (3 g, 8.6 mmol) in anhydrous Et_2O (100 cm^3) was added with stirring pyridine (2.74 g, 34.6 mmol) in anhydrous Et_2O (10 cm^3). The diol (3.8 g, 17.3 mmol) was then added to the previous mixture with stirring. Following the procedure as for (**a**), a major product was obtained [accompanied by a minor product (compound **5**) (15%), which was already obtained in (**a**)] by using

TABLE IV

Characterization details for compounds (**5A**–**7A**)

				Elemental analysis/percentage Composition					
		M		Calc.			Found		
Compound	Formula	Calc.[a]	Obs.	C	H	N	C	H	N
(**5A**)	$C_9H_{14}O_6N_3P_3Cl_4$	493	494[b]	21.8	2.8	8.5	21.9	2.9	8.45
(**6A**)	$C_{18}H_{28}O_{12}N_3P_3Cl_2$	641	642[b]	33.7	4.4	6.45	33.5	4.3	6.5
(**7A**)	$C_{27}H_{42}O_{18}N_3P_3$	789	792[c]	41.1	5.3	5.3	41.3	5.2	5.4

[a] Based on the mass of the most abundant isotope.

[b] $(M + H).^+$

[c] $(M + 3H)^+$ (see discussion section and ref. 6).

benzene/dichloromethane mixture (1:4) and recrystallised from light petroleum (b.p. 40–60°C)/dichloromethane mixture (4:1). It was characterised as the bis derivative, (**6**), m.p. 115°C, yield 1.4 g (46%).

(c) With an excess of diol. Reaction of $N_3P_3Cl_6$ (3 g, 8.6 mmol) in THF (100 cm^3) with about six equivalents of malonate (11.4 g, 51.6 mmol) in the presence of anhydrous pyridine (8.22 g, 103 mmol) carried out as in (**a**). T.l.c. examination revealed the formation of large amounts of pyridine hydrochloride, polymeric products and small spot. The reaction mixture was filtered. The filtrate was concentrated and column chromotographed using silica gel (30 g) and eluted with light petroleum/THF mixture (4:1). The product was obtained admixed with some pyridine hydrochloride and polymeric product. This product was recolumned using the same eluent and recrystallised from benzene. It was identified as the tris derivative, (**7**), m.p. 243°C (dec.), yield 0.65 g (22%). Characterisation details are in Table IV.

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