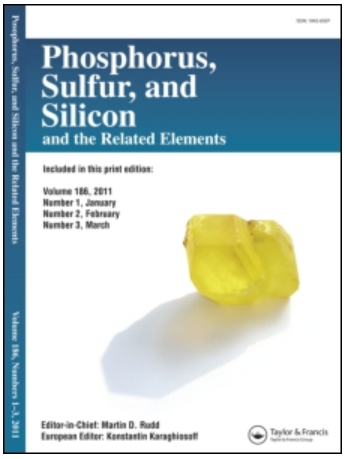

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STUDIES OF PHOSPHAZENES PART XXVI: BI(CYCLOPHOSPHAZENES) CONTAINING A P-O-P BRIDGE

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STUDIES OF PHOSPHAZENES PART XXVI†: BI(CYCLOPHOSPHAZENES) CONTAINING A P—O—P BRIDGE

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Penta(phenoxy)chlorocyclotriphosphazene $[N_3P_3(OPh)_5Cl$ (**1**)] reacts with "(hydroxy)"phosphazenes, $N_3P_3(OPh)_5(OH)$ (**2**), $N_3P_3(OMe)_5(OH)$ (**3**) and *gem*-$N_3P_3(NHBu^t)_2(OMe)_2(OH)$ (**4**) to give P—O—P bridged cyclophosphazenes, $[N_3P_3(OPh)_5]_2O$ (**5**), $[N_3P_3(OPh)_5]O[N_3P_3(OMe)_5]$ (**6**) and $[N_3P_3(OPh)_5]O[N_3P_3(NHBu^t)_2(OMe)_3]$ (**7**) respectively. The products are characterised by IR and NMR spectroscopy and mass spectrometry. The P—O—P bridge of compound **5** is readily cleaved by various nucleophiles.

INTRODUCTION

Cyclophosphazenes containing hydroxy substituents are a subject of current interest.[1-5] Although phosphorus-31 NMR spectroscopy indicates that (hydroxy) phosphazenes exist in solution only as oxophosphazanes,[1,2,6] reactions of these compounds appear to involve the P—OH form. Thus, the pentamethoxy derivative, $N_3P_3(OMe)_5(OH)$, reacts with acetyl chloride[7] or trimethylchlorosilane[8] to give $N_3P_3(OMe)_5(OCOCH_3)$ and $N_3P_3(OMe)_5(OSiMe_3)$ respectively. Similarly, the pentaphenyl derivative, $N_3P_3(Ph)_5(OH)$ reacts with the chloro analogue, $N_3P_3(Ph)_5Cl$, in the presence of an excess of pyridine to give the P—O—P bridged cyclophosphazene, $(N_3P_3Ph_5)_2O$.[9] Such P—O—P bridged compounds have also been prepared by the oxidation of hydrido cyclophosphazenes.[10] In this study we report further examples of P—O—P bridged compounds obtained by condensing the penta(phenoxy) derivative, $N_3P_3(OPh)_5Cl$, with (hydroxy)phosphazenes. In addition, the susceptibility of the P—O—P bridge to nucleophilic substitution reactions is investigated. The preparation of other P—O—P bridged phosphazene compounds using the same synthetic approach was reported[11] in 1984 by Fedorov *et al.*

† Part XXV: K. C. Kumaraswamy, M. D. Poojari, S. S. Krishnamurthy and H. Manohar, *J. Chem. Soc. Dalton Trans.*, (in press).

RESULTS AND DISCUSSION

The pentaphenoxy derivative (**1**) reacts with the (alkoxy)("hydroxy")cyclophosphazenes, (**2**), (**3**) and (**4**), in boiling benzene and an excess of pyridine to give the P—O—P bridged compounds, (**5**), (**6**) and (**7**), respectively (Figure 1). The molecular formula of these derivatives is established by mass spectrometry; parent ions are clearly observed in each case. The fragmentation pattern reveals that the P—O—P bridge is cleaved initially. Subsequent loss of alkoxy or aryloxy substituents follows until finally the cyclophosphazene ring itself fragments. The pattern observed for the symmetrical P—O—P derivative (**5**) is shown in Figure 2. A similar fragmentation has been observed in the mass spectrum of spirocyclic phosphazenes containing alkanedioxy substituents.[18]

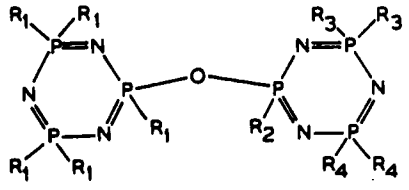

FIGURE 1 Structures of P—O—P bridged cyclophosphazenes,

$R_1 - R_4 = OPh$ (**5**);

$R_1 = OPh$, $R_2 - R_4 = OMe$ (**6**);

$R_1 = OPh$, $R_2, R_3 = OMe$, $R_4 = NHBu^t$ (**7**).

The IR spectra of the P—O—P compounds (**5–7**) show bands in the region 1200–1260 cm^{-1} (P=N ring stretch). A band of medium intensity at 975–980 cm^{-1} is observed which is absent in the spectra of the uncoupled reagents (**1–4**). This band can be assigned to the asymmetric stretching frequency of the P—O—P bridge.[9]

The reactivity of the P—O—P bridge towards nucleophiles has received little attention in acyclic phosphorus chemistry[19] and there are no reports of such reactions in cyclophosphazene chemistry. The reactions of the bi-cyclophosphazene (**5**) with a few nucleophiles are summarised in Table I. The P—O—P bridge is easily cleaved by Cl^-, F^-, OH^-, OPh^- and OMe^- to give the hydroxyphosphazene (**1**) and $N_3P_3(OPh)_5X$ (Figure 3); the cyclophosphazene ring remains intact in these reactions.

The formation of P—O—P cross-links has been postulated during the thermolysis of linear poly(organo)phosphazene polymers.[20] It is possible that nucleophiles such as OMe^- or OPh^- may be useful for breaking down these cross-links while retaining the linear polymeric structure intact.

EXPERIMENTAL

The cyclophosphazenes, $N_3P_3(OR)_5X$ [R=Ph, X=Cl[12] or OH[13]; R=Me, X=OH[8]] and $N_3P_3(NHBu^t)_2(OMe)_3(OH)$[1] were prepared by literature methods.

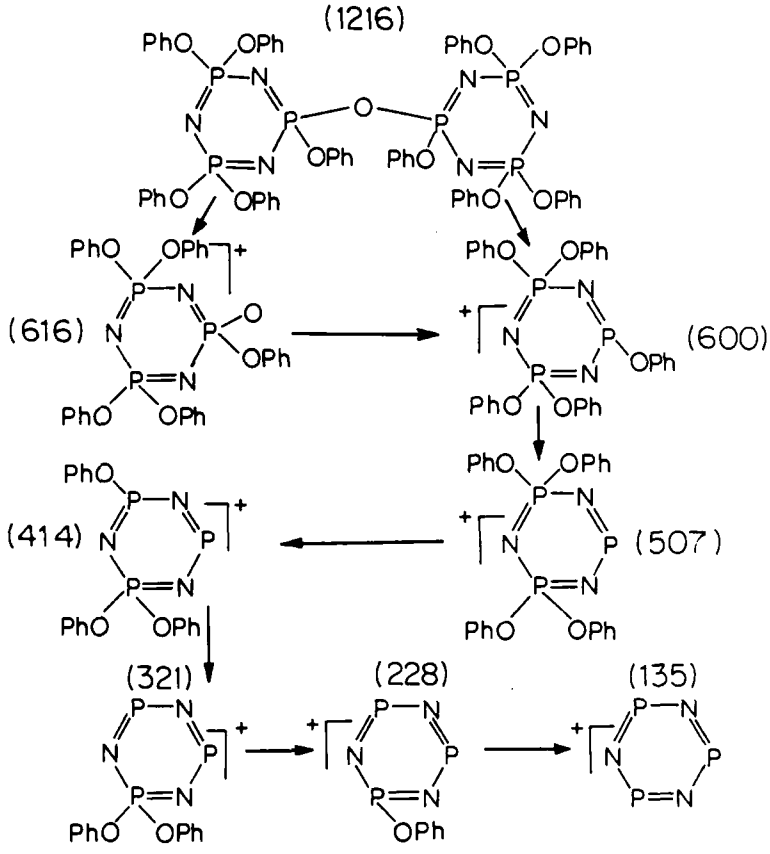

FIGURE 2 Mass spectral fragmentation pattern of $[N_3P_3(OPh)_5]_2O$ (**5**). Numbers in parentheses denote m/e values.

TABLE I

Nucleophilic substitution reactions[a] of $[N_3P_3(OPh)_5]_2O$ (**5**)

Compound (**5**) g; mmol	Reagent	Products isolated[b]	Yield g; %	mp °C
1.00; 0.82	Anhydrous HCl	$N_3P_3(OPh)_5Cl$[c]	0.48; 92	68
1.50; 1.23	Anhydrous HF (30% pyridinium hydrofluoride)[d]	$N_3P_3(OPh)_4F$[e]	0.72; 94	49
1.50; 1.23	Ethanolic KOH (5 mmol)	$N_3P_3(OPh)_5(OH)$	1.30; 85	165
1.50; 1.23	NaOPh (2 mmol)	$N_3P_3(OPh)_6$[c]	0.75; 88	111
1.00; 0.82	NaOMe (2 mmol)	$N_3P_3(OPh)_5(OMe)$[f]	0.45; 90	91

[a] Reactions carried out in boiling methyl cyanide for 2 h.

[b] In all reactions $N_3P_3(OPh)_5(OH)$ (**2**) is formed in 85–90% yield; characterised by comparison with an authentic sample (mp and IR)[13].

[c] Characterised by comparison with authentic samples (mp, IR and ^{31}P NMR).[12]

[d] Prepared by literature method.[15]

[e] Characterised by comparison with an authentic sample (mp, IR and ^{31}P NMR).[16,17]

[f] Analysis-Found: C, 58.7; H, 4.3; N, 6.6. Calculated for $C_{31}H_{28}P_3N_3O_6$: C, 58.9; H, 4.4; N, 6.6. ^1H NMR ($CDCl_3$): δ 3.23 (d, 3 H, OCH_3, $^3J(P—H) = 12.1$ Hz) 7.2 (m, 25 H, OC_6H_5).

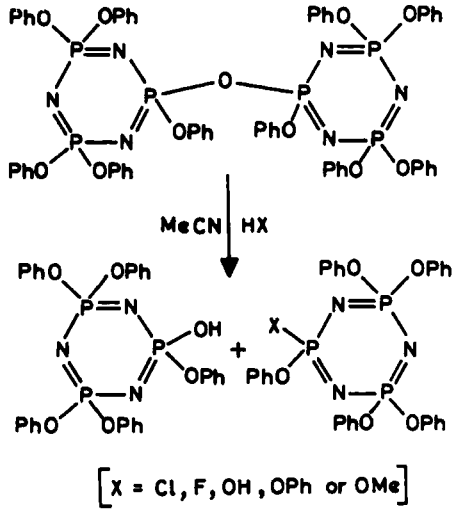

FIGURE 3 Nucleophilic substitution reactions of $[N_3P_3(OPh)_5]_2O$ (**5**).

Proton NMR spectra were obtained from a Brucker FT 270 MHz spectrometer. The ^{31}P NMR spectra were recorded using Brucker WH 90 (36.43 MHz) and Varian FT 80A (32.20 MHz) spectrometers. The spectra were obtained in $CDCl_3$ solution with ~ 85% H_3PO_4 as external reference; upfield shifts are negative. Infrared spectra were recorded in potassium bromide discs using a Perkin Elmer spectrophotometer. Mass spectrometric data were obtained from an AEI MS 902 spectrometer.

Preparation of the bridged cyclophosphazene $[N_3P_3(OPh)_5]_2O$ (**5**). Penta(phenoxy)(hydroxy)cyclotriphosphazene, $N_3P_3(OPh)_5(OH)$ (**2**) (1.0 g; 1.6 mmol), dissolved in benzene (50 ml) and pyridine (25 ml), was added to a solution of $N_3P_3(OPh)_5Cl$ (**1**) (1.03 g; 1.6 mmol) in benzene (25 ml). The mixture was heated under reflux for 2 h. After evaporation of the solvent, the residual oil was dissolved in diethyl ether (100 ml). This solution was washed with water (2 × 50 ml), dried over sodium sulphate and evaporated to obtain a viscous residue which solidified by the addition of light petroleum (bp 60–80°)-methylene chloride (1 : 2) and cooling to 0°C. Recrystallisation from the same solvent gave compound **5**, mp 167–169°C (1.65 g; 83%). [Found: C, 59.2; H, 4.1; N, 6.9 calculated for $C_{60}H_{50}P_6N_6O_{11}$: C, 59.2; H, 4.1; N, 6.9]. IR 980, 1170, 1190, 1200, 1260 cm^{-1}. ^1H NMR($CDCl_3$): δ 7.2(m, OC_6H_5). Mass spectrum: m/e = 1216.

The phosphorus-31 NMR spectrum of **5** is very complex and shows the presence of a small amount of the (hydroxy)phosphazene **2** even though a freshly recrystallised sample of **5** was used.[14] It was not possible to fully analyse this complex spectrum by computer simulation. However, approximate values of chemical shifts could be obtained which show a reasonable fit for an $A_2BB'A'_2$ spin system [δ $\underline{P}(OPh)_2$ = 8.8, δ ($\underline{P}$—O—$\underline{P}$) = 4.4].

Compounds **6** and **7** were prepared by treating **1** with **3** and **4** respectively. The reaction conditions and the work-up procedure were the same as described above for compound **5**.

Compound **6** (65% yield) is a viscous oil, m/e = 906 corresponding to parent ion $(C_{35}H_{40}N_6O_{11}P_6)^+$. IR 975, 1180, 1200, 1225, 1270. ^1H NMR($CDCl_3$): δ 3.65 (d, 3 H, OCH_3, ^3J(P—H) = 12.1 Hz), 3.73 (d, 6 H, OCH_3, ^3J(P—H) = 12.0 Hz), 3.77 (d, 6 H, OCH_3, ^3J(P—H) = 12.2 Hz), 7.2 (m, 25 H, OC_6H_5): ^{31}P NMR δ 20.8 to −6.7 (complex multiplet).

Compound **7** (75% yield) is a solid, mp 142–144°C, recrystallised from light petroleum (60–80°)-methylene chloride (1 : 2); m/e = 988 corresponding to parent ion $(C_{41}H_{52}N_8O_9P_6)^+$. IR 980, 1170, 1190, 1220, 1260, 3340, 3370 cm^{-1}. ^1H NMR($CDCl_3$): δ 3.54 (d, 3 H, OCH_3, ^3J(P—H) = 12.5 Hz), 3.67 (d, 6 H, OCH_3, ^3J(P—H) = 12.5 Hz); 3.68 (d, 6 H, OCH_3, ^3J(P—H) = 12.1 Hz), 3.1 (broad, 2 H, NH), 1.29 (18 H, $2C(CH_3)_3$). ^{31}P NMR: δ 15.1 to −4.6 (complex multiplet).

Nucleophilic substitution reactions of the bridged cyclophosphazene **5**. Reactions of compound **5** with Cl^-, F^-, OH^-, OPh^- and OMe^- in boiling methyl cyanide are summarised in Table I. The work-up procedure involved the evaporation of the solvent and neutralisation of the residue with an acid or a base. The residue was extracted with diethyl ether (2 × 50 ml) and dried over sodium sulphate. Partial removal of

diethyl ether led to the precipitation of $N_3P_3(OPh)_5(OH)$ (**2**) as a colourless solid and the other product was left behind in solution.

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