Studies of Phosphazenes. Part 13.[1] Thermal Rearrangement Reactions of Some Methoxycyclophosphazenes

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The methoxycyclophosphazenes $[NP(OMe)_2]_n$ (n = 3—6) rearrange on heating to give oxocyclophosphazanes, $[N(Me)PO(OMe)]_n$. Isomeric products are formed when n = 4—6. The ^1H, ^{31}P, and ^{13}C n.m.r. data for the starting materials and the products are presented. The ethoxy- and n-propoxy-derivatives $N_3P_3(OR)_6$ do not undergo the above rearrangement. The geminal derivatives $N_3P_3R_2(OMe)_4$ (R = Ph or $NHBu^t$) on heating yield both fully and partially rearranged products, namely dioxophosphaz-1-enes and oxophosphazadienes, as shown by 270-MHz ^1H n.m.r. spectroscopy. The non-geminal derivative $N_3P_3(NMe_2)_2(OMe)_4$ gives only the fully rearranged product $N_3Me_3P_3(NMe_2)_2O_3(OMe)$, whose structure has been established from its ^1H and ^{31}P n.m.r. spectra.

THE rearrangement of some alkoxycyclophosphazenes to oxocyclophosphazanes was previously investigated by Shaw and co-workers.[2,3] The rearrangement was effected by heating these esters either alone or in the presence of an alkyl halide as a catalyst. The formation of two partially rearranged products during the reaction of the hexaethoxide $N_3P_3(OEt)_6$ in the presence of ethyl iodide was suggested from t.l.c. evidence but these compounds were not characterised.[3] Bullen *et al.*[4] re-investigated the rearrangement of the octamethoxide $N_4P_4(OMe)_8$ catalysed by methyl iodide and isolated two isomeric oxocyclophosphazanes $N_4Me_4P_4O_4(OMe)_4$, whose structures were established by *X*-ray crystallography. Rallo[5] heated the higher-membered methoxycyclophosphazenes $[NP(OMe)_2]_n$ (n = 5 or 6) at *ca.* 200 °C under vacuum and concluded that the vitreous hygroscopic mass obtained in each case was a decomposition product.

Spectroscopic data for cyclotriphosphazanes (and higher oligomers) are scanty.[6] In contrast, extensive data are available for numerous cyclodiphosphazanes.[6,7] In this paper, we describe a more detailed study of the thermal rearrangement of the methoxycyclophosphazenes $[NP(OMe)_2]_n$ (n = 3—6), and the ^1H, ^{31}P, and ^{13}C n.m.r. spectra of the products. In addition, we discuss the complex thermal transformations undergone by methoxycyclotriphosphazenes that also contain other organic substituents.

EXPERIMENTS

A mixture of oligomeric chlorocyclophosphazenes, $(NPCl_2)_n$ (n = 3—6) (BASF, Ludwigshafen or Ethyl Corporation), was separated by a standard procedure.[8] The methoxycyclophosphazenes[5,9] $[NP(OMe)_2]_n$ (n = 3—6) (1)—(4) were prepared in 60—80% yield by allowing a solution of the appropriate chlorocyclophosphazene in dry benzene to react with a stirred solution of sodium methoxide in dry methanol initially at 0 °C (1 h) and then at 25 °C (24 h). The hexaethoxide $N_3P_3(OEt)_6$ was prepared similarly; the n-propoxy-analogue, $N_3P_3(OPr^n)_6$, was synthesised by treating the hexachloride $N_3P_3Cl_6$ with n-propanol in the presence of pyridine.[9] The geminal derivatives, $N_3P_3Ph_2Cl_4$ and $N_3P_3Cl_4(NHBu^t)_2$, and the non-geminal ones, *trans*-$N_3P_3Cl_4(NMe_2)_2$ and *trans*-$N_3P_3Cl_3(NMe_2)_3$, were obtained by literature methods.[10-12]

Hydrogen-1 n.m.r. spectra were recorded with JEOL MH 100 and Bruker WH 270 spectrometers, ^{31}P-{^1H} n.m.r. spectra on a Bruker HFX-90 instrument operating at 36.43 MHz, and ^{13}C-{^1H} n.m.r. spectra on a Bruker WH 270 spectrometer at 67.9 MHz. Mass spectrometric data were obtained from the P.C.M.U. Service, Harwell.

Preparations—2,2:4,4,6,6-$N_3P_3Ph_2(OMe)_4$ (5). This compound was prepared as reported in the literature.[13] N.m.r.: ^1H, δ(OMe) 3.66, $^3J^*$(P–H) 12.4 Hz; ^{31}P, δ[$P(OMe)_2$] 18.3, δ(PPh_2) 21.0, ^2J(P–P) 34.3 Hz.

2,2:4,4,6,6-$N_3P_3(NHBu^t)_2(OMe)_4$ (6). The geminal bis(t-butylamino)-derivative[11] $N_3P_3Cl_4(NHBu^t)_2$ (5.0 g, 0.012 mol) was allowed to react with an excess of sodium methoxide in methanol (75 cm³) at 25 °C. The mixture was heated under reflux for 4 h. After evaporation of the solvent, a syrup was obtained which was extracted with light petroleum (b.p. 40—60 °C) (3 × 75 cm³). The extract was rapidly washed with water and dried over anhydrous sodium sulphate. Removal of the solvent gave an oil which slowly solidified at 0 °C. Recrystallisation from cold light petroleum gave 2,2,4,4-*tetramethoxy*-6,6-*bis*(*t-butylamino*)-*cyclotriphosphazatriene* (6) (1.1 g, 20%), m.p. 72—73 °C (Found: C, 35.6; H, 8.0; N, 17.4. $C_{12}H_{22}N_5O_4P_3$ requires C, 35.7; H, 7.9; N, 17.4%). N.m.r.: ^1H, δ(OMe) 3.66, $^3J^*$(P–H) 12.0 Hz, δ(CMe_3) 1.35, δ(NH) 2.3; ^{31}P, δ[$P(OMe)_2$] 18.9, δ[$P(NHBu^t)_2$] 11.6, ^2J(P–P) 63.7 Hz.

trans-2,2,4,6:4,6-$N_3P_3(NMe_2)_2(OMe)_4$ (7). The dimethylamino-derivative *trans*-2,2,4,6:4,6-$N_3P_3Cl_4(NMe_2)_2$, m.p. 103 °C[12] (5.0 g, 0.014 mol), was treated with an excess of sodium methoxide in methanol (75 cm³) at 0 °C. The mixture was heated under reflux (6 h), cooled to *ca.* 25 °C, and diethyl ether (200 cm³) was added. The solution was filtered and the filtrate was washed with dilute hydrochloric acid (50 cm³), sodium hydrogencarbonate (50 cm³), and finally with water (3 × 50 cm³). The ether layer was dried (anhydrous sodium sulphate) and the solvent was evaporated to obtain an oil (0.2 g). The combined water washings were neutralised with dilute hydrochloric acid and extracted with chloroform using a continuous-extraction device. The chloroform solution was dried (anhydrous sodium sulphate) and evaporation yielded more (2.8 g) of the same oil (t.l.c., i.r., n.m.r. evidence). Distillation *in vacuo* gave trans-4,6-*bis*(*dimethylamino*)-2,2,4,6-*tetramethoxycyclotriphosphazatriene* (7) (2.5 g, 60%), b.p.

150 °C (0.5 mmHg *) (*m/e* = 347, $C_8H_{24}N_5O_4P_3$ requires *m/e* = 347). N.m.r.: ^1H, δ(OMe) 3.48 and 3.56, ^3J*(P–H) 12.4 and 12.4 Hz, δ(NMe_2) 2.56, ^3J*(P–H) 11.6 Hz; ^{31}P, δ[$P(OMe)_2$] 14.8, δ[$P(NMe_2)(OMe)$] 20.7, ^2J(P–P) 64.5 Hz.

An analogous preparation using *trans*-2,4,6:2,4,6-$N_3P_3Cl_3(NMe_2)_3$ [12] gave *trans*-2,4,6-tris(dimethylamino)-2,4,6-trimethoxycyclotriphosphazatriene (8) (52%), b.p. 160 °C (1 mmHg) [lit.,[14] b.p. 135 °C (0.6 mmHg)] (*m/e* = 360, $C_9H_{27}N_6O_3P_3$ requires *m/e* = 360). N.m.r.: ^1H, δ(OMe) 3.46(2) and 3.52(1), ^3J*(P–H) 11.8 and 11.8 Hz, δ(NMe_2) 2.56(2) and 2.60(1), ^3J*(P–H) 10.4 and 10.4 Hz; ^{31}P, δ[$P(NMe_2)(OMe)$] 26.0.

Thermal Rearrangement Reactions.—$N_3P_3(OMe)_6$ (1). The hexamethoxide (1) (1 g, 3.1 mmol) was placed in a round-bottomed flask (100 cm^3) which was evacuated to a pressure of 1—2 mmHg. It was immersed in an oil-bath maintained at 160 ± 2 °C for 3.5 h. The flask was then cooled and opened under an atmosphere of dry nitrogen. The product, which was free of compound (1) [t.l.c. (acetone)], was dissolved in dry dichloromethane and the solution was filtered. The filtrate was concentrated (10 cm^3) and light petroleum (b.p. 40—60 °C) (50 cm^3) was added. Two crude crops of crystals were obtained which were recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) (1 : 2) to give 2,4,6-trimethoxy-1,3,5-trimethyl-2,4,6-trioxocyclotriphosphazane (1a), m.p. 128 °C (lit.,[2] m.p. 127—127.5 °C) (0.7 g, 70%).

The experiment was repeated using the following conditions: (*i*) 160 °C, 3 h, atmosphere of dry nitrogen, yield of compound (1a) 30%; (*ii*) 160 °C, 2 h, in dry air, a black insoluble mass was obtained and (1a) was not detected; (*iii*) 140 °C, 64 h, in *m*-xylene solution, yield of (1a) 40%.

$N_4P_4(OMe)_8$ (2). The octamethoxide (2) (1.0 g, 2.3 mmol) was heated at 160 °C (1—2 mmHg) for 6.5 h as above. The crude product was dissolved in dry dichloromethane. Addition of light petroleum (b.p. 60—80 °C) induced crystallisation. The crystals obtained were recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) (1 : 3) to give 2,4,6,8-tetramethoxy-1,3,5,7-tetramethyl-2,4,6,8-tetraoxocyclotetraphosphazane (2a) (0.4 g, 40%), m.p. 190—192 °C (decomp.). The mother-liquor was cooled at 0 °C for 24 h and a second crop of crystals appeared. Recrystallisation from dichloromethane–light petroleum (1 : 3) gave the isomeric oxocyclotetraphosphazane (2b) (0.2 g, 20%), m.p. 183—185 °C (decomp.). The isomeric oxocyclotetraphosphazanes do not interconvert on heating [0.8 g, 150 °C (1—2 mmHg)] but decompose to insoluble resins.

The methoxide (2) decomposed completely when heated under an atmosphere of nitrogen at 160 °C for 4 h to give a resinous material which was insoluble in common organic solvents.

$N_5P_5(OMe)_{10}$ (3) *and* $N_6P_6(OMe)_{12}$ (4). The decamethoxide (3) (1.0 g, 1.9 mmol) was heated at 150 °C (1—2 mmHg) for 3 h as before. Thin-layer chromatography (acetone) of the oily reaction mixture showed the presence of three products with very close R_f values and the absence of starting material (3). This oil (0.8 g) did not solidify even at −78 °C. Its ^1H and ^{13}C-{^1H} n.m.r. spectra (Table 1) indicated that complete rearrangement to oxocyclopentaphosphazanes had taken place (parent ion at *m/e* = 535 corresponding to $C_{10}H_{30}N_5O_{10}P_5^+$). Attempts to separate individual components from the mixture were unsuccessful.

The methoxide $N_6P_6(OMe)_{12}$ (4) also rearranges completely when heated at 150 °C (1—2 mmHg) for 12 h to give a very complex mixture of cyclohexaphosphazanes (t.l.c., ^1H n.m.r.). Both methoxides (3) and (4) decompose rapidly to insoluble resinous materials if they are heated in air at *ca.* 170 °C for 1 h. These materials are probably cross-linked polymers.

gem-$N_3P_3Ph_2(OMe)_4$ (5). Compound (5) was heated at 170 °C (1—2 mmHg) for 7.5 h (no reaction occurred at 150 °C). The ^1H n.m.r. spectrum of the hygroscopic product showed that it was a 2 : 1 mixture of the fully rearranged compound $N_3Me_2P_3Ph_2O_2(OMe)_2$ (5b) and a partially rearranged compound $N_3MeP_3Ph_2(O)(OMe)_3$ (5a) (intense parent ion at *m/e* = 412 corresponding to $C_{16}H_{21}N_3O_4P_3^+$). Attempts to separate the two products were unsuccessful. Heating the starting material at 200 °C (1—2 mmHg) (3.5 h) did not increase the proportion of fully rearranged product (5b) to any significant extent.

TABLE 1

Hydrogen-1, ^{31}P, and ^{13}C n.m.r. data [a]

Compound	^1H δ(OCH_3) [b]	^1H δ(NCH_3) [c]	^{31}P δ(P)	^{13}C δ(OCH_3)	^{13}C δ(NCH_3)
(1) $N_3P_3(OMe)_6$	3.72		21.7	52.7	
(1a) $N_3Me_3P_3O_3(OMe)_3$	3.31 (2) [d]	2.91 (2)	6.6 (2)	53.6 (1)	31.2 (2)
	3.54 (1)	3.14 (1)	9.4 (1) [e]	53.9 (2)	33.6 (1)
(2) $N_4P_4(OMe)_8$	3.66		2.8	53.0	
(2a) $N_4Me_4P_4O_4(OMe)_4$ 2-*trans*-4-*cis*-6-*trans*-8	3.83	3.00	8.0 [f]	53.9	33.9
(2b) $N_4Me_4P_4O_4(OMe)_4$ 2-*cis*-4-*trans*-6-*trans*-8	3.90	3.06	7.5 [f]	54.1	34.3
(3) $N_5P_5(OMe)_{10}$	3.53		−2.5	52.9	
(3a,b,c) $N_5Me_5P_5O_5(OMe)_5$	3.9 [g]	3.0 [g]	−2.5 to +9.2 [h]	53.0 [g]	33.0 [g]
(4) $N_6P_6(OMe)_{12}$	3.67		−4.2	52.9	
(4x) $N_6Me_6P_6O_6(OMe)_6$	3.7 [g]	2.9 [g]	−12.1 to +12.7 [h]	53.0 [g]	33.0 [g]
$N_3P_3(OEt)_6$	3.92 [i]		14.3	62.1 [j]	
$N_3Et_3P_3O_3(OEt)_3$	4.1 [g,i]	3.56 (2) [k]	4.9 (2)	63.0 [j]	41.0 (2) [m]
		3.46 (1)	7.0 (1) [l]		42.5 (1)

[a] ^1H, in $CDCl_3$ solution; internal reference $SiMe_4$ (100 or 270 MHz); ^{31}P, in $CDCl_3$ solution; external reference 85% H_3PO_4: upfield shifts are negative (36.43 MHz); ^{13}C in $CDCl_3$ solution; internal reference $SiMe_4$ (67.9 MHz). [b] ^3J*(P–H) values are: 12.4, (1)—(3); 12.0, (1a); 12.2, (2a); and 11.5 Hz, (2b). [c] ^3J*(P–H) values are: 10.0, (1a); 9.6, (2a); and 10.0 Hz, (2b). [d] All numbers in parentheses refer to relative intensities. [e] ^2J(P–P) 23.1 Hz. [f] Sharp singlet. [g] Approximate centre of multiplet. [h] Complex multiplet(s). [i] OCH_2; ^3J*(P–H) 8.1 Hz. [j] $O^{13}CH_2$. [k] NCH_2; ^3J*(P–H) 6.9 Hz. [l] ^2J(P–P) 25.0 Hz. [m] $N^{13}CH_2$.

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

gem-$N_3P_3(NHBu^t)_2(OMe)_4$ (6). Compound (6) (1.0 g, 2.5 mmol) was heated at 150 °C (1—2 mmHg) for 6.5 h. The product was a viscous hygroscopic liquid. Although t.l.c. (acetone, ethyl acetate, or methanol) indicated the absence of starting material, the number of components formed in the thermolysis could not be clearly discerned. The mass spectrum of the product showed a strong parent ion at m/e = 403 ($C_{12}H_{32}N_5O_4P_3^+$) which suggests that ring degradation does not occur to any significant extent. The ^1H n.m.r. spectrum (270 MHz) of the product clearly indicated that it was a mixture of two partially rearranged isomers of formula $N_3MeP_3(NHBu^t)_2O(OMe)_3$ (6a, b) and the fully rearranged compound $N_3Me_2P_3(NHBu^t)_2O_2(OMe)_2$ (6c) in the ratio 3 : 2 (see Results and Discussion section). If the experiment is carried out at 170 °C (1—2 mmHg) for 4 h, the proportion of the latter increases at the expense of the partially rearranged isomers but, in addition, a brittle glassy substance is deposited on the walls of the flask. The ^1H n.m.r. spectrum of this glassy substance showed broad absorption bands in the $-OCH_3$ and $>NCH_3$ regions. At 200 °C (1—2 mmHg), thermolysis of compound (6) for 4.5 h gave only a brittle glassy mass which could not be characterised.

trans-2,2,4,6:4,6-$N_3P_3(NMe_2)_2(OMe)_4$ (7). Compound (7) (2.5 g, 3 mmol) was heated at 170 °C (1—2 mmHg) for 4.5 h. The product contained starting material and one other compound (t.l.c.; acetone). It was extracted with dichloromethane and distilled *in vacuo*. An oil (2.0 g, 80%) was collected [150 °C (0.5 mmHg)] which was identified as the starting material (i.r., n.m.r. spectroscopy). The brown residual mass was highly hygroscopic. Its ^1H n.m.r. spectrum indicated that it was the rearranged product $N_3Me_3P_3(NMe_2)_2O_3(OMe)$ (7a) (mass spectrum: m/e = 347 corresponding to $C_8H_{24}N_5O_4P_3^+$) (see Results and Discussion section).

Attempted Rearrangement Reactions of $N_3P_3(OR)_6$, R = Et *or* Pr^n.—These compounds decomposed on heating. A summary of reactions involving the hexaethoxide is given in Table 2.

TABLE 2

Attempted thermal rearrangement reactions of $N_3P_3(OEt)_6$

Experimental conditions	Duration of heating/h	Products obtained
200 °C/Air	1	Insoluble resin
200 °C/N_2	1	Insoluble resin
200 °C (1—2 mmHg)	1	Insoluble resin + hexaethoxide (30%)
150 °C (1—2 mmHg)	2	Insoluble resin + hexaethoxide (50%)
125 °C (1—2 mmHg)	1.5	Insoluble resin + hexaethoxide (70%) *

* 30% Yield after heating for 4 h.

RESULTS AND DISCUSSION

Rearrangement of the methoxycyclophosphazene $N_3P_3(OMe)_6$ (1) takes place readily at 150—160 °C (1—2 mmHg) to give the oxocyclophosphazane $N_3Me_3P_3O_3(OMe)_3$ (1a), m.p. 128 °C (70% yield), previously obtained as an involatile residue in low yield [2] during the distillation of compound (1) under vacuum. The crystal structure of (1a) has been reported by Ansell and Bullen.[15] The compound has a distorted boat shape. The non-equivalence of the $-OCH_3$ and $>NCH_3$ protons observed in the ^1H n.m.r. spectrum (and the non-equivalence of $-O^{13}CH_3$ and $>N^{13}CH_3$ carbon nuclei, Table 1) suggests that the molecule probably retains its distorted boat form in solution.

Cheng *et al.*[16] have recently reported the ^{31}P n.m.r. spectrum of a substance obtained from the thermal treatment of the hexamethoxide $N_3P_3(OMe)_6$ at 140 °C for 3 h. Their spectrum has been analysed for an ABC spin pattern (δ_A 9.6, δ_B 7.3, δ_C 6.6 p.p.m.). It was suggested that such a spectrum could arise from the oxocyclophosphazane with a *trans* arrangement of phosphoryl groups [as found by Ansell and Bullen [15] in their crystallographic study of compound (1a)]. The ^{31}P n.m.r. spectrum of our pure sample of (1a) is clearly an AB_2 pattern (illustrated elsewhere [17]) and consequently the validity of the spectrum described by Cheng *et al.*[16] must be viewed with scepticism. Furthermore, one of the P–N–P couplings in the ABC analysis of these workers [16] has a large negative value which is very unusual: most P–N–P couplings, whose signs have been determined, are positive for cyclic phosphorus–nitrogen compounds.[18]

The octamethoxide $N_4P_4(OMe)_8$ (2) undergoes rearrangement on heating at 160 °C (1—2 mmHg) to give the isomeric oxocyclotetraphosphazanes $N_4Me_4P_4O_4(OMe)_4$ (2a), m.p. 190—192 °C (decomp.) and (2b), m.p. 183—185 °C (decomp) (relative yield *ca.* 2 : 1). Although a cyclotetraphosphazane of this type could exist in four isomeric forms, it is difficult to discriminate between them solely on the basis of n.m.r. data [17] (Table 1). Crystallographic data (cell dimensions) indicate that the isomers (2a, b) are identical to those described by Bullen *et al.*[4] in a study of the rearrangement of compound (2) catalysed by methyl iodide. The 2-*trans*-4-*cis*-6-*trans*-8 isomer (2a) also predominates in the purely thermal preparation but it is interesting to note that the relative yield of isomer (2b) (2-*cis*-4-*trans*-6-*trans*-8) is considerably enhanced. The claim of Mochel and Cheng [16,19] that only one isomeric oxocyclotetraphosphazane (2-*trans*-4-*cis*-6-*trans*-8) is formed in the thermolysis of the octamethoxy-derivative, $N_4P_4(OMe)_8$, at 140—160 °C is untenable.

In contrast to an earlier report,[5] we observe that the decamethoxide $N_5P_5(OMe)_{10}$ (3) undergoes complete rearrangement when heated at 150 °C under reduced pressure for 3 h. Thin-layer chromatography indicates the presence of three products (3a, b, c) with very close R_f values and the absence of starting material (3). The 270-MHz ^1H n.m.r. spectrum of this mixture of oxocyclopentaphosphazanes $N_5Me_5P_5O_5(OMe)_5$ (3a, b, c) shows complex multiplets centred at δ 3.8 ($-OCH_3$) and 3.0 ($>NCH_3$) in the ratio 1 : 1. The ^{13}C-{^1H} n.m.r. spectrum consists of multiplets centred at δ 53.0 ($-O^{13}CH_3$) and 33.0 ($>N^{13}CH_3$) as anticipated for a mixture of cyclopentaphosphazanes. The ^{31}P-{^1H} n.m.r. spectrum of this mixture contains at least 25 lines. Similar n.m.r. data (Table 1) indicate that the hexameric derivative $N_6P_6(OMe)_{12}$ (4) also undergoes complete rearrangement at 150 °C (1—2 mmHg) (but only after

12 h) to give a complex mixture of isomeric products (4x).

It has been reported [2] that the hexaethoxide $N_3P_3(OEt)_6$ undergoes rearrangement to the cyclotriphosphazane $N_3Et_3P_3O_3(OEt)_3$ after heating in air at 200 °C for 1 h. This oxocyclophosphazane was also obtained in a reaction catalysed by ethyl iodide (mixed m.p. and i.r. spectrum).[2] We have made numerous unsuccessful attempts to repeat this thermal rearrangement reaction using various experimental conditions (see Table 2). In most cases, an insoluble material and/or starting material were obtained.

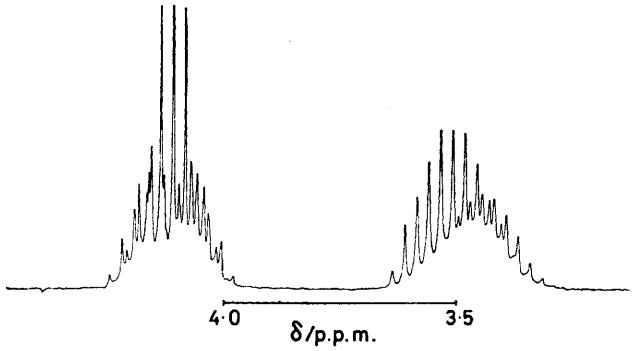


FIGURE 1 The 270-MHz ^1H n.m.r. spectrum of $N_3Et_3P_3O_3(OEt)_3$ in $CDCl_3$ solution

In 1969, Buslaev *et al.*[20] also reported an apparent thermal rearrangement of $N_3P_3(OEt)_6$ to its oxocyclotriphosphazane during a study of the reaction of the hexaethoxide with titanium tetrachloride or zirconium tetrachloride in a sealed ampoule at 200 °C for 2 h. The ^1H n.m.r. spectrum of their product is illustrated in their paper [20] and demonstrates that their claim that an oxocyclophosphazane is formed is clearly in error. The cyclotriphosphazane $N_3Et_3P_3O_3(OEt)_3$ should exhibit signals due to $-OCH_2$ and $>NCH_2$ groups in its ^1H n.m.r. spectrum in the intensity ratio 1 : 1. The published spectrum [20] shows only signals in the $-OCH_2$ region and a complex pattern for CH_3 protons. The ^1H n.m.r. spectrum of an authentic sample of the above compound (prepared by the method of Rätz and Hess [21]) is shown in Figure 1 (note the multiplets for both $-OCH_2$ *and* $>NCH_2$ protons).

Four products (excluding geometrical and conformational isomers) could be anticipated from the thermal rearrangement of a geminal derivative, $N_3P_3R_2(OMe)_4$ (Figure 2). The mono-rearranged product (C) formed by methylation at the γ ring-nitrogen atom seems inherently unlikely for either an inter- or intra-molecular pathway for the rearrangement. Hence, we have not considered structure (C) in the discussion that follows.

The thermal rearrangements of the geminal compounds $N_3P_3Ph_2(OMe)_4$ (5) and $N_3P_3(NHBu^t)_2(OMe)_4$ (6) have been investigated by ^1H and ^{31}P n.m.r. spectroscopy. The $-NCH_3$ region of the ^1H n.m.r. spectrum of a rearranged product with structure (A) or (B) (Figure 2) should give a doublet of doublets; this region of the spectrum of product (D) should show a ' triplet ' and a doublet of doublets. If the three compounds of struc-

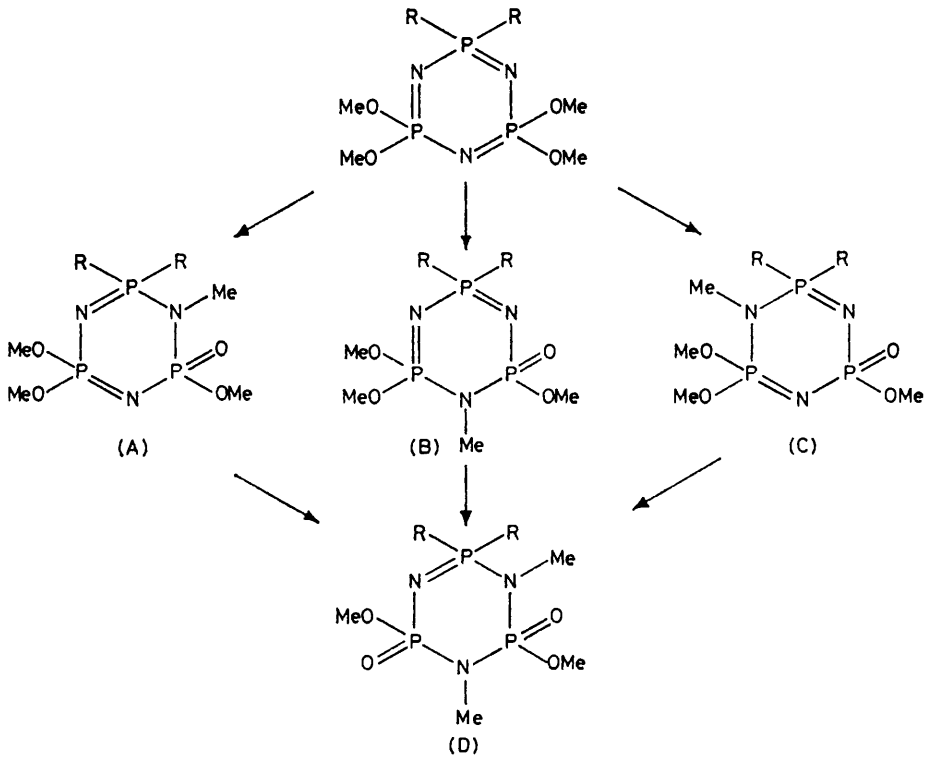


FIGURE 2 Possible products from the thermal rearrangement of *gem*-$N_3P_3R_2(OMe)_4$

tures A, B, or D are all present, the $-OCH_3$ region of the spectrum could in principle give rise to eight methoxy-doublets.

The rearrangement reaction of the methoxycyclophosphazene *gem*-$N_3P_3Ph_2(OMe)_4$ (5) has been studied at temperatures in the range 150—200 °C (1—2 mmHg). Rearrangement is not observed at 150 °C for 12 h. The ^1H n.m.r. spectra of the products obtained from the reactions at 170 (7.5), 170 (14), and 200 °C (3.5 h) are very similar and indicate that the same products are formed in each case. Some resinous material is also formed in the experiment carried out at 200 °C (3.5 h) (featureless absorptions beneath the $-NCH_3$ signals in the ^1H n.m.r. spectrum). The 270-MHz ^1H n.m.r. spectrum of a typical reaction mixture is shown in Figure 3. The

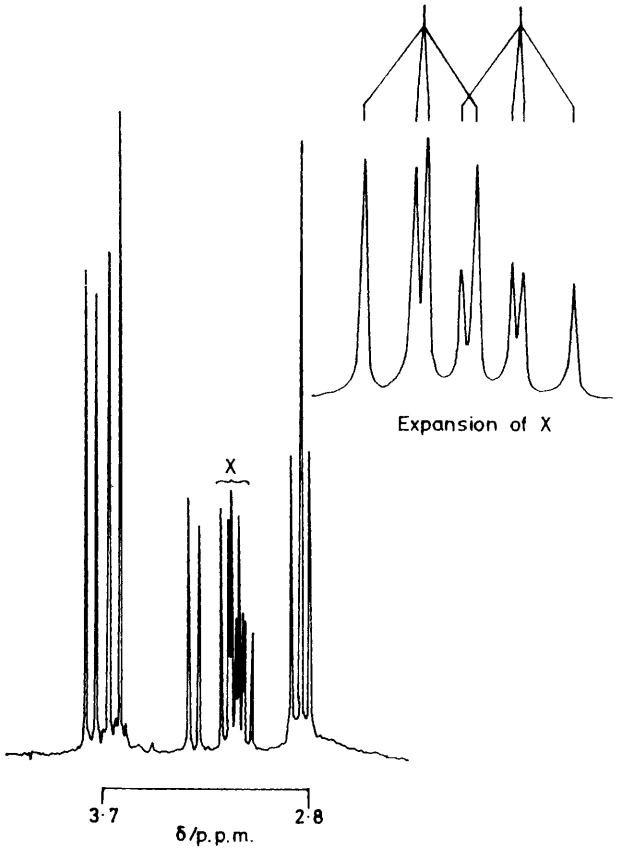


FIGURE 3 The ^1H n.m.r. spectrum (270 MHz, $CDCl_3$) ($-OCH_3$ and $>NCH_3$ regions) of the products (5a,b) obtained by heating $N_3P_3Ph_2(OMe)_4$ (5) at 170 °C (1—2 mmHg) for 7.5 h

$>NCH_3$ region consists of a ' triplet ' at δ 2.84 [^3J(P–H) 10.5 Hz] and two doublets of doublets at δ 3.10 (10.9 and 9.0 Hz) and 3.15 (10.9 and 9.0 Hz). From intensity considerations, the ' triplet ' must be paired with the multiplet at δ 3.15; the intensity of the latter is almost double that of the multiplet at δ 3.10. In the $-OCH_3$ region of the spectrum only three doublets [δ 3.31, 3.66, and 3.76; ^3J(P–H) 12.5 Hz in each case] can be readily discerned. The ^{31}P-{^1H} n.m.r. spectrum of this mixture consists of two overlapping AMX patterns of relative intensity *ca.* 2 : 1. The major group of signals can be analysed to give the following parameters: δ_A 17.4, δ_M 7.7, δ_X −4.4; ^2J(AM) 13.4, ^2J(AX) 20.6, and ^2J(MX) 14.8 Hz. The other AMX pattern is difficult to analyse accurately owing to its lower intensity, overlap on the δ 7 and −4 regions, and to the low ^2J(P–N–P) values. Only the A part of the spectrum is clearly visible (δ *ca.* 16.0).

The ^1H and ^{31}P n.m.r. spectra of the above reaction mixture are clearly compatible with the presence of the fully rearranged compound $N_3Me_2P_3Ph_2O_2(OMe)_2$ (5b) (major product) and only one of the possible partially rearranged compounds. We favour structure (5a) (Figure 4) for the minor product because (*a*) δ(PPh_2) is very similar to that of the fully rearranged product (5b), and (*b*) further rearrangement to give product (5b) would appear to be sterically less favoured. We do not exclude formation of the cyclophosphazadiene with an $>NMe$ group α to the $\equiv PPh_2$ substituent [see Figure 2(A)] in this rearrangement reaction. This product is pro-

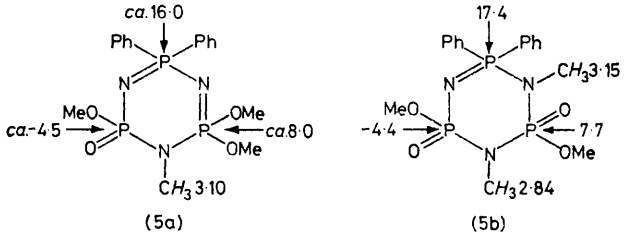


FIGURE 4 Structures of products (5a,b) with assignment of δ(NCH_3) and δ(*P*) (values in p.p.m.)

bably formed but further rearrangement to product (5b) would be relatively facile (see later). Assignments of δ(N*Me*) and δ(*P*) for products (5a, b) are given in Figure 4.

The geminal derivative $N_3P_3(NHBu^t)_2(OMe)_4$ (6) undergoes thermal rearrangement to give three products (5a, b, c). The 270-MHz ^1H n.m.r. spectrum of a mixture of these products obtained by heating compound (6) at 150 °C under reduced pressure for 6.5 h is shown in Figure 5. The presence of a ' triplet ' and three doubles of doublets in the $>NCH_3$ region of the spectrum indicates that two cyclotriphosphazadienes and the fully rearranged cyclotriphosphaz-1-ene are formed in this rearrangement reaction (Figure 6). A comparison of the ^1H n.m.r. spectra of the products obtained at 150 and 170 °C is informative. There is a considerable increase in the intensity of the ' triplet ' (δ 2.92) and the doublet of doublets (δ 3.09), and a comparable decrease in the intensity of the doublet of doublets at δ 2.87; the remaining multiplet (δ 2.99) remains virtually unchanged. These observations confirm that the signals at δ 2.92 and 3.09 arise from the fully rearranged product (6c). They strongly suggest that the signals at δ 2.87 should be assigned to compound (6a) in Figure 6 as this cyclotriphosphazadiene possesses a ring-nitrogen atom with minimal steric inhibition to further rearrangement. Moreover, it is reasonable to suppose that compound (6a)

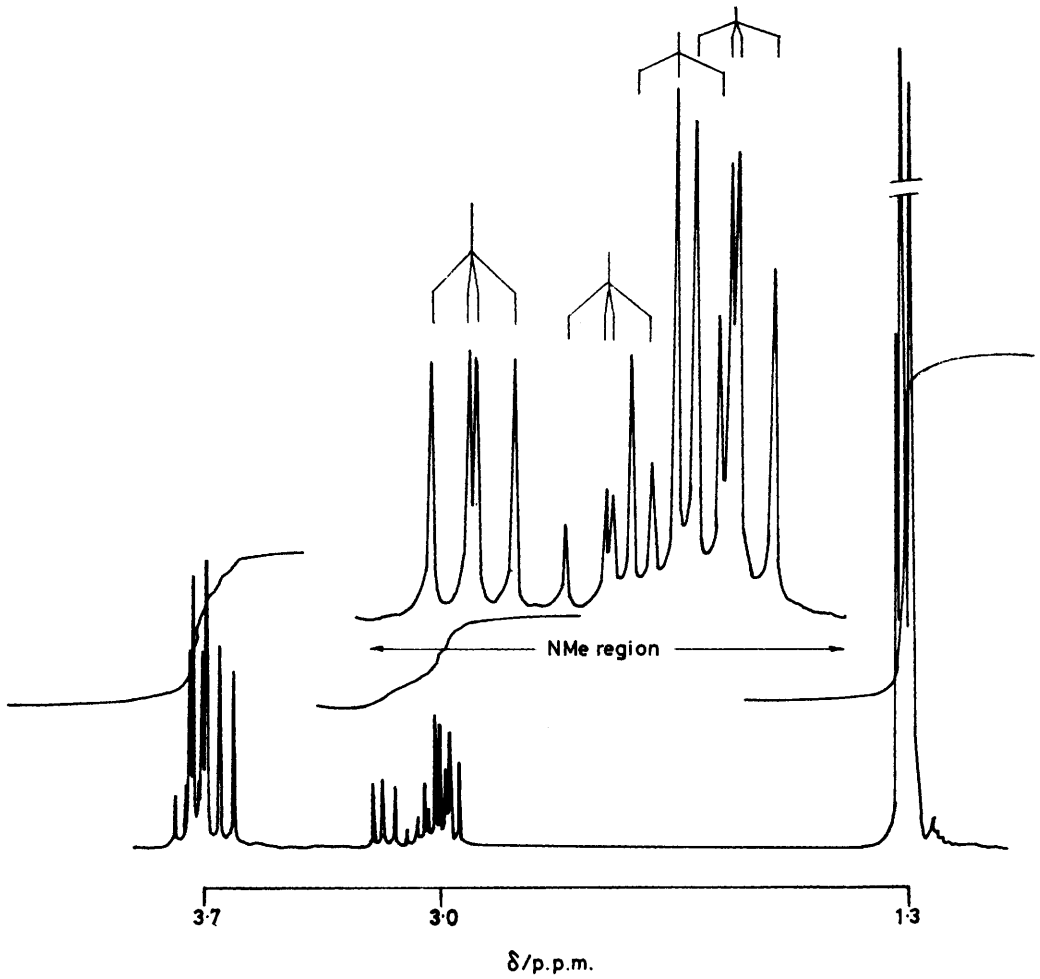


FIGURE 5 The ^1H n.m.r. spectrum (270 MHz, $CDCl_3$–D_2O) of the products (6a, b, c) obtained by heating $N_3P_3(NHBu^t)_2(OMe)_4$ (6) at 150 °C (1—2 mmHg) for 6.5 h

would be the major mono-rearranged product owing to the greater electron density at the ring-nitrogen atoms α to the $\equiv P(NHBu^t)_2$ group.

The ^1H n.m.r. spectrum of the mixture of compounds (6a,b,c) also contains five doublets in the $-OCH_3$ region [δ 3.61, 3.69, 3.71, 3.72, and 3.76; ^3J(P–H) 12.5, 11.8, 12.1, 12.1, and 13.2 Hz respectively]. The assignment of these doublets is unclear. The ^{31}P-{^1H} n.m.r. spectrum is very complex (*ca.* 40 lines from 17 to −9 p.p.m.) as anticipated for a mixture of three compounds, each of which possesses three non-equivalent phosphorus nuclei.

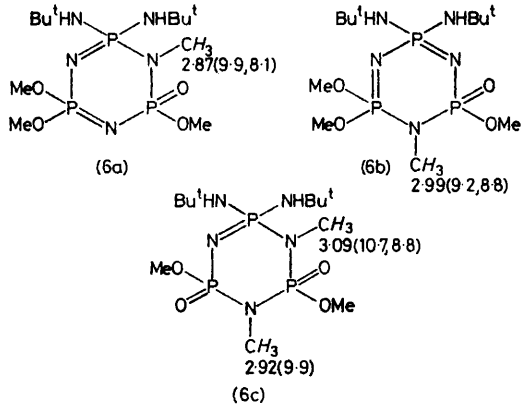
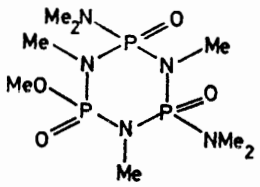


FIGURE 6 Structures of products (6a, b, c) with assignment of δ(NCH_3) (values in p.p.m.); ^3J(P–H) values (Hz) are given in parentheses

If the cyclophosphazene derivative *trans*-$N_3P_3(NMe_2)_2(OMe)_4$ (7) is heated at 170 °C (1—2 mmHg) for 4.5 h, the t.l.c. of the product shows the presence of starting compound and a small quantity of a very hygroscopic compound (7a) having a lower R_f value. The ^1H n.m.r. spectrum of (7a) consists of a broad signal (with some splitting) at *ca.* δ 2.6 (NCH_3) and a low-intensity doublet centred at δ 3.48 [$^3J^*$(P–H) 12.0 Hz] which arises from $-OCH_3$ protons. These two signals are in the ratio 7 : 1. There is also an intense singlet (δ 3.5) in the spectrum which may arise from the presence of occluded methylamine. The latter would be formed by hydrolysis of a rearranged product. The ^{31}P n.m.r. spectrum of product (7a) consists of a doublet [δ 9.6, $=P(NMe_2)O$] and a triplet [δ −5.9, $=PO(OMe)$] with ^2J(P–P) 17.7 Hz. In principle, nine rearranged pro-

ducts are possible from the thermolysis of *trans*-$N_3P_3(NMe_2)_2(OMe)_4$ (7) but only the fully rearranged product shown below is compatible with both the ^1H and ^{31}P n.m.r. data. In contrast, the cyclophosphazene, *trans*-



(7a)

2,4,6:2,4,6-$N_3P_3(NMe_2)_3(OMe)_3$ (8) does not rearrange even when heated at 200 °C under reduced pressure: the starting material is recovered quantitatively. This observation corroborates a previous report by Wende and Joel.[14]

Conclusions.—The methoxycyclophosphazenes $[NP(OMe)_2]_n$ (n = 3—6) (1)—(4) undergo thermal rearrangement to oxocyclophosphazanes. Analogous products are not obtained by heating the ethoxy- and n-propoxy-derivatives $N_3P_3(OR)_6$, R = Et or Pr^n; extensive decomposition occurs to give intractable resins. This difference in behaviour may be attributed to steric factors and implies the involvement of an intermolecular pathway [2] for the alkoxyphosphazene–oxophosphazane rearrangement. The geminal derivatives $N_3P_3R_2(OMe)_4$, R = Ph or $NHBu^t$, also rearrange on heating but in these examples both partially and fully rearranged products are obtained. The formation of the former (cyclophosphazadienes) has been convincingly established in such a thermal rearrangement reaction by 270-MHz ^1H n.m.r. spectroscopy. The results obtained here suggest that rearrangement reactions of methoxycyclophosphazenes containing different substituent groups will be controlled by a variable balance of electronic and steric effects associated with ring-nitrogen atoms.

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