Studies of Phosphazenes. Part 33.[1] Thermal Rearrangement of Alkoxy(*p*-methylphenoxy)cyclophosphazenes: A Synthetic Route to Oxocyclophosphazanes, Phosphazadienes and Phosphaz-1-enes†

Sakthivel Karthikeyan and Setharampattu S. Krishnamurthy*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

The aryloxy(alkoxy)cyclotriphosphazenes $N_3P_3(OR)_{6-m}(OC_6H_4Me\text{-}p)_m$ (R = Me, n = 1–3; R = Et or CH_2Ph, n = 3) rearrange on heating to give trioxocyclotriphosphazanes; the di- and mono-methoxy derivatives, $N_3P_3(OMe)_{6-n}(OC_6H_4Me\text{-}p)_n$($n$ = 4 or 5), yield dioxophosphaz-1-enes and an oxophosphazadiene respectively. The ^1H, ^{13}C and ^{31}P NMR data for the starting materials and the products are presented. No evidence has been found for partially rearranged products. The geometrical disposition of the aryloxy groups in the starting material is retained in the rearranged products. Some aspects of the mechanism of the thermal rearrangement are discussed.

We have earlier reported that thermolysis of the methoxy(aryloxy)cyclotriphosphazene derivatives *cis*- and *trans*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$ gives the respective *cis*- and *trans*-trioxo-*N*-methylcyclotriphosphazanes.[2] In this paper we elaborate this synthetic approach to obtain a range of trioxocyclotriphosphazanes and the mixed six-membered cyclic phosphazene–phosphazane derivatives from the thermolysis of a series of alkoxy(aryloxy)cyclotriphosphazenes $N_3P_3(OR)_{6-n}(OC_6H_4Me\text{-}p)_n$ (R = Me, n = 1–5; R = Et or CH_2Ph, n = 3). In contrast to the extensive literature available on cyclodiphosphazanes, cyclotriphosphazanes are sparsely investigated. Trioxocyclotriphosphazanes may be accessible from oxidation reactions of cyclotri-λ^3-phosphazanes but these reactions have not been explored in detail.[3] Recently, Murray and co-workers[4] reported the isolation of trioxo-*N*-arylcyclotriphosphazanes by a direct condensation reaction between $POCl_3$ and an aromatic primary amine hydrochloride.

Experimental

The chloro(*p*-methylphenoxy)cyclotriphosphazenes $N_3P_3Cl_{6-n}(OC_6H_4Me\text{-}p)_n$ (n = 1–5) were prepared by treating hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) with sodium *p*-methylphenoxide in tetrahydrofuran (thf) as described previously.[5] The chloro(aryloxy) derivatives were converted into the alkoxy(aryloxy) derivatives by treatment with an excess of sodium alkoxide in boiling thf. The preparative details are summarised in Table 1. A typical procedure is given below.

Preparation of $N_3P_3(OEt)_3(OC_6H_4Me\text{-}p)_3$ **7**.—A solution of sodium ethoxide (45 mmol), prepared from sodium metal (1.0 g) in absolute ethanol (75 cm^3), was added dropwise to a stirred solution of $N_3P_3Cl_3(OC_6H_4Me\text{-}p)_3$ (5.0 g, 9 mmol) in anhydrous thf (100 cm^3). The reaction mixture was heated under reflux for 36 h. A TLC examination showed the absence of the starting material. Solvent was removed under reduced pressure and the residue dissolved in benzene–Et_2O (1:1, 200 cm^3). The solution was filtered to remove sodium chloride; the filtrate was washed successively with a 5% NaOH solution (1 × 50 cm^3), 0.2 mol dm^{-3} HCl (1 × 50 cm^3), and water (2 × 50 cm^3) and dried over anhydrous Na_2SO_4. Solvent was evaporated from the solution to obtain $N_3P_3(OEt)_3(OC_6H_4Me\text{-}p)_3$ **7** as a colourless oil (4.1 g, 79%). ^1H NMR: δ 3.80 (OCH_2), 1.20 (CH_3) and 2.30 ($p\text{-}CH_3$).

Sodium hydride was used instead of sodium metal for the preparation of sodium benzyl oxide. The methoxy(*p*-methylphenoxy)cyclotriphosphazenes were isolated by filtering the reaction mixtures through a silica gel column intead of the work-up procedure described above.

Fractional crystallisation was effective in the separation of *trans*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$ **5** from its *cis* and *gem* isomers. The residual mixture (enriched in *cis* and *gem* isomers) was subjected to multiple development preparative TLC over silica gel using benzene as the eluent to isolate pure *cis*- and *gem*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$, **4** and **6**. Column chromatography over silica gel was employed to separate the isomers of other methoxy(*p*-methylphenoxy) derivatives. The yields of geminal isomers were very low. In particular, the *gem*-$N_3P_3(OMe)_4(OC_6H_4Me\text{-}p)_2$ was only detected by ^1H NMR spectroscopy; it could not be isolated in a pure state. No attempt was made to separate the isomers of ethoxy and benzyloxy derivatives **7** and **8**. The details of the chromatographic separations are given in Table 1.

Thermal Rearrangement of Alkoxy(p-*methylphenoxy*)*cyclotriphosphazenes* **1–11**.—Alkoxy(*p*-methylphenoxy)cyclotriphosphazenes **1–11** were subjected to thermal rearrangement under reduced pressure either in a sealed tube or under continuous pumping using a rotary pump.[2,6] The experimental details are given in Table 2.

Analytical and Spectroscopic Measurements.—The analytical data for alkoxy(*p*-methylphenoxy)cyclotriphosphazenes **1–11** and their rearranged *N*-alkyl(*p*-methylphenoxy)oxocyclophosphazanes **12–21** are given in Table 3. Details of ^1H, ^{13}C and ^{31}P NMR spectroscopic measurements were described previously.[2,6] The data are summarised in Tables 4–6 and also Fig. 1.

Results and Discussion

Alkoxy(p-*methylphenoxy*)*cyclotriphosphazenes: Synthesis and NMR Spectra*.—The alkoxy(*p*-methylphenoxy)cyclotriphosphazenes $N_3P_3(OR)_n(OC_6H_4Me\text{-}p)_{6-n}$ (n = 1–5, R = Me; n = 3, R = Et or CH_2Ph) have been obtained by treatment of

† *Non-SI unit employed*: Torr ≈ 133 Pa.

Table 1 Experimental details of the preparation of alkoxy(*p*-methylphenoxy)cyclotriphosphazenes[a]

Reaction	Chloro precursor			Sodium metal		Reaction time/h	Product	TLC R_f	Yield[b]	
		g	mmol	g	mmol				g	%
(1)	$N_3P_3Cl_5(OC_6H_4Me\text{-}p)$	10.0	24	3.8	167	26	**1**	0.72[c]	7.6.	80
(2)	$N_3P_3Cl_4(OC_6H_4Me\text{-}p)_2$	10.0	20	2.8	122	28	**2**	0.55[c]	7.5	79
							3	0.58[c]		
(3)	$N_3P_3Cl_3(OC_6H_4Me\text{-}p)_3$	10.0	18	2.0	89	24	**4**	0.22[d]		
							5	0.28[d]	7.9	82
							6	0.25[d]		
(4)	$N_3P_3Cl_3(OC_6H_4Me\text{-}p)_3$	5.0	9	1.0	45	36	**7**	0.62[d]	4.1	79
(5)	$N_3P_3Cl_3(OC_6H_4Me\text{-}p)_3$	5.0	9	1.3[e]	53	25	**8**	0.45[d]	5.8	84
(6)	$N_3P_3Cl_2(OC_6H_4Me\text{-}p)_4$	10.0	16	1.5	63	20	**9**	0.41[d]	7.3	77
							10	0.43[d]		
(7)	$N_3P_3Cl(OC_6H_4Me\text{-}p)_5$	10.0	14	0.7	28	24	**11**	0.67[d]	7.9	80

[a] An excess of alcohol [50 cm^3 methanol in reactions (1)–(3), (6) and (7); 50 cm^3 ethanol in (4); 6.7 g benzyl alcohol in (5)] was used. Solvent: boiling thf (250 cm^3). [b] Separation of isomers effected by column chromatography or preparative-scale TLC over silica gel (see text). [c] Eluent: benzene–acetone (1:1). [d] Eluent: benzene. [e] Sodium hydride was used instead of sodium metal.

Table 2 Experimental details of the thermal rearrangement reactions of alkoxy (*p*-methylphenoxy)cyclotriphosphazenes

Reaction	Alkoxy derivative	Amount /mg	Temperature[a] /°C	Time /h	Product	Yield[b] (%)
1	**1**	500	160[c]	2.0	**12**	95[d]
2	**1**	500	160	2.0	**12**	100
3	**2**	250	165	4.0	**13**	95[d]
4	**3**	250	165	4.0	**14**	95[d]
5	**4**	200	185	5.0	**15**	100
6	**5**	200	180	5.0	**16**	95[e]
7	**5**	200	185	5.0	**16**	100
8	**6**	150	185	5.0	*f*	95[d]
9	**7**	200	285	5.0	**17**	90[e]
10	**8**	250	185	5.0	**18**	100
11	**9**	200	190	4.0	**19**	95[d]
12	**10**	200	190	4.0	**20**	95[d]
13	**11**	200	205	5.5	**21**	90[d]
14	**5** + **8**[g]	300	185	5.0	**22**[h]	100

[a] Variation in temperature ±5 °C; reactions carried out in a sealed tube evacuated to 0.1 Torr before being sealed. [b] Based on ^1H NMR data. [c] Carried out under continuous pumping at 0.5 Torr. [d] Remainder is insoluble material. [e] Remainder is starting material. [f] A complex mixture of fully and partially rearranged products (NMR evidence). [g] A 1:1 mixture. [h] A mixture of fully rearranged products (see Fig. 5).

Table 3 Analytical data (calculated values in parentheses) for alkoxy(*p*-methylphenoxy)cyclotriphosphazenes and *N*-alkyl(*p*-methylphenoxy)cyclophosphazanes

Compound		M.p./°C	Analysis (%) C		H	
1	$N_3P_3(OMe)_5(OC_6H_4Me\text{-}p)$	Liquid	36.20	(36.25)	5.95	(5.55)
2	*cis*-$N_3P_3(OMe)_4(OC_6H_4Me\text{-}p)_2$	Liquid	45.10	(45.65)	6.15	(5.50)
3	*trans*-$N_3P_3(OMe)_4(OC_6H_4Me\text{-}p)_2$	60	45.65	(45.65)	5.85	(5.50)
4	*cis*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$	Liquid	51.95	(52.45)	6.00	(5.45)
5	*trans*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$	87	52.40	(52.45)	5.75	(5.45)
6	*gem*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$	Liquid	51.75	(52.45)	6.05	(5.45)
7	$N_3P_3(OEt)_3(OC_6H_4Me\text{-}p)_3$	Liquid	54.00	(54.80)	6.20	(6.10)
8	$N_3P_3(OCH_2Ph)_3(OC_6H_4Me\text{-}p)_3$	100	64.40	(64.85)	5.90	(5.40)
9	*cis*-$N_3P_3(OMe)_2(OC_6H_4Me\text{-}p)_4$	83	57.70	(57.60)	5.85	(5.45)
10	*trans*-$N_3P_3(OMe)_2(OC_6H_4Me\text{-}p)_4$	Liquid	58.15	(57.60)	5.75	(5.45)
11	$N_3P_3(OMe)(OC_6H_4Me\text{-}p)_5$	80	61.45	(61.65)	5.90	(5.40)
12	$N_3Me_3P_3O_3(OMe)_2(OC_6H_4Me\text{-}p)$	Liquid	35.85	(36.25)	6.05	(5.55)
13	*cis*-$N_3Me_3P_3O_3(OMe)(OC_6H_4Me\text{-}p)_2$	Liquid	44.80	(45.65)	6.10	(5.50)
14	*trans*-$N_3Me_3P_3O_3(OMe)(OC_6H_4Me\text{-}p)_2$	Liquid	44.85	(45.65)	5.75	(5.50)
15	*cis*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$	101	52.00	(52.45)	5.95	(5.45)
16	*trans*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$	117	52.20	(52.45)	5.70	(5.45)
17	$N_3Et_3P_3O_3(OC_6H_4Me\text{-}p)_3$	Liquid	53.80	(54.80)	7.75	(6.10)
18	$N_3(CH_2Ph)_3P_3O_3(OC_6H_4Me\text{-}p)_3$	Liquid	64.15	(64.85)	5.85	(5.40)
19	*cis*-$N_3Me_2P_3O_2(OC_6H_4Me\text{-}p)_4$	Liquid	56.45	(57.60)	5.90	(5.45)
20	*trans*-$N_3Me_2P_3O_2(OC_6H_4Me\text{-}p)_4$	Liquid	56.50	(57.60)	5.95	(5.45)
21	$N_3MeP_3O(OC_6H_4Me\text{-}p)_5$	Liquid	60.10	(61.65)	5.90	(5.40)

chloro precursors with the respective alkoxides. The geometrical and positional isomers of $N_3P_3(OMe)_n(OC_6H_4Me\text{-}p)_{6-n}$ (n = 2–4) were separated by column chromatography or TLC over silica gel. The yields of the pure compounds are low mainly

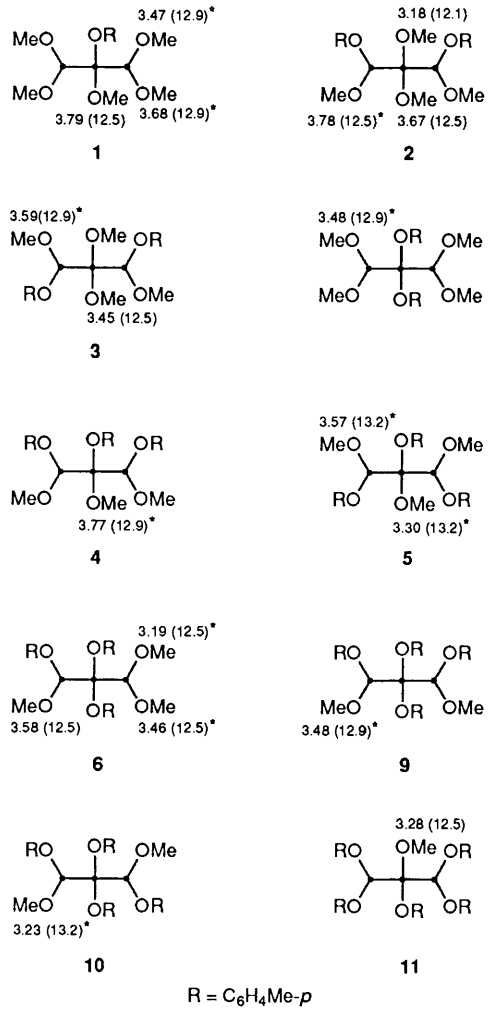

Fig. 1 Proton NMR data (OCH_3 chemical shifts) for methoxy (*p*-methylphenoxy)cyclotriphosphazenes **1–6** and **9–11**; $^3J_{PH}$ values are shown in parentheses. Signals marked * show virtual coupling. The three ring phosphorus atoms are projected on the plane of the paper with the substituents lying above and below this plane.

owing to the closeness of the R_f values of the isomers and partly as a result of hydrolytic decomposition of the alkoxy-(aryloxy)phosphazenes on the column. The elution sequence of the positional and geometrical isomers is found to be $R_f(trans) > R_f(gem) > R_f(cis)$. This sequence may be compared with that observed for aminocyclotriphosphazenes, *viz.* $R_f(trans) > R_f(cis) > R_f(gem)$.[7]

The structures of the methoxy(*p*-methylphenoxy)cyclotriphosphazenes **1–6** and **9–11** have been established from their ^1H NMR spectroscopic data which are summarised in Fig. 1. The spectral patterns are almost the same as those of the corresponding dimethylamino derivatives, $N_3P_3(NMe_2)_n(OC_6H_4Me\text{-}p)_{6-n}$ (n = 1–5);[5] however the $^3J_{PH}$ values for the methoxy derivatives do not follow the trend observed for the dimethylamino derivatives. The $^3J_{PH}$ values for the methoxy derivatives **1–6** and **9–11** are higher than those for the corresponding dimethylamino derivatives; the benzyloxy derivative **8** [δ_{CH_2} = 4.98 (*cis* isomer); 4.75, 4.51 (*trans* isomer)] on the other hand shows a low $^3J_{PH}$ value (7–8 Hz). The $^{13}C\text{-}\{^1H\}$ NMR data for the alkoxy(*p*-methylphenoxy)cyclotriphosphazenes (Table 5) support the structures assigned on the basis of ^1H NMR data. The $^2J_{PC}$ value associated with the alkoxy group decreases with increasing number of *p*-methylphenoxy groups. This coupling is not observed for several compounds (Table 5) and the reasons for this are not clear.

The phosphorus-31 chemical shifts of the methoxy(*p*-methylphenoxy)cyclotriphosphazenes **1–6** and **9–11** move slightly downfield as the number of aryloxy groups increases. However, the $^2J_{PP}$ value does not vary significantly throughout the series (Table 6). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of *gem*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$ **6** is that of an ABC spin system and its analysis has been carried out by iterative computation.[8] The three phosphorus–phosphorus couplings lie in a narrow range (84–88 Hz) but follow the order ^2J[P(OR)(OMe)–P(OR)$_2$] > ^2J[P(OMe)$_2$–P(OR)$_2$] > ^2J[P(OMe)$_2$–P(OMe)(OR)] [R = $C_6H_4Me\text{-}p$].

N-*Alkyl*(p-*methylphenoxy*)*oxocyclophosphazanes: Synthetic and NMR Spectroscopic Studies.*—Thermolysis of alkoxy(*p*-methylphenoxy)cyclotriphospha*zenes* leads to a rearrangement to *N*-alkyl(oxo)cyclophospha*zanes*, in which a geminal $\equiv P(OC_6H_4Me\text{-}p)_2$ centre is retained. An increase in the number of aryloxy groups or a lengthening of the alkyl chain (R = Me to Et) results in an increase in the rearrangement temperature (Table 2). The geometric disposition of the aryloxy groups in the starting material is retained in the rearranged products. All oxocyclophosphazanes are moisture-sensitive; exposure of these products to atmospheric moisture even for a short time leads to hydrolytic ring cleavage and formation of phosphonic acids and alkylamines (^1H and ^{31}P NMR evidence).

In analogy with cyclohexane derivatives, cyclotriphosphazanes may be represented as having either a chair or a boat type of conformation. Crystallographic investigations on *trans*-$N_3Me_3P_3O_3(OR)_3$ (R = Me[9] or $C_6H_4Me\text{-}p$[2]) and *trans*-$N_3Ph_3P_3O_3Cl_3$[4] show that the N_3P_3 ring adopts a twist-boat conformation. Recently Murray and Woodward[10] reported that the N_3P_3 ring in *cis*-$N_3Ph_3P_3O_3Cl_3$ is flat. It is not yet clear how general this result is. On the basis of NMR data we had earlier proposed a chair conformation for the N_3P_3 ring in *cis*-$N_3Me_3P_3O_3(OC_6H_4Me\text{-}p)_3$.[2] On steric grounds a chair conformation is more likely than a planar arrangement when bulky substituents are attached to the phosphorus centres. Hess and Zeiss[11] reported that the symmetrical isomer of the cyclotri-λ^3-phosphazane $[MeNP(OC_6H_4Br\text{-}p)]_3$ has a chair conformation with the *p*-bromophenoxy groups occupying the axial positions. In the absence of any other evidence, we assume that the N_3P_3 ring in *cis*-oxocyclotriphosphazanes adopts a chair conformation. The NMR data for the mixed phospha*zene*–phospha*zane* derivatives (Tables 4–6) can also be interpreted on the above basis, *viz.* products derived from *cis*-(aryloxy)cyclotriphosphazene precursors have a chair conformation of the ring whereas those derived from *trans*-(aryloxy)cyclotriphosphazenes have a boat conformation. The NMR data for the *cis* isomers would also be consistent with a planar ring. The structures proposed for all the rearranged N-methyl derivatives are shown in Fig. 2 and the spectroscopic data in support of these structures are discussed below.

$N_3Me_3P_3O_3(OMe)_2(OC_6H_4Me\text{-}p)$ **12**. Thermal rearrangement of the hexamethoxy derivative $N_3P_3(OMe)_6$ gives *trans*-$N_3Me_3P_3O_3(OMe)_3$;[9,12] although the formation of a *cis* isomer has been reported, it has not been adequately characterised.[13–15] However, $N_3P_3(OMe)_5(OC_6H_4Me\text{-}p)$ **1**, upon thermal rearrangement yields an isomeric pair of oxocyclotriphosphazanes, $N_3Me_3P_3O_3(OMe)_2(OC_6H_4Me\text{-}p)$ **12**, as indicated by the ^1H and ^{13}C NMR spectra of the product (Fig. 3, Tables 4 and 5). The two isomers are formed in the ratio 3:2. A *trans* configuration of phosphoryl groups is proposed for the more-abundant isomer **12b** and a *cis* configuration for the less-abundant isomer **12a** based on the NMR data. The signals arising from the NCH_3 protons of **12b** lie in between those arising from **12a** in both the ^1H and ^{13}C NMR spectra. Presumably the NCH_3 protons of the *cis* isomer experience more shielding and deshielding by the phosphoryl and/or the aryl groups than do those of the *trans* isomer. The protons of the two OCH_3 groups in each of the isomers are magnetically equivalent; accordingly, a doublet is observed for each isomer (Fig. 3). The ^{31}P NMR spectrum of isomer **12b** is of an AMX type; the *cis* isomer **12a** exhibits an ABX spin pattern. The

Table 4 Proton NMR data for *N*-alkyl(oxo)cyclophosphazanes[a]

Compound	δ(OMe)	^3J(PH)/Hz	δ(NMe)	^3J(PH)/Hz	δ(CH_3-*p*)
12a[b]	3.62	12.1	3.26[1]	9.7	2.33
			3.02[2]	9.9	
12b[c]	3.84	12.1	3.17[1]	11.0	2.33
			3.09[2]	10.1	
13	3.78	12.1	3.08[2]	10.1	2.22
			3.06[1]	9.7	
14	3.62	12.1	3.31[1]	9.6	2.33[1]
			3.09[1]	10.1	2.32[1]
			3.07[1]	10.1	
15	—	—	3.21	9.9	2.30
16	—	—	3.27[1]	9.7	2.32[1]
			3.14[2]	10.1	2.30[2]
17	—	—	2.80[d,e]	*f*	2.24[1]
					2.20[2]
18a[b]	—	—	4.76[d]	14.2	2.29
18b[c]	—	—	4.87[1,d]	14.0	2.24
			4.75[2,d]	14.6	
19	—	—	3.21[1]	10.1	2.33[2]
			2.99[1,g]	10.9,	2.30[1]
				9.0	2.26[1]
20	—	—	3.28[1]	10.1	2.28[1]
			2.90[1,g]	10.9,	2.27[2]
				9.4	2.24[1]
21	—	—	3.22[g]	10.5,	2.29[3]
				8.3	2.26[2]
22	—	—	4.72[2]	*f*	2.25
			3.20[3]	*f*	

[a] Superscripts denote relative intensities. [b] *cis* isomer. [c] *trans* isomer. [d] NCH_2 protons. [e] A complex multiplet is observed at δ 1.2 for NCH_2CH_3 protons. [f] Complex multiplet, $^3J_{PH}$ could not be determined. [g] Doublet of doublets.

phosphorus nuclei of the PO(OMe) groups resonate downfield compared to that of the PO(OC_6H_4Me-*p*) group.

$N_3Me_3P_3O_3$(OMe)(OC_6H_4Me-*p*)$_2$, **13** *and* **14**. The thermal rearrangement of *cis* **2** and *trans* **3** isomers of N_3P_3(OMe)$_4$(OC_6H_4Me-*p*)$_2$ yields the respective *cis* **13** and *trans* **14** isomers of $N_3Me_3P_3O_3$(OMe)(OC_6H_4Me-*p*)$_2$. The ^{1}H NMR spectrum of isomer **13** (Fig. 4) shows two partially overlapping triplets at δ 3.08 and 3.06 (intensity ratio 2:1) for the NCH_3 protons. The protons of the two NCH_3 groups flanking the PO(OC_6H_4Me-*p*) and PO(OMe) groups (Fig. 4) are magnetically equivalent and resonate downfield of the region associated with the protons of the remaining NCH_3 group. The ^{1}H NMR spectrum of the *trans* isomer **14** (also illustrated in Fig. 4) shows three triplets for the NCH_3 protons. The protons of the two NCH_3 groups that flank the PO(OC_6H_4Me-*p*) and PO(OMe) groups [Me(2) and Me(3) in Fig. 4] are nearly equivalent and their signals appear upfield of those arising from the remaining NCH_3 protons. The non-equivalence of the NMe groups is corroborated by ^{13}C NMR data (Table 5).

The ^{31}P NMR spectrum of the *cis* isomer **13** shows a simple AX_2 pattern whereas a more complex ABX pattern is observed for the *trans* isomer **14**. The ^{31}P nucleus of the PO(OMe) group is deshielded compared to the ^{31}P nuclei of the two PO(OC_6H_4Me-*p*) groups for both the isomers; however, this deshielding is more pronounced for the *cis* isomer **13**.

$N_3Me_3P_3O_3$(OC_6H_4Me-*p*)$_3$, **15** *and* **16**. We have earlier reported that the thermolysis of the *cis* or *trans* isomer of N_3P_3(OMe)$_3$(OC_6H_4Me-*p*)$_3$, **4** or **5**, yields the respective isomeric trioxocyclotriphosphazanes $N_3Me_3P_3O_3$(OC_6H_4Me-*p*)$_3$, **15** and **16**. In the same paper we discussed the assignments of the NMR (^{1}H and ^{13}C) signals on the basis of the X-ray crystal structure of the *trans* isomer **16**.[2] In contrast to the behaviour of isomers **4** and **5**, the *geminal* isomer **6** gives a complex mixture of products (NMR evidence) when subjected to thermal rearrangement.

$N_3Et_3P_3O_3$(OC_6H_4Me-*p*)$_3$ **17** *and* $N_3(CH_2Ph)_3P_3O_3$-(OC_6H_4Me-*p*)$_3$ **18**. The thermal rearrangement reaction of N_3P_3(OR)$_3$(OC_6H_4Me-*p*)$_3$ (R = Et **7** or CH_2Ph **8**) (in each case a 1:5 *cis*–*trans* mixture) affords the N-ethyl, **17a** and **17b** and N-benzyl, **18a** and **18b**, cyclotriphosphazanes, $N_3R_3P_3$-O_3(OC_6H_4Me-*p*)$_3$ (R = Et or CH_2Ph), as an isomeric mixture in each case. The NMR spectroscopic features of the N-benzyl derivatives are similar to those of the analogous N-methyl derivatives, **15** and **16** (Tables 4–6), suggesting that they have similar structures in solution. Proton NMR spectroscopy is less informative for the N-ethyl derivatives as only broad signals are observed for the CH_2 and CH_3 protons. The ^{13}C NMR spectrum shows two resonances at δ 46.1 and 41.8 (relative intensities 1:2) for the N–$^{13}CH_2$ carbon nuclei attributable to the *trans* isomer **17b**. The $^{13}CH_3$ resonances appear at δ 10.9 and 8.6 (relative intensities 2:1); the intensity pattern is thus the reverse of that found for the $^{13}CH_2$ resonances. The signals arising from the *cis* isomer **17a** are presumably buried underneath those of the *trans* isomer **17b**.

cis- and trans-$N_3Me_2P_3O_2$(OC_6H_4Me-*p*)$_4$, **19** *and* **20**. The isomeric configurations are retained in the thermal rearrangement reactions of *cis*- and *trans*-N_3P_3(OMe)$_2$(OC_6H_4Me-*p*)$_4$ to afford the dioxophosphaz-1-enes **19** and **20**. The ^{1}H NMR spectrum of **19** as well as that of **20** shows a triplet for the protons of the NCH_3 groups flanked by the two PO(OC_6H_4Me-*p*) groups and a doublet of doublets for the protons of the remaining NCH_3 group which is flanked by P(OC_6H_4Me-*p*)$_2$ and PO(OC_6H_4Me-*p*) moieties. The signals due to the non-equivalent *p*-CH_3 groups on the aryl rings are well resolved in the spectra of both isomers.

The ^{13}C NMR spectrum of the *cis* isomer **19** shows two singlets for the N–$^{13}CH_3$ groups; on the other hand only a single line is observed for the N–$^{13}CH_3$ groups for the *trans* isomer **20**. A possible explanation for the accidental coincidence of the chemical shifts of the two non-equivalent N–$^{13}CH_3$ carbon-13 nuclei is that whereas the protons of the NCH_3 groups are influenced by the magnetic anisotropy of the phosphoryl group, the ^{13}C nuclei are far less affected. The 'ring current' associated with the phenyl ring may also contribute to the accidental equivalence of the ^{13}C nuclei. The ^{31}P NMR spectra of both isomers **19** and **20** are of the ABX type; of the

Table 5 ^{13}C-{^1H} NMR data for alkoxy (*p*-methylphenoxy)cyclotriphosphazenes and *N*-alkyl(oxo)cyclophosphazanes[a]

Compound	δ(OMe)	^2J(PC)/Hz	δ(NMe)	δ(CH_3-*p*)
1	53.1[1]	6.3	—	20.7
	52.6[4]	—		
2	53.1[2]	—	—	20.7
	52.7[1]	5.0		
	52.4[1]	5.2		
3	53.0[1]	—	—	20.7
	52.6[1]	4.8		
4	53.1	—	—	20.7
5	53.0[2]	—	—	20.7
	52.8[1]	—		
6	53.0[1]	4.2	—	20.7
	52.6[1]	6.2		
	52.4[1]	6.3		
7a[b]	62.5[c]	—	—	20.7
				15.9[d]
7b[e]	62.4[2,c]	—	—	20.7
	62.1[1,c]	—		15.9[d]
8a[b]	68.1[c]	—	—	20.7
8b[e]	67.8[2,c]	—	—	20.7
	67.5[1,c]	—		
9	53.0	—	—	20.7
10	52.8	—	—	20.7
11	52.8	4.2	—	20.7
12a[b]	53.7	6.3	33.9[1]	20.7
			31.3[2]	
12b[e]	53.9	6.3	33.7[1]	20.7
			31.5[2]	
13	53.8	6.0	31.8[2]	20.7
			31.6[1]	
14	53.0	5.5	33.0[1]	19.70[1]
			30.51[1]	19.67[1]
			30.45[1]	
15	—	—	32.6	20.7
16	—	—	33.8[1]	20.7
			31.8[2]	
17b[e]	—	—	46.1[1,f]	20.7
			41.8[2,f]	10.9[2,g]
				8.6[1,g]
18a[b]	—	—	50.8[f]	20.6
18b[e]	—	—	51.4[1,f]	20.6
			49.9[2,f]	
19	—	—	32.5[1]	20.7
			31.3[1]	
20	—	—	31.1	20.7
21	—	—	30.0	20.7

[a] Superscripts indicate the relative intensities. [b] *cis* Isomer. [c] Signal assigned to OCH_2 carbon. [d] Signal assigned to OCH_2CH_3 carbon. [e] *trans* isomer. [f] Signal assigned to the NCH_2 carbon. [g] Signal assigned to the NCH_2CH_3 carbon.

three types of phosphorus nuclei, the $P(OC_6H_4Me\text{-}p)_2$ phosphorus is the most deshielded.

$N_3MeP_3O(OC_6H_4Me\text{-}p)_5$ **21**. The compound **21**, a mono(oxo)phosphazadiene, is obtained from the thermal rearrangement of the mono(methoxy)cyclotriphosphazene $N_3P_3(OMe)(OC_6H_4Me\text{-}p)_5$ **11**; a small amount (<5%) of a ring-degraded material is also formed in this reaction. The formation of **21** is clearly shown by the appearance of a doublet of doublets at δ 3.22 in the ^1H NMR spectrum and a singlet at δ 30.0 in the ^{13}C NMR spectrum which are assigned to the lone $N\text{–}^{13}CH_3$ group. The ^{31}P NMR spectrum is of the ABX type and is consistent with the oxophosphazadiene structure of **21**. The $^2J_{PP}$ values across the formal P–N double bonds (49 Hz) are only slightly higher than the other $^2J_{PP}$ coupling (46 Hz) involving a formal P–N single bond. In general, P–P coupling constants decrease as the formal unsaturation within the P–N ring decreases (Table 6).

Mechanistic Aspects.—Both inter- and intra-molecular mech-

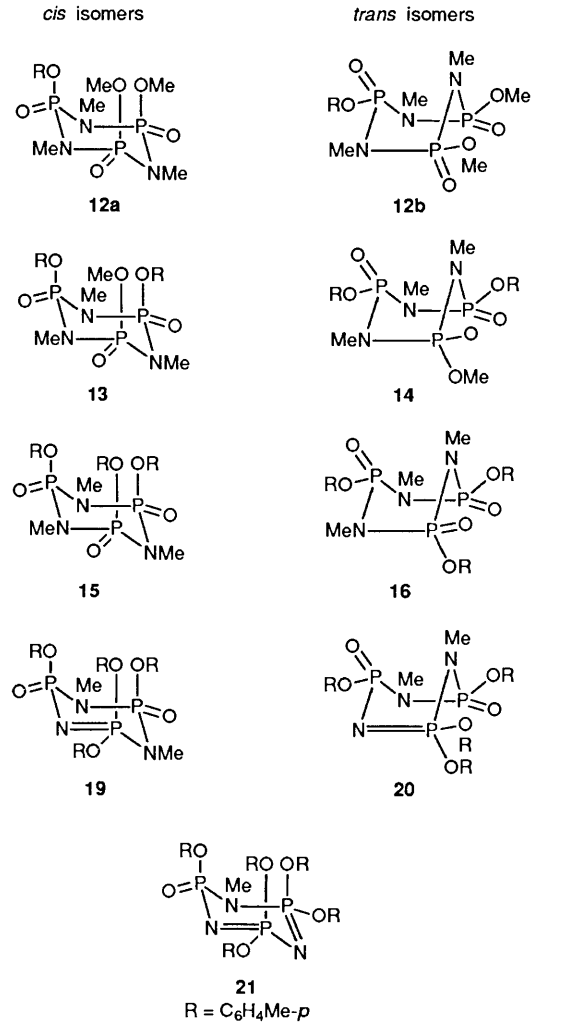

Fig. 2 Structures proposed for *N*-methyloxocyclophosphazanes

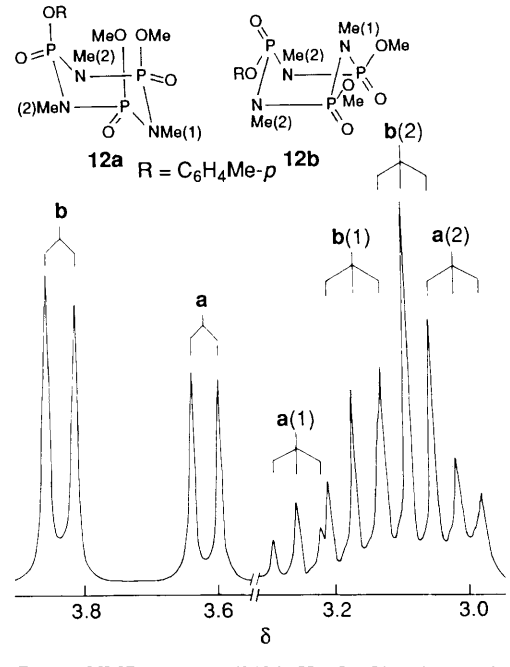

Fig. 3 Proton NMR spectrum (270 MHz, $CDCl_3$ solvent) of a mixture of *cis*- and *trans*-$N_3Me_3P_3O_3(OMe)_2(OC_6H_4Me\text{-}p)$, **12a** and **12b** ($OCH_3$ and NCH_3 regions only). The numbers in parentheses represent the assignment of the different NCH_3 resonances.

Table 6 ^{31}P-{^1H} NMR data for alkoxy(*p*-methylphenoxy)cyclotriphosphazenes and *N*-alkyl(oxo)cyclophosphazanes[a]

Compound	δ[P(OR′)$_2$]	δ[P(OR′)(OR)]	δ[P(OR)$_2$]	δ[PO(OR)]	δ[PO(OR′)]	^2J(PP)/Hz
1	—	15.5	19.7	—	—	84.2
2	—	14.7	18.7	—	—	85.2
3	—	14.7	18.8	—	—	84.3
4	—	14.1	—	—	—	—
5	—	14.3	—	—	—	—
6	9.9(A)	14.5(B)	18.7(C)	—	—	84.0(BC) 85.2(AC) 88.4(AB)
7a[b]	—	12.7	—	—	—	—
7b[c]	—	12.9	—	—	—	—
8a[b]	—	13.0	—	—	—	—
8b[c]	—	13.3	—	—	—	—
9	9.4	14.0	—	—	—	87.3
10	9.5	14.2	—	—	—	87.0
11	8.7	13.3	—	—	—	87.2
12a[b]	—	—	—	5.0[1,d](A) 4.8[1,d](B)	0.6[d](X)	—
12b[c]	—	—	—	9.5[1](A) 6.2[1](M)	1.4(X)	24.0(AM) 24.0(MX) 24.0(AX)
13	—	—	—	8.1	0.2	23.4
14	—	—		4.7(A)	3.6(B) −0.2(X)	25.3(AB) 12.6(AX) 24.5(BX)
15	—	—	—	—	−1.1	—
16	—	—	—	—	2.6[1] −0.9[2]	22.7
18a[b]	—	—	—	—	−0.5	—
18b[c]	—	—	—	—	3.7[1] −0.4[2]	23.7
19	5.1(X)	—	—	—	−9.9[1](A) −6.5[1](B)	68.7(AB) 20.5(AX) 38.1(BX)
20	5.1(X)	—	—	—	−10.3[1](A) −6.2[1](B)	51.9(AB) 26.8(AX) 41.0(BX)
21	7.2[1](A) 3.6[1](B)	—	—	—	−4.7(X)	49.5(AB) 49.0(AX) 45.8(BX)

[a] Superscripts indicate the relative intensities; R = Me, R′ = OC_6H_4Me-*p*. [b] *cis* Isomer. [c] *trans* Isomer. [d] Centre of complex multiplets.

anisms have been proposed for the thermal rearrangement of alkoxycyclotriphosphazenes.[12] Evidence in favour of the intermolecular mechanism has been obtained from the thermal rearrangement of a mixture of $N_3P_3(OMe)_6$ and its deuteriated analogue $N_3P_3(OCD_3)_6$.[15] The derivative $N_3P_3(OMe)_6$ undergoes rearrangement when heated at 150 °C. For the series of methoxy(*p*-methylphenoxy) derivatives $N_3P_3(OMe)_n(OC_6H_4Me\text{-}p)_{6-n}$ (n = 1–5) an increase of 10 °C in the rearrangement temperature is observed upon the introduction of each aryloxy group. This observation is again consistent with an intermolecular mechanism for the rearrangement. In order to gain further insight into the mechanistic aspects of this rearrangement reaction, the thermolysis of a 1:1 mixture of *trans*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$ **5** and $N_3P_3(OCH_2Ph)_3(OC_6H_4Me\text{-}p)_3$ (*cis*:*trans* = 1:5) **8** has been studied. This system was chosen because both the cyclotriphosphazenes **5** and **8** undergo rearrangement at almost the same temperature (*ca.* 185 °C). If the rearrangement were to occur entirely by an *intramolecular* mechanism no interchange of substituents would be expected in the products; in such a case only the unscrambled products **16** and **18** would be formed (Fig. 5). On the other hand, in an *intermolecular* process the probability of obtaining scrambled products would be high compared to the individual unscrambled products **16** and **18**. Both scrambled, **22**, and unscrambled products are obtained in this experiment and the relative yields of the three products **16**, **18** and **22** are nearly equal as shown by ^1H NMR spectroscopy. This ratio of the scrambled and unscrambled products cannot be explained solely on the basis of an intermolecular mechanism; an intramolecular mechanism is also probably involved.

In the thermal rearrangement reactions of all non-geminal alkoxy(*p*-methylphenoxy)cyclotriphosphazenes no partially rearranged products are detected by NMR spectroscopy. The first stage of the rearrangement appears to be much slower compared to the subsequent stages. Even in a few incomplete reactions only the fully rearranged product and the starting material could be detected. These results can be explained by assuming that the first stage of the thermal rearrangement proceeds by a slow intermolecular pathway whilst the subsequent stages involve a relatively faster intramolecular mechanism.

In an earlier study it was shown that methoxycyclotriphosphazenes $N_3P_3R_2(OMe)_4$ (R = Ph or NHBu^t) containing a geminally substituted PR_2 centre undergo thermolysis to yield both partially and fully rearranged products whereas the non-geminally substituted bis(dimethylamino) derivative *trans*-$N_3P_3(NMe_2)_2(OMe)_4$ gives only the fully rearranged product.[6] We find in the present study that methoxy(*p*-methylphenoxy) cyclophosphazenes except *gem*-$N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$ do not give any partially rearranged products. The reasons for these differences are not clear.

Conclusions

Controlled thermolysis of alkoxycyclophosphazenes containing other substituents such as aryloxy, aryl or alkylamino groups

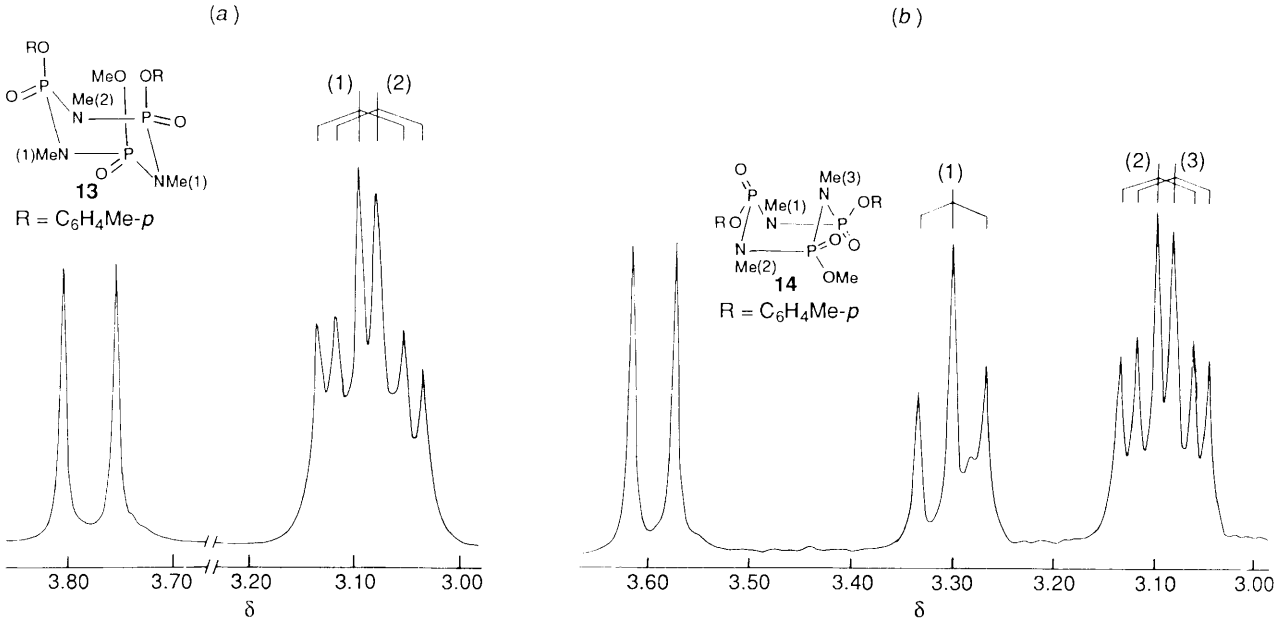

Fig. 4 Proton NMR spectra (270 MHz, $CDCl_3$ solvent) of (*a*) *cis*-$N_3Me_3P_3O_3(OMe)(OC_6H_4Me\text{-}p)_2$ **13** and (*b*) *trans*-$N_3Me_3P_3O_3(OMe)(OC_6H_4Me\text{-}p)_2$ **14** (OCH_3 and NCH_3 regions only). The numbers in parentheses represent the assignment of the different NCH_3 resonances.

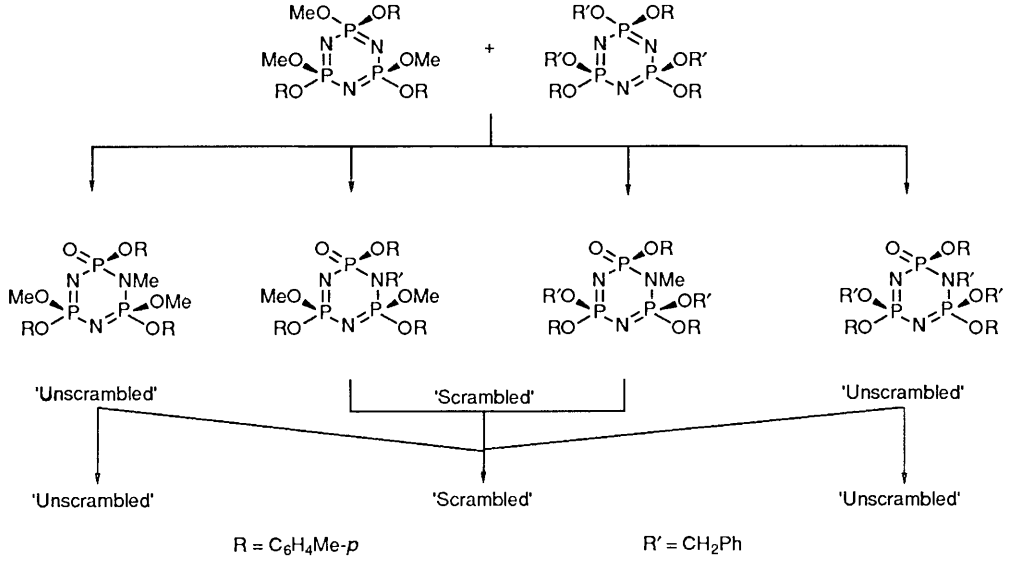

Fig. 5 Thermal rearrangement of a mixture of $N_3P_3(OMe)_3(OC_6H_4Me\text{-}p)_3$ and $N_3P_3(OCH_2Ph)_3(OC_6H_4Me\text{-}p)_3$. Formation of scrambled and unscrambled products.

that are inert to thermal degradation/rearrangement provides a convenient route to a range of trioxocyclotriphosphazanes, dioxocyclotriphosphaz-1-enes and oxocyclotriphosphazadienes. Such mixed phospha*zene*–phospha*zane* systems are not readily accessible by other routes. The thermal rearrangement of aryloxy(alkoxy)cyclotriphosphazenes proceeds with retention of the orientation of the aryloxy substituents with respect to the phosphazene ring.

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References

1 Part 32, S. Ganapathiappan, K. S. Dhathathreyan and S. S. Krishnamurthy, *Macromolecules*, 1987, **20**, 1501.
2 S. Karthikeyan, K. Vyas, S. S. Krishnamurthy, T. S. Cameron and B. R. Vincent, *J. Chem. Soc., Dalton Trans.*, 1988, 1371.
3 R. Keat, *Top. Curr. Chem.*, 1982, **102**, 89; *The Chemistry of Inorganic Homo- and Heterocycles*, eds. I. Haiduc and D. B. Sowerby, Academic Press, London, 1987, vol. 2, p. 467.
4 O. Johnson, M. Murray and G. Woodward, *J. Chem. Soc., Dalton Trans.*, 1989, 821.
5 S. Karthikeyan and S. S. Krishnamurthy, *Z. Anorg. Allg. Chem.*, 1984, **513**, 231.
6 K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1981, 1928.
7 J. M. E. Goldschmidt, in *Analytical Chemistry of Phosphorus Compounds*, ed. H. Halmann, Wiley, New York, 1972, p. 523.
8 P. Diehl, P. H. Kellerhaus and W. Niederberger, *J. Magn. Reson.*, 1971, **4**, 352.
9 G. B. Ansell and G. J. Bullen, *J. Chem. Soc. A*, 1968, 3026.
10 R. Murray and G. Woodward, XI International Conference on Phosphorus Chemistry, Tallinn, July 1989, Abstract No. 2–27.
11 H. Hess and W. Zeiss, unpublished work cited in W. Zeiss, A. Pointner, C. Engelhardt and H. Klehr, *Z. Anorg. Allg. Chem.*, 1981, **475**, 256.

12 B. W. Fitzsimmons, C. Hewlett and R. A. Shaw, *J. Chem. Soc.*, 1964, 4450; 1965, 7432.
13 V. D. Mochel and T. C. Cheng, *Macromolecules*, 1978, **11**, 176.
14 T. C. Cheng, V. D. Mochel, H. F. Adams and T. F. Longo, *Macromolecules*, 1980, **13**, 158.
15 W. T. Ferrar, F. V. DiStefano and H. R. Allcock, *Macromolecules*, 1980, **13**, 1345.

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