Articles

Ring Expansion and Polymerization of Transannular Bridged Cyclotriphosphazenes and Their Spirocyclic Analogues

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Received February 21, 1992; Revised Manuscript Received September 10, 1992

ABSTRACT: The ring expansion and polymerization reactions of the transannular substituted cyclotriphosphazenes 1,3-[$N_3P_3(OCH_2CF_3)_4(X_2R)$] ($X_2R$ = 1,2-dioxyphenyl, 2,2′-dioxybiphenyl, 1,8-dioxynaphthyl, and 1,8-diaminonaphthyl) are described and are compared to the behavior of the analogous spirocyclic cyclotriphosphazenes 1,1-[$N_3P_3(OCH_2CF_3)_4(X_2R)$] ($X_2R$ = 2,2′-dioxybiphenyl, 1,8-dioxynaphthyl, and 1,8-diaminonaphthyl). When heated at temperatures above 200 °C, transannular 1,3-[$N_3P_3(OCH_2CF_3)_4$(2,2′-$O_2C_{12}H_8$)] and spirocyclic 1,1-[$N_3P_3(OCH_2CF_3)_4$(2,2′-$O_2C_{12}H_8$)], 1,1-[$N_3P_3(OCH_2CF_3)_4$(1,8-$O_2C_{10}H_6$)], and 1,1-[$N_3P_3(OCH_2CF_3)_4${1,8-$(NH)_2C_{10}H_6$}] underwent ring–ring equilibration to yield higher cyclic species that ranged from the cyclic tetramer to dodecamer. When heated in the presence of 1% $(NPCl_2)_3$, as a polymerization initiator, small amounts of low molecular weight polymer are also formed. By contrast, thermolysis of transannular 1,3-[$N_3P_3(OCH_2CF_3)_4${1,8-$(NH)_2C_{10}H_6$}], 1,3-[$N_3P_3(OCH_2CF_3)_4$(1,8-$O_2C_{10}H_6$)], and 1,3-[$N_3P_3(OCH_2CF_3)_4$(1,2-$O_2C_6H_4$)] at temperatures above 200 °C, in the presence or absence of $(NPCl_2)_3$, resulted in ring-opening polymerization to give low molecular weight poly(organophosphazenes). The balance between ring–ring equilibration and ring-opening polymerization is discussed in relation to the ability of the transannular organic group to generate ring strain and destabilize the cyclic trimer with respect to the linear polymer.

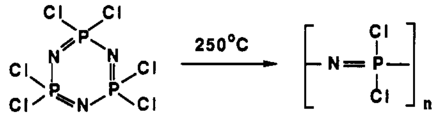
Introduction

The most widely used synthetic route to poly(organophosphazenes) involves the ring-opening polymerization of hexachlorocyclotriphosphazene (1) to give un-cross-linked, soluble, high molecular weight poly(dichlorophosphazene) (2). The chloro side groups of 2 are then replaced by reaction with suitable nucleophiles to yield a wide variety of stable, substituted high polymers.[1,2] The macromolecular substitution step is essential because P–Cl units will sensitize the polymer to thermal and hydrolytic breakdown.

In principle, a simpler and more direct method would involve the ring-opening polymerization of organo-substituted cyclic trimers, with the halogen-replacement reactions occurring in high yield at the small-molecule level.[3,4] However, previous work has shown that cyclic trimers that bear only organic side groups, such as $(NPMe_2)_3$,[5] $(NPPh_2)_3$,[6] $[NP(OCH_2CF_3)_2]_3$,[7] or $[NP(OPh)_2]_3$,[8] undergo ring expansion and ring–ring equilibration at elevated temperatures but do not polymerize.

Recent synthetic advances in our program have allowed the preparation of cyclic phosphazenes that bear transannular metallocenyl side groups (3).[9] Structural studies have shown that these species possess a phosphorus–nitrogen ring that is considerably distorted from planarity, and this suggests substantial strain within the ring.[10] Indeed, during thermolysis in the presence of small amounts of $(NPCl_2)_3$ as an initiator, the species with both metallocenyl and trifluoroethoxy side groups can be induced to undergo ring-opening polymerization to produce a high molecular weight polymer (4).[9] Furthermore, cyclic trimers 3 with trifluoroethoxy and methyl or phenyl groups, as well as transannular metallocenyl units, provide the first examples of fully organo-substituted cyclic phosphazenes that will undergo uncatalyzed ring-opening polymerization.[11] Thus, it appears that the introduction of ring strain destabilizes the fully organo-substituted trimers enough to favor polymerization. The thermolysis of ferrocenyl trimer 3, which bears more sterically demanding cosubstituents, such as phenoxy groups, results in ring expansion (in the presence or absence of an initiator) to produce the cyclic hexamer.[9,11] This reduced tendency for polymerization may be explained by an increase in the steric crowding of the side groups in a prospective linear polyphosphazene compared to the situation in a cyclic oligomer.[1] Clearly, this effect must be taken into consideration when designing new strained cyclic trimers as precursors to poly(organophosphazenes).

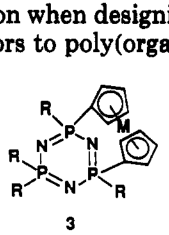
Scheme I



1

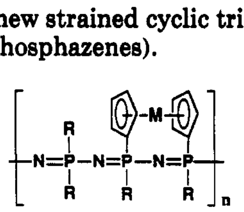
2

n = 15,000



3

M = Fe or Ru
R = OCH_2CF_3 or OPh

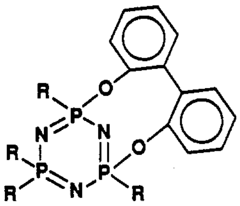


4

M = Fe
R = OCH_2CF_3

In this paper we describe an extension of the above work to a study of fully organosubstituted cyclic trimers 5–8. These species possess a transannular *organic* bridge derived from a difunctional alcohol or amine. Variations in the transannular bridge from 2,2′-biphenylenedioxy to 1,8-naphthalenediyldioxy and 1,8-naphthalenediyldiamino to 1,2-phenylenedioxy allowed a study to be made of the effects of increasing the size of the bridge and of the resultant ring strain on the balance between ring–ring equilibration and polymerization. Trifluoroethoxy groups were chosen as the cosubstituents in order to provide a direct comparison with the behavior of the transannular metallocenyl trimer 3 (where M = Fe and R = OCH_2CF_3).[9]

In addition, comparisons were made with the thermal behavior of *spirocyclic* organosubstituted cyclic trimers 9–11, in which a difunctional nucleophile is allowed to cyclize at a single phosphorus atom. These structures should impose minimal strain on the phosphorus–nitrogen ring.



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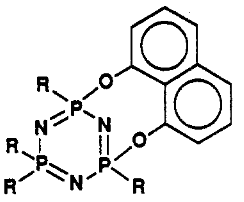

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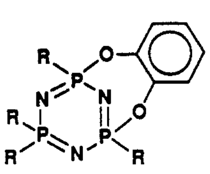

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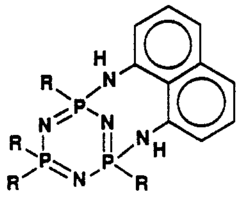
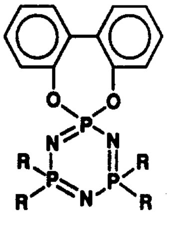


8

R = OCH_2CF_3



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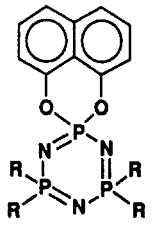

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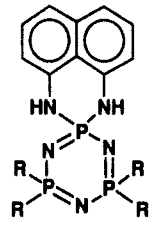


11

Earlier work in our program suggested that the trisubstituted spirocyclic trimers $[NP(2,2'\text{-}O_2C_{12}H_8)]_3$, $[NP(1,8\text{-}O_2C_{10}H_6)]_3$, and $[NP\{1,2\text{-}(NH)_2C_6H_4\}]_3$ are stable at temperatures up to 300 °C.[12] However, spirocyclic substituted trimers with five-membered side unit rings at the phosphorus atoms, such as $[NP(1,2\text{-}O_2C_6H_4)]_3$ and the 2,3-dioxynaphthyl analogue, are known to undergo side-group rearrangements as well as phosphazene ring cleavage.[13]

Thus, the questions of interest are (1) can the transannular derivatives 5–8 be induced to undergo ring-opening polymerization at elevated temperatures, (2) how do their thermal reactions differ from those of spirocyclic phosphazene trimers 9–11, and (3) what do these differences reveal about the balance between ring–ring equilibration and polymerization in fully organo-substituted cyclotriphosphazenes. The syntheses of cyclic trimers 5–11 are described elsewhere.[14] Attempts to synthesize a spirocyclic 1,2-dioxyphenyl analogue of 9–11 have so far proved unsuccessful.

Results and Discussion

Procedure. The transannular bridged cyclic trimers 5–8 were prepared by the reactions of $1,3\text{-}[N_3P_3(OCH_2CF_3)_4Cl_2]$ (12) with difunctional nucleophiles 2,2′-biphenol, 1,8-dihydroxynaphthalene, catechol, and 1,8-diaminonaphthalene, respectively.[14] The spirocyclic phosphazenes 9–11 were prepared directly from $(NPCl_2)_3$ (1) in a two-step, one reaction vessel process, which involved an initial addition of the difunctional nucleophile, followed by treatment with an excess of sodium trifluoroethoxide.[14]

Samples of these compounds were sealed in evacuated glass tubes either by themselves [tube a; (a) in Experimental Section] or in the presence of 1% $(NPCl_2)_3$ as a polymerization initiator or accelerator [tube b; (b) in Experimental Section].[11,15] They were then heated at temperatures between 150 and 250 °C. The contents of the tubes were analyzed by a combination of NMR spectroscopy, FAB mass spectrometry, gel permeation chromatography (GPC), and thin-layer chromatography (TLC). Generally, the ^{31}P NMR spectra provided little detailed information about the products of the reactions due to their complexity and the multitude of phosphorus environments present. However, they did indicate clearly whether or not a reaction had taken place. The GPC and FAB mass spectral data were more informative, with the presence of both higher cyclic oligomers and polymer being detected by GPC techniques. The nature of the higher cyclic oligomers produced by ring–ring equilibration was estimated by FAB mass spectrometry, and the ratio of cyclic oligomers to polymer was determined by integration of the GPC traces.

Comparisons between Transannular Substituted Cyclic Trimers 5–8. Initial thermal studies were performed on the biphenylenedioxy derivative 5. Tubes containing 5 were heated at 150, 200, and 250 °C for 2 weeks, both in the presence and absence of 1% $(NPCl_2)_3$ (1). No increase in melt viscosity was observed for any of these experiments, and this suggested an absence of extensive polymerization. No reaction at all was detected when the system was heated for 2 weeks at 150 °C: 5 was recovered unchanged. At 200 °C or higher temperatures, cyclic trimer 5 underwent ring–ring equilibration exclusively, with the higher cyclic species (detected by FAB mass spectrometry) ranging from cyclic tetramer to decamer (see Table I). In the presence of 1% $(NPCl_2)_3$, ring–ring equilibration predominated (as indicated by GPC analyses), with cyclic species up to dodecamer detected by FAB mass spectrometry. Small amounts of low molecular weight polymer ($M_n \approx 10^4$) were also produced. The ratio of cyclic oligomers to polymer was estimated by GPC analysis to be 6:1 (see Figure 1).

Thermolysis of the 1,8-naphthalenedioxy derivative 6 at 200 or 250 °C induced ring expansion and polymerization, both in the presence and absence of $(NPCl_2)_3$. When heated alone at 200 °C cyclic species up to the hexamer were detected by FAB mass spectrometry (Table II). GPC analysis showed that the ratio of cyclic species to polymer was ca. 1:1 (Figure 2). Similar results were obtained in the presence of $(NPCl_2)_3$ but with an increase evident in the amount of polymer produced, to give a ratio of ca. 1:2. When the thermolysis was carried out at 250 °C, the higher cyclic species produced were identical to those formed at

Table I
FAB Mass Spectral Data for the Thermolysis Products from 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (5) and 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (9)

	starting cyclotriphosphazene and temperature (°C) of experiment											
cyclic oligomer (R = CH_2CF_3)	**5** 150	**5**[a] 150	**9** 150	**9**[a] 150	**5** 200	**5**[a] 200	**9** 200	**9**[a] 200	**5** 250	**5**[a] 250	**9** 250	**9**[a] 250
[$N_3P_3(OR)_4(O_2C_{12}H_8)$]					+	+	+	+	+	+	+	+
[$NP(OR)_2]_3$	+	+	+	+				+			+	
[$N_4P_4(OR)_4(O_2C_{12}H_8)_2$]								+	+	+	+	+
[$N_4P_4(OR)_6(O_2C_{12}H_8)$]					+	+	+	+	+	+	+	+
[$NP(OR)_2]_4$								+	+	+		
[$N_5P_5(OR)_6(O_2C_{12}H_8)_2$]					+	+	+	+		+	+	+
[$N_5P_5(OR)_8(O_2C_{12}H_8)$]					+	+	+	+	+	+	+	+
[$NP(OR)_2]_5$										+		
[$N_6P_6(OR)_8(O_2C_{12}H_8)_2$]					+	+	+	+	+	+	+	+
[$N_6P_6(OR)_{10}(O_2C_{12}H_8)$]							+	+	+	+		
[$N_7P_7(OR)_{10}(O_2C_{12}H_8)_2$]						+			+		+	+
[$N_8P_8(OR)_{10}(O_2C_{12}H_8)_3$]					+	+						+
[$N_8P_8(OR)_{12}(O_2C_{12}H_8)_2$]									+		+	+
[$N_9P_9(OR)_{12}(O_2C_{12}H_8)_3$]					+	+			+		+	+
[$N_9P_9(OR)_{14}(O_2C_{12}H_8)_2$]												
[$N_{10}P_{10}(OR)_{14}(O_2C_{12}H_8)_3$]					+	+					+	+
[$N_{11}P_{11}(OR)_{14}(O_2C_{12}H_8)_4$]					+	+					+	+
[$N_{12}P_{12}(OR)_{16}(O_2C_{12}H_8)_4$]						+					+	+
polymer						+		+		+		+

[a] Tube b, in the presence of [$NPCl_2]_3$; + indicates molecular ion observed [with losses of OR and ($O_2C_{12}H_8$)].

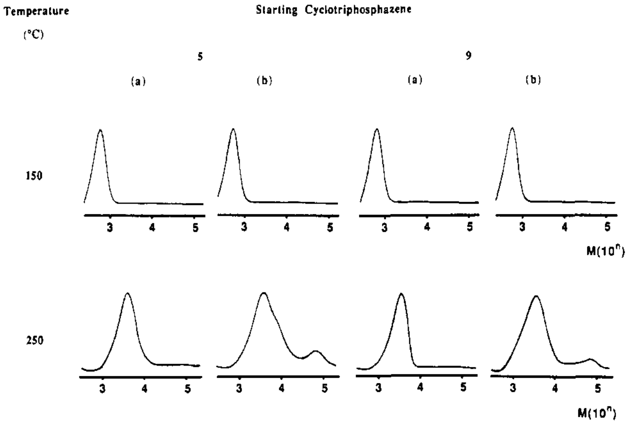


Figure 1. Estimated molecular weights by GPC analysis of the tube contents after thermolysis of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (5) and 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (9): (a) heated alone; (b) heated in the presence of 1% $(NPCl_2)_3$.

200 °C, but the ratio of cyclic to polymeric species was reduced to ca. 3:2, independent of the presence of $(NPCl_2)_3$.

Thermolysis of the 1,2-phenylenedioxy transannular bridged trimer (7) resulted in an increase in melt viscosity after 4 days at 250 °C, and a darkening of the reaction mixture both in the presence or absence of $(NPCl_2)_3$. Analysis of the products indicated a complete disappearance of the cyclic trimer 7 in both systems a and b, accompanied by the formation of a mixture of higher cyclic species and polymer, in a ratio of ca. 1:4 (see Table III and Figure 3). Isolation of the polymers **13a** and **13b** from tubes a and b, respectively, was achieved by repeated precipitation from THF into hexane. Characterization data are shown in the Experimental Section. GPC experiments gave estimated molecular weights of $M_w = 9.4 \times 10^4$ ($n = 147$) and $M_n = 5.7 \times 10^4$ for **13a** and $M_w = 1 \times 10^5$ ($n = 156$) and $M_n = 6.1 \times 10^4$ for **13b**. Both materials were isolated as off-white powders that were insoluble in chloroform and hydrocarbons but readily soluble in acetone or THF.

Heating of the transannular 1,8-diaminonaphthalene derivative 8 at 200 °C for 5 h led to an increase in the melt viscosity both in the presence and absence of 1% $(NPCl_2)_3$. The ^{31}P NMR spectra of both reaction mixtures were identical and contained very broad resonances approximately 25 ppm upfield from those of 8. GPC experiments revealed the presence of low molecular weight polymer as the major product, together with small amounts of higher cyclic species. FAB mass spectrometry indicated that these higher cyclic species consisted exclusively of integral multiples of the starting trimer 8, i.e. hexamer, nonamer, and dodecamer. These results are collected in Figure 4 and Table IV.

Table II
FAB Mass Spectral Data for the Thermolysis Products from 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (6) and 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (10)

	starting cyclotriphosphazene and temperature (°C) of experiment					
cyclic oligomer (R = CH_2CF_3)	**6** 200	**6**[a] 200	**6** 250	**6**[a] 250	**10** 250	**10**[a] 250
[$N_3P_3(OR)_4(O_2C_{10}H_6)$]	+	+	+	+	+	+
[$NP(OR)_2]_3$			+			+
[$N_4P_4(OR)_4(O_2C_{10}H_6)_2$]			+	+	+	+
[$N_4P_4(OR)_6(O_2C_{10}H_6)$]	+	+	+	+	+	+
[$NP(OR)_2]_4$		+	+	+		+
$N_5P_5(OR)_4(O_2C_{10}H_6)_3$]			+	+	+	+
[$N_5P_5(OR)_6(O_2C_{10}H_6)_2$]	+	+	+	+	+	+
[$N_5P_5(OR)_8(O_2C_{10}H_6)$]	+	+	+	+	+	+
[$NP(OR)_2]_5$						+
[$N_6P_6(OR)_6(O_2C_{10}H_6)_3$]			+	+	+	+
[$N_6P_6(OR)_8(O_2C_{10}H_6)_2$]	+	+	+	+	+	+
[$N_6P_6(OR)_{10}(O_2C_{10}H_6)$]			+	+	+	+
[$N_7P_7(OR)_8(O_2C_{10}H_6)_3$]					+	+
[$N_7P_7(OR)_{10}(O_2C_{10}H_6)_2$]					+	+
polymer	+	+	+	+		

[a] Tube b, in the presence of [$NPCl_2]_3$; + indicates molecular ion observed [with losses of OR and ($O_2C_{12}H_6$)].

The polymers from both the uncatalyzed and catalyzed reactions, **14a** and **14b**, respectively, were isolated by repeated precipitations from THF or dichloromethane into hexane, and the structures were examined by GPC methods [**14a**, $M_w = 8.0 \times 10^4$ ($n = 113$), $M_n = 5.6 \times 10^4$; **14b**, $M_w = 2.3 \times 10^4$ ($n = 32$), $M_n = 1.2 \times 10^4$], IR, ^{31}P, ^1H, and ^{13}C NMR spectroscopy, and elemental analysis (see Experimental Section). A strong NH stretch at 3000 cm^{-1} in the IR spectra of **14a** and **14b**, confirmed the retention of the amine proton of 8. The ^{31}P NMR spectrum of **14b** is shown in Figure 5. The detection of numerous phos-

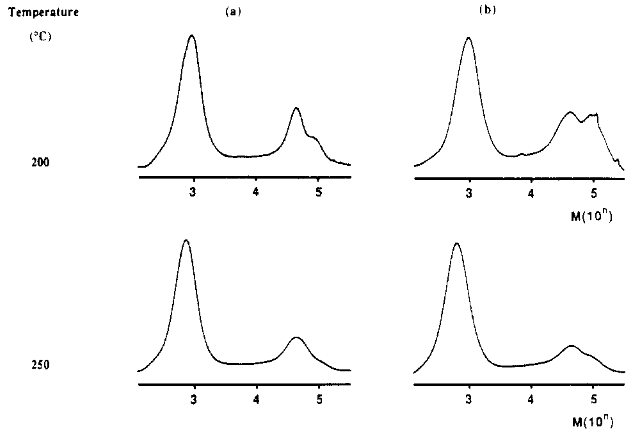


Figure 2. Estimated molecular weights by GPC analysis of the products formed by thermolysis of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (**6**): (a) heated alone; (b) heated in the presence of 1% $(NPCl_2)_3$.

Table III
FAB Mass Spectral Data for the Thermolysis Products from 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_6H_4)$] (7) at 250 °C

cyclic oligomer ($R = CH_2CF_3$)	7	7[a]
[$N_3P_3(OR)_4(O_2C_6H_4)$]		
[$NP(OR)_2]_3$	+	
[$N_4P_4(OR)_4(O_2C_6H_4)_2$]	+	+
[$N_4P_4(OR)_6(O_2C_6H_4)$]	+	+
[$NP(OR)_2]_4$	+	+
[$N_5P_5(OR)_4(O_2C_6H_4)_3$]		
[$N_5P_5(OR)_6(O_2C_6H_4)_2$]	+	+
[$N_5P_5(OR)_8(O_2C_6H_4)$]	+	+
[$NP(OR)_2]_5$		
[$N_6P_6(OR)_6(O_2C_6H_4)_3$]		
[$N_6P_6(OR)_8(O_2C_6H_4)_2$]	+	+
[$N_6P_6(OR)_{10}(O_2C_6H_4)$]	+	+
[$NP(OR)_2]_6$		
[$N_7P_7(OR)_8(O_2C_6H_4)_3$]	+	+
[$N_7P_7(OR)_{10}(O_2C_6H_4)_2$]	+	+
[$N_7P_7(OR)_{12}(O_2C_6H_4)$]		+
[$NP(OR)_2]_7$		
[$N_8P_8(OR)_{10}(O_2C_6H_4)_3$]	+	+
[$N_8P_8(OR)_{12}(O_2C_6H_4)_2$]	+	+
[$N_8P_8(OR)_{14}(O_2C_6H_4)$]		
[$NP(OR)_2]_8$		
[$N_9P_9(OR)_{10}(O_2C_6H_4)_4$]		
[$N_9P_9(OR)_{12}(O_2C_6H_4)_3$]	+	+
[$N_9P_9(OR)_{14}(O_2C_6H_4)_2$]		

[a] Tube b, in the presence of [$NPCl_2]_3$; + indicates molecular ion observed [with losses of OR and ($O_2C_6H_4$)].

phorus environments suggests that the polymer microstructure is complex. Both **14a** and **14b** were off-white in color but darkened slowly unless stored in the dark under an inert atmosphere. Both polymers are readily soluble in non-hydrocarbon organic solvents.

Comparisons between the Spiro Substituted Cyclic Trimers. Thermal studies of the spirocyclic biphenylenedioxy derivative **9** were conducted at 150, 200, and 250 °C. At moderate temperatures (150 °C) no reaction was detected either in the presence or absence of 1% $(NPCl_2)_3$. At higher temperatures (200–250 °C) extensive ring–ring equilibration was detected by FAB mass spectrometry, as shown in Table I. In the presence of 1% $(NPCl_2)_3$ small amounts of low molecular weight polymer were also detected by GPC methods, as shown in Figure 1.

Thermolysis of spirocyclic cyclic trimer **10** for 2 weeks at 250 °C produced little change, with only trace amounts of higher cyclic species, up to the cyclic hexamer, detected by FAB mass spectrometry. However, in the presence of $(NPCl_2)_3$, more extensive ring expansion was detected which consumed trimer **10** and produced a number of higher cyclic species (see Figure 6 and Table II).

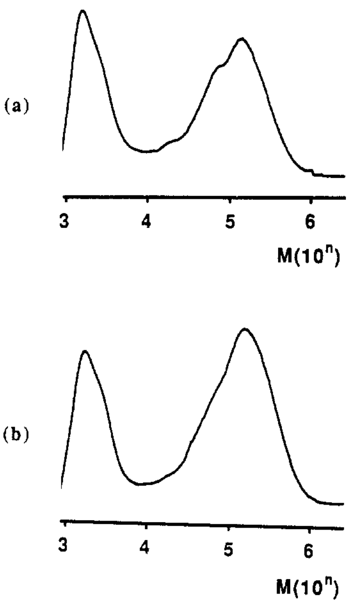


Figure 3. Estimated molecular weights by GPC analysis of the products formed by thermolysis of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_6H_4)$] (**7**), at 250 °C: (a) heated alone; (b) heated in the presence of 1% $(NPCl_2)_3$.

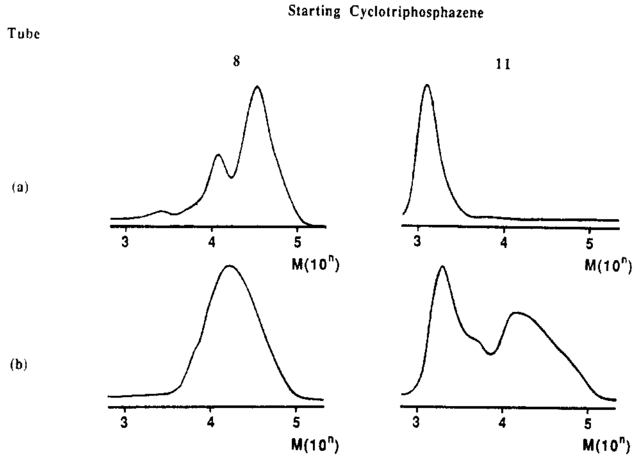


Figure 4. Estimated molecular weights by GPC analysis of the products formed by thermolysis of 1,3-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (**8**) and 1,1-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (**11**), at 200 °C: (a) heated alone; (b) heated in the presence of 1% $(NPCl_2)_3$.

Cyclic trimer **11** was recovered virtually unchanged after being maintained at 200 °C for 24 h. Formation of a small amount (<1%) of a cyclic hexamer was confirmed by TLC and FAB mass spectroscopy. However, thermolysis of **11** in the presence of 1% $(NPCl_2)_3$ resulted in extensive ring–ring equilibration (see Table IV and Figure 4), with significant amounts of low molecular weight polymer detected by GPC analysis.

Comparisons between Transannular and Spirocyclic Systems. Very little differences was detected in the thermal behavior of the transannular and spirocyclic biphenylenedioxy derivatives **5** and **9**. At moderate temperatures (150 °C) no ring–ring equilibration or polymerization occurred in the presence or absence of 1% $(NPCl_2)_3$. At higher temperatures (200–250 °C) extensive ring expansion occurred, with the higher cyclic species detected ranging from tetramers to dodecamers. This is similar to the behavior of [$NP(OCH_2CF_3)_2]_3$ at high temperatures, as reported previously.[7] In that system, cyclic species such as tetramer, pentamer, and hexamer

Table IV
FAB Mass Spectral Data for the Thermolysis Products from 1,3-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (8) and 1,1-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (11) at 200 °C

	starting cyclotriphosphazene			
cyclic oligomer (R = CH_2CF_3)	8	8[a]	11	11[a]
[$N_3P_3(OR)_4\{(NH)_2C_{10}H_6\}$]	+	+	+	+
[$NP(OR)_2]_3$				+
[$N_4P_4(OR)_6\{(NH)_2C_{10}H_6\}$]				+
[$NP(OR)_2]_4$				+
[$N_5P_5(OR)_6\{(NH)_2C_{10}H_6\}_2$]				+
[$N_5P_5(OR)_8\{(NH)_2C_{10}H_6\}$]				+
[$N_6P_6(OR)_8\{(NH)_2C_{10}H_6\}_2$]	+	+	+	+
[$N_6P_6(OR)_{10}\{(NH)_2C_{10}H_6\}$]				+
[$N_7P_7(OR)_8\{(NH)_2C_{10}H_6\}_3$]				+
[$N_7P_7(OR)_{10}\{(NH)_2C_{10}H_6\}_2$]				+
[$N_8P_8(OR)_8\{(NH)_2C_{10}H_6\}_4$]				+
[$N_8P_8(OR)_{10}\{(NH)_2C_{10}H_6\}_3$]				+
[$N_8P_8(OR)_{12}\{(NH)_2C_{10}H_6\}_2$]				+
[$N_9P_9(OR)_{10}\{(NH)_2C_{10}H_6\}_4$]				+
[$N_9P_9(OR)_{12}\{(NH)_2C_{10}H_6\}_3$]	+	+		+
[$N_9P_9(OR)_{16}\{(NH)_2C_{10}H_6\}$]	+	+		+
[$N_{12}P_{12}(OR)_{16}\{(NH)_2C_{10}H_6\}_4$]	+	+		
[$N_{12}P_{12}(OR)_{20}\{(NH)_2C_{10}H_6\}_2$]	+	+		
polymer	+	+		+

[a] Tube b, in the presence of [$NPCl_2]_3$; + indicates molecular ion observed [with loss of OR].

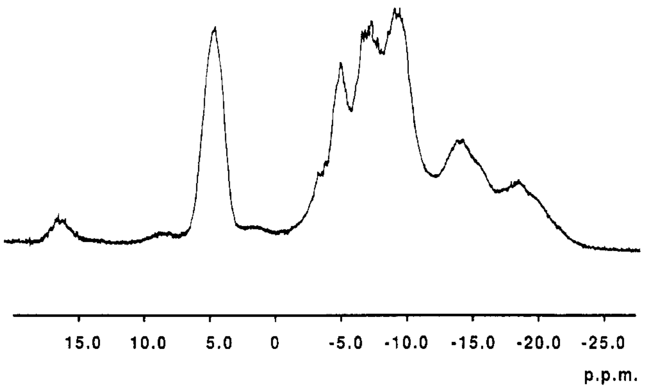


Figure 5. ^{31}P NMR spectrum ($CDCl_3$, 148 MHz) of polymer [$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}]_n$ (14a).

were isolated following heating at 250 °C. It appears that the presence of a transannular biphenylenedioxy moiety has little influence on the ring expansion or polymerization behavior of 5. Apparently, the flexible seven-membered side unit ring of 5 imposes few constraints on the phosphazene ring. This view is supported by the X-ray crystal structures of 5 and 9, reported in an earlier publication.[14] These show only a slight puckering of the phosphazene ring of 5, compared to the planar phosphorus–nitrogen ring of 9. Also, the angle at the nitrogen atom between the two aryloxy rings in 5 is only slightly narrower than those at the other two nitrogen atoms (117 vs 120°), and this too is indicative of only minimal ring strain.

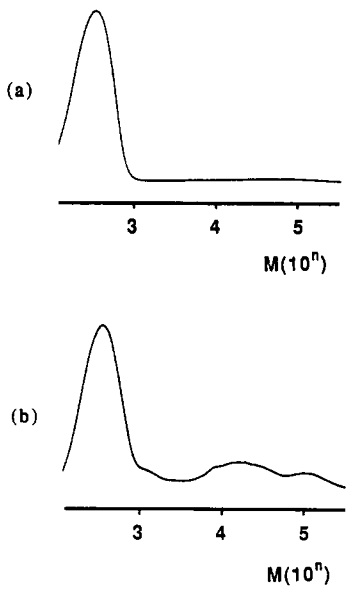
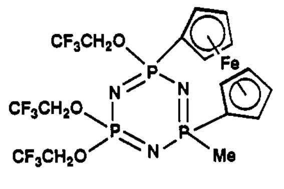


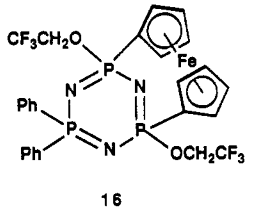
Figure 6. Estimated molecular weights by GPC analysis of the products formed by thermolysis of 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (10): (a) heated alone; (b) heated in the presence of 1% $(NPCl_2)_3$.

The formation of small amounts of polymer during the thermolysis of 5 or 9 in the presence of 1% $(NPCl_2)_3$, suggests that $(NPCl_2)_3$ may act as a polymerization initiator at temperatures above 200 °C. Previous studies in our program have shown that equimolar mixtures of [$NP(OCH_2CF_3)_2]_3$ and $(NPCl_2)_3$ will copolymerize at 200 °C.[7] Similar results have also been reported when BCl_3 was employed as a polymerization initiator. However, small amounts of $(NPCl_2)_3$ accelerate the ring expansion of [$NP(OCH_2CF_3)_2]_3$ but do not initiate polymerization.[7] The present results show a similar acceleration of ring expansion in the presence of $(NPCl_2)_3$ but only a limited amount of polymerization. The yield of polymer from these reactions was very low, with ring–ring equilbration being favored at temperatures above 200 °C.

The smaller "bite angle" of the 1,8-naphthalenedioxy side group in the transannular 1,8-dioxynaphthalene derivative 6 is known to increase the distortion of the phosphorus–nitrogen ring.[14] In theory this increase in ring strain should favor polymerization at high temperatures.[11] The results are consistent with this reasoning, since striking differences exist between the thermal behavior of transannular trimer 6 and that of the spiro-substituted trimer 10. Thermolysis of 6 at 200 °C did not favor ring–ring equilibration over polymerization at this temperature, since the ratio of higher cyclic species to polymer was approximately 1:1. Thermolysis in the presence of 1% $(NPCl_2)_3$ led to an increase in the proportion of polymer produced (to ca. 1:2), although, the molecular weight of the polymer did not change. *The uncatalyzed ring-opening polymerization of 6 at 200 °C is the first example of this process by a cyclotriphosphazene with a purely organic bridge structure.* Previous reports have described the uncatalyzed polymerization of species such as [$N_3P_3Me(OCH_2CF_3)_3(n\text{-}C_5H_4)_2Fe$] (15) and [$N_3P_3Ph_2(OCH_2CF_3)_2(n\text{-}C_5H_4)_2Fe$] (16).[11] X-ray crystallography has shown that 6, 15, and 16 all possess a highly puckered and presumably strained phosphorus–nitrogen ring, and it is the release of this strain that provides the driving force for polymerization.[10,14]



15



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Thus, the important point to be noted is that the polymerization of 6 indicates that this is a *general* phenomenon that is not dependent on the presence of organometallic bridge structures. Presumably, any strain-inducing transannular unit that can withstand the thermolysis conditions should assist polymerization.

However, the molecular weights of the higher polymers are very different, with those produced by the thermolysis of **15** and **16**[11] being higher than those formed during the thermolysis of **6** (≈10^6 compared with ≈10^4). At 250 °C *both* ring–ring equilibration and polymerization are detected, and the product mixture does not change in the presence or absence of 1% $(NPCl_2)_3$. However, the ratio of cyclic species to polymer increased from 1:2 to 3:2, when the thermolysis was performed at 250 °C. This suggests that the position of equilibrium is sensitive to temperature, with cyclic oligomers being favored over polymers as the temperature is raised and with the average molecular weight of the polymer declining at the higher temperature. Related effects have been suggested for the depolymerization of poly[bis(trifluoroethoxy)phosphazene] at temperatures above 200 °C.[16] This suggests the existence of a ceiling temperature at temperatures above 250 °C.

Heating of the spirocyclic naphthalenedioxy phosphazene **10** at 250 °C brought about virtually no change, with only trace amounts of ring expansion species being detected by ^{31}P NMR spectroscopy or FAB mass spectrometry. However, in the presence of $(NPCl_2)_3$, **10** underwent extensive ring expansion, but no polymerization. These results too are similar to those reported for $[NP(OCH_2CF_3)_2]_3$ and confirm that small amounts of $(NPCl_2)_3$ accelerate the ring–ring equilibration of trifluoroethoxy-substituted phosphazenes.[7] The differences in the thermal behavior of **6** and **10** again suggest that a strained phosphazene ring is needed before polymerization occurs, at least in this temperature range. This view is supported by the X-ray crystal structure of **10** which shows an essentially planar phosphorus–nitrogen ring, virtually devoid of ring strain.[14]

Thermolysis of the 1,2-phenylenedioxy transannular bridged trimer (**7**) at 250 °C gave identical results in both the presence and absence of $(NPCl_2)_3$. Both ring expansion and polymerization products were detected, with the ratio of higher cyclic species to polymer being 1:4 (see Table III and Figure 3). The proportion of polymer formed was independent of the presence of $(NPCl_2)_3$, and was twice that produced by thermolysis of the 1,8-naphthalenedioxy derivative **6**. This increase in the conversion to polymer can perhaps be related to the increase in the strain imposed on the phosphazene ring, as a consequence of the decrease in the "bite angle" of the transannular unit. As the size of the transannular bridge is decreased from 2,2′-biphenylenedioxy to 1,8-naphthalenedioxy to 1,2-phenylenedioxy in cyclic trimers **5**–**7**, the proportion of polymer rose from <10% to ca. 80% of the detected products. This suggests that in this system the ratio of the cyclic to polymeric products can be controlled by the size of the transannular bridge.

Thermolysis of **8** at 200 °C produced almost exclusively low molecular weight polymer, both in the presence or absence of $(NPCl_2)_3$, together with a small amount of higher cyclic oligomers. The ring expanded species detected by FAB mass spectrometry were identified as cyclic hexamer, nonamer, and dodecamer. These results are similar to those for polymerization of the transannular ferrocenyl trimer **3** ($M = Fe$, $R = OCH_2CF_3$), and this suggests a similarity between these two processes.[9] The structure of **8** in the solid state has not yet been determined, and the conformation of the phosphazene ring and the implied degree of ring strain is not known. The present results suggest that the phosphazene ring of **8** may be more highly strained than the corresponding 1,8-naphthalenedioxy derivative **6**, because **6** undergoes both ring expansion and polymerization at 200 °C. The approximate molecular weights of polymers **14a** and **14b**, determined by GPC analysis, were lower than those of macromolecules produced from ferrocenyl trimers **3**, **15**, and **16**.[9,11] However, the absence of ring-expanded species, such as the cyclic tetramer $[N_4P_4(OCH_2CF_3)_6\{(NH)_2C_{10}H_6\}]$, in the FAB mass spectra suggests that polymers **14a** and **14b** do not depolymerize readily at 200 °C.

The 1,8-naphthalenediamino spirocyclic trimer **11** was unchanged after heating at 200 °C for 24 h, but it underwent extensive ring expansion and polymerization in the presence of 1% $(NPCl_2)_3$. The formation of significant amounts of polymer is suprising and cannot be explained solely on the basis of ring strain.

Role Played by $(NPCl_2)_3$. Hexachlorocyclotriphosphazene accelerates virtually all of the reactions described in this paper. In previous papers it was concluded that the polymerization of $(NPCl_2)_3$ alone proceeds through a process that involves an initial ionization of chloride ions from phosphorus, followed by a cationic chain propagation process.[17] It has also been proposed that the ring expansion reactions of fully organo-substituted cyclic phosphazenes may take place via ring cleavage to give zwitterion intermediates that can undergo ring fusion.[18] Both mechanisms appear to be operative in the reactions described here. The presence of P–Cl bonds introduced via $(NPCl_2)_3$ may provide a low activation energy route to polymer formation and perhaps also to ring expansion. But the absence of P–Cl units slows both reactions and may favor ring expansion over linear polymerization.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (30 °C, 0.05 mmHg) before use. Compounds **5**–**11** were synthezied as described previously.[14,19,20]

Equipment. ^{31}P (36.2 MHz) NMR spectra were recorded using a JEOL FX 90Q NMR spectrometer. High-field ^{31}P (146 MHz), ^{13}C (90 MHz), and ^{1}H (360 MHz) NMR spectra were obtained by use of a Bruker WM 360 NMR spectrometer. Both ^{31}P and ^{13}C NMR spectra were proton decoupled unless otherwise specified. ^{31}P NMR spectra were referenced relative to external 85% H_3PO_4 with positive shifts recorded downfield of the reference. ^{1}H and ^{13}C NMR spectra were referenced relative to external tetramethylsilane. Reactions were routinely followed by ^{31}P NMR spectroscopy and thin-layer chromatography. All NMR spectra were recorded in $CDCl_3$ unless otherwise stated. Gel permeation chromatography was carried out with the use of a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 3392 refractive index detector. A detailed description of the procedure has been previously reported.[11] FAB mass spectra were recorded by use of a Kratos MS-50 mass spectrometer. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Thermal Equilibration and Polymerization. The cyclic trimers **5**–**11** were purified extensively by recrystallization, followed by high-vacuum sublimation. Thermal studies were carried out by sealing samples under vacuum (50 μmHg) in thick-walled Pyrex tubes (5 × 0.5 cm). The tubes were rigorously cleaned before use by immersion in an ethanolic KOH solution followed by rinsing with dilute HCl and numerous washings with distilled/deionized water. The tubes were then dried at elevated temperatures. Heating was accomplished using thermoregulated ovens equipped with a mechanical rocking device to ensure continuous agitation of the tube contents. For each experiment, two tubes (a and b) were charged with the appropriate cyclotriphosphazene (0.5 g), in a nitrogen-filled drybox. One mole percent of $(NPCl_2)_3$ (ca. 3 mg) was added to one tube (b), and both were connected to a vacuum line and evacuated for 30 min at pressures <50 μmHg. The tubes were then sealed, wrapped in aluminum gauze, and placed in a preheated oven at the desired temperature. Heating was continued until a change in the reaction mixture was detected, such as an increase in melt viscosity or the onset of discoloration. All tubes were removed from the oven after 2 weeks, regardless of detectable changes. The tubes were then opened and their contents extracted with dry THF. The extracts were filtered and analyzed by ^{31}P NMR spectroscopy, TLC and GPC. Other samples were also filtered through silica gel to remove insoluble polymeric products, and were analyzed by FAB mass spectrometry. FAB mass spectra recorded before and after filtration through silica gel were identical, indicating that the polymeric products did not affect the distribution of species detected by mass spectrometry. More detailed experimental procedures are described below.

Heating of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (5). 1. At 150 °C. (a) When heated alone for 2 weeks, the melt remained clear, colorless, and fluid. After the tube was opened, ^{31}P NMR spectroscopy, FAB mass spectrometry, TLC, and GPC of the tube contents showed no evidence of change. (b) Identical results to those in (a) were obtained in the presence of 1% $(NPCl_2)_3$.

2. At 200 °C. (a) A slight darkening of the tube contents was detected after 2 weeks. After extraction of the material with THF, the only resonances found in the ^{31}P NMR spectrum were those from unchanged **5** [27.0 (dd, *J* 79, 88 Hz), 25.6 (dd, *J* 79, 91 Hz), and 22.0 (dd, *J* 88, 91 Hz) ppm]. The most intense ion detected in the FAB mass spectrum was also that for **5** (*m/z* 716, MH$^+$), although a number of higher cyclic species were also detected (see Table I). GPC analysis gave a single peak, at an elution volume of 28.2 mL, for cyclic trimer **5**. (b) In the presence of 1% $(NPCl_2)_3$ a slight darkening of the tube contents occurred after 2 weeks, but the reaction mixture remained clear and fluid. After extraction with THF, ^{31}P NMR spectra of the extract contained resonances from unchanged **5** (see above) and numerous upfield resonances between −2 and −20 ppm. The most intense ion detected in the FAB mass spectrum was that for the cyclic tetramer [$N_4P_4(OCH_2CF_3)_6(O_2C_{12}H_8)$] (*m/z* 959, MH$^+$). The higher cyclic species detected are shown in Table I. Two peaks were detected in the GPC trace at elution volumes of 28 and 24 mL, in a ratio of 6:1.

3. At 250 °C. (a) The molten material remained clear and colorless after being heated for 2 weeks. ^{31}P NMR spectroscopy showed resonances for trace amounts of **5** plus a complex series of peaks shifted upfield to regions between −3 and −23 ppm. The most intense ion detected in the FAB mass spectrum was that for the cyclic tetramer [$N_4P_4(OCH_2CF_3)_6(O_2C_{12}H_8)$] (*m/z* 959, MH$^+$). The higher cyclic species detected are shown in Table I. GPC analysis showed only one peak at an elution volume of 26.2 mL. (b) No change in the color or viscosity of the melt was detected after heating for 2 weeks. After extraction with THF, ^{31}P NMR spectroscopy showed resonances for trace amounts of **5** plus numerous upfield resonances at between −2 and −20 ppm. The higher cyclic species detected by FAB mass spectrometry are shown in Table I, and the most intense ion found was from [$N_4P_4(OCH_2CF_3)_6(O_2C_{12}H_8)$] (*m/z* 959, MH$^+$). The GPC trace contained two peaks at elution volumes of 26.5 and 23.1 mL, in a ratio of 5:1.

Behavior of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (6). 1. At 200 °C. (a) The melt remained clear and colorless for 6 days but then began to discolor. The tube was cooled to room temperature and opened, and the contents were extracted with THF. ^{31}P NMR spectroscopy showed a large number of resonances at 1.1 (br), −0.7 (br), −4.5 (br), −9.7 (br), −17.2 (br), −19.6 (s), and −22.7 (br) ppm. The higher cyclic species detected by FAB mass spectrometry are shown in Table II. The most intense peak was identified as the cyclic trimer, [$N_4P_4(OCH_2CF_3)_6(O_2C_{10}H_6)$] (*m/z* 933, MH$^+$). Two peaks were detected in the GPC trace at 27.8 and 24.0 mL (with a shoulder at 22.8 mL), in a ratio of ca. 1:1. (b) The molten trimer remained clear, colorless, and fluid for 6 days; however, discoloration occurred at longer times. After 6 days the tube was opened and the contents were extracted with THF. A complex series of peaks were found in the ^{31}P NMR spectrum at 15.0 (m), −0.4 (m), −4.0 (m), −5.0 (br), −10.3 (br), −17.1 (br), −19.6 (s), and −22.7 (br) ppm. The most intense ion in the FAB mass spectrum was identified as [$N_4P_4(OCH_2CF_3)_6(O_2C_{10}H_6)$] (*m/z* 933, MH$^+$), and the higher cyclic species detected are shown in Table II. GPC analysis gave two peaks at elution volumes of 27.8 and 24.2 mL (with a shoulder at 22.5 mL), in a ratio of 1:2.

2. At 250 °C. (a) The molten material became slightly discolored after heating for 3 days. No increase in melt viscosity was observed. The tube contents were extracted with THF. The ^{31}P NMR spectrum of the extract showed a large number of resonances at 15.0 (m), 1.4 (br), −0.5 (br), −4.5 (br), −10 (br), −17.0, −19.6 (s), and −22.4 (br) ppm. The higher cyclic species detected by FAB mass spectrometry are shown in Table II. The most intense signal was identified as [$N_4P_4(OCH_2CF_3)_6(O_2C_{10}H_6)$] (*m/z* 933, MH$^+$). Two peaks were detected in the GPC trace at 27.8 and 24.0 mL, in a ratio of ca. 3:2. (b) The molten trimer, **6**, became heavily discolored after heating for 3 days. The ^{31}P NMR spectrum of the THF extract showed a complex series of peaks at 15.0 (m), 1.1 (br), −0.6 (br), −4.6 (br), −10 (br), −17.0 (br), −19.7 (s), and −22.7 (br) ppm. The most intense ion in the FAB mass spectrum was identified as [$N_4P_4(OCH_2CF_3)_6(O_2C_{10}H_6)$] (*m/z* 933, MH$^+$) and the higher cyclic species detected are shown in Table II. GPC gave two peaks at elution volumes of 27.8 and 24 mL, in a ratio of 3:2.

Attempts to separate the higher polymeric products from the higher cyclic oligomers produced during thermolysis of **6** at 200 or 250 °C proved to be unsuccessful for both reactions in tubes a and b, due to the close similarity of their solubilities.

Behavior of 1,3-[$N_3P_3(OCH_2CF_3)_4(O_2C_6H_4)$] (7) at 250 °C. (a) The tube contents darkened and became viscous after 4 days at 250 °C. ^{31}P NMR spectroscopy of the THF extracts showed a large number of peaks at 17.2 (m), 9.5 (br), 4.9 (s), 2.5 (m), −1.9 (s), −3.2 (m), −5.6 (m), and −7.2 (br) ppm. Two peaks in the ratio of 1:4 were found in the GPC trace at elution volumes of 27.8 and 21.8 mL.

Polymer **13a** was isolated as a pale brown powder (0.27 g, 54%) by repeated precipitation from a viscous solution in THF (ca. 1 mL) into a large excess of hexane (200 mL). Anal. Calcd for $C_{14}H_{12}F_{12}N_3O_6P_3$: C, 26.31; H, 1.89; N, 6.58. Found: C, 24.98; H, 2.31; N, 6.57. NMR: δ_H (acetone-d_6) 7.3–6.8 (br, Ph, 4 H) and 4.5 (br, OCH_2CF_3, 8 H); δ_P (acetone-d_6) 10.3, 2.0, −0.8, −2.2, −5.2, −7.1, −10.8, and −20.0 (all br) ppm; δ_C (acetone-d_6) 149.4, 142.3, 128.1, 126.6, 125.5, 122.7, 122.4, 120.9, 120.4, 119.3, 118.4, and 64.1 (all br) ppm. GPC: $M_w = 9.4 \times 10^4$ ($n = 147$), $M_n = 5.7 \times 10^4$.

(b) Molten trimer **7** darkened in color, and the melt became viscous after 4 days at 250 °C. ^{31}P NMR spectra contained a number of peaks upfield from those of **7** at 17.2 (m), 9.5 (br), 4.9 (s), 2.3 (m), −3.5 (m), −4.3 (m), and −7.2 (br) ppm. GPC analyses gave two peaks in a ratio of 1:4 at elution volumes of 27.8 and 21.8 mL.

Polymer **13b** (0.2 g, 40%) was isolated by repeated precipitations from a viscous solution in THF (ca. 1 mL) into a large excess of hexane (200 mL). (Anal. Calcd for $C_{14}H_{12}F_{12}N_3O_6P_3$: C, 26.31; H, 1.89; N, 6.58. Found: C, 24.57; H, 1.87; N, 6.44). NMR: δ_H (acetone-d_6) 7.3–6.8 (br, Ph, 4 H), 6.1 (br, OCH_2CF_3, 2 H) and 4.5 (br, OCH_2CF_3, 6 H) ppm; δ_P (acetone-d_6) 10.3, 1.2, −2.3, −7.1 (−5.9, sh), −10.5, and −20.0 (all br) ppm; δ_C (acetone-d_6) 149.4, 142.3, 140.0, 128.8, 126.6, 125.4, 124.2, 122.5, 120.8, 119.1, 118.3, and 64.1 (all br) ppm. GPC: $M_w = 1 \times 10^5$ ($n = 156$), $M_n = 6.1 \times 10^4$.

Behavior of 1,3-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (8) at 200 °C. (a) The tube contents became viscous and darkened in color after 5 h. The tube and contents were cooled to room temperature, and the contents were extracted with THF. ^{31}P NMR spectroscopy showed a broad resonance between 6 and 3 ppm and a complex series of peaks at 4.5, −5.1, −8.1, −10 and −15 ppm. The higher cyclic species detected by FAB mass spectrometry are shown in Table IV. The most intense peak was tentatively identified as the cyclic hexamer [$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$]$_2$ (*m/z* 1376, MH$^+$). Three peaks were found in the GPC trace at elution volumes of 27, 25.6, and 24.5 mL, in a ratio of 1:10:40.

Polymer **14a** was isolated as an off-white powder (0.11 g, 22%) by repeated precipitation from a viscous solution in dichloromethane (ca. 2 mL) into a large excess of hexane (300 mL). (Anal. Calcd for $C_{18}H_{16}F_{12}N_5O_4P_3$: C, 31.45; H, 2.35; N, 10.19. Found: C, 31.79; H, 2.26; N, 10.85). NMR: δ_H 7.3–7.2 (br, Ph, 6 H), 6.6 (br, NH, 2 H), and 4.2 (br, OCH_2CF_3, 8 H) ppm; δ_P 16.0, 4.5, −4.9, −7.2, −9.1, and −14.1 (all br) ppm (see Figure 5); δ_C 135.0, 134.5, 127.5, 124.2, 122.0, 121.0, 110.9, and 60.3 (all br) ppm GPC: $M_w = 8 \times 10^4$ ($n = 116$), $M_n = 5.6 \times 10^4$.

(b) The tube contents became viscous after 1 h and darkened after 5 h. After 5 h of thermolysis, the tube was cooled to room temperature and opened, and the contents were extracted with THF. The ^{31}P NMR and FAB mass spectra were identical to those described in (a). GPC analysis showed a single peak with an elution volume of 25.3 mL.

This polymer **14b** (0.19 g, 38%) was isolated by repeated precipitations from a viscous solution in dichloromethane (ca. 2 mL) into a large excess of hexane (300 mL). (Anal. Calcd for $C_{18}H_{16}F_{12}N_5O_4P_3$: C, 31.45; H, 2.35; N, 10.19. Found: C, 31.90; H, 2.37; N, 10.63). NMR: δ_H 7.3–7.15 (br, Ph, 6 H), 6.55 (br, NH, 2 H), and 4.2 (br, OCH_2CF_3, 8 H) ppm; δ_P 15.5, 4.4, −4.8, −6.7, −8.0, −14.0, and −18.0 (all br) ppm; δ_C 135.1, 127.0, 126.0, 120.9, 110.8, and 62.8 (all br) ppm. GPC: $M_w = 2.3 \times 10^4$ ($n = 32$), $M_n = 1.2 \times 10^4$.

Behavior of 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{12}H_8)$] (9). 1. At 150 °C. (a) When heated alone for 2 weeks the melt remained clear, colorless, and fluid. After the tube was opened ^{31}P NMR spectroscopy, FAB mass spectrometry, TLC, and GPC of the tubes contents showed no change. (b) Identical results to those in (a) were obtained in the presence of 1% $(NPCl_2)_3$.

2. At 200 °C. (a) The molten trimer **9** remained clear, colorless, and fluid when heated for 2 weeks. Extraction with THF gave a colorless solution, the ^{31}P NMR spectrum of which contained resonances for cyclic trimer **9** [25.2 (dd, *J* 92 Hz) and 18.2 (d, *J* 92 Hz) ppm] plus a minor peak at −3.75 ppm. The most intense ion detected in the FAB mass spectrum was also that from **9** (m/z 716, MH^+), although weak signals for a number of higher cyclic species were also detected (see Table I). GPC analysis gave a single peak, at an elution volume of 28.1 mL, for cyclic trimer **9**. (b) When heated for 2 weeks in the presence of 1% $(NPCl_2)_3$ molten trimer **9** remained clear, colorless, and fluid. After extraction with THF, ^{31}P NMR spectroscopy showed resonances for trace amounts of **9** (see above) and a new intense peak at −3.75 ppm. Several other broad resonances were also present between +4 and −10 ppm. The most intense ion detected in the FAB mass spectrum was that from the cyclic tetramer [$N_4P_4(OCH_2CF_3)_6(O_2C_{12}H_8)$] ($m/z$ 959, MH^+). The higher cyclic species detected are shown in Table I. Two major peaks in a ratio of 1:1 were detected in the GPC trace, at elution volumes of 28 and 24.5 mL, with shoulders at 27.2 and 26 mL, respectively.

3. At 250 °C. (a) The tube contents remained clear, colorless, and fluid after heating for 2 weeks. ^{31}P NMR spectroscopy showed a complex series of peaks at 15.1 (m), 5.4–3.5 (br), −3 (br), and −9 (br) ppm. The most intense ion detected in the FAB mass spectrum was that for the cyclic tetramer [$N_4P_4(OCH_2CF_3)_6(O_2C_{12}H_8)$] ($m/z$ 959, MH^+). The higher cyclic species detected are shown in Table I. GPC analysis showed only one peak at an elution volume of 26.5 mL. (b) No change in the color or viscosity of the melt was detected after heating for 1 week. However, after 10 days a slight precipitate was formed, at which point the tube was cooled to room temperature. After extraction with THF, ^{31}P NMR spectroscopy of the extract showed resonances at 15.1 (m), 5.4–3.5 (br), −3 (br), −10 (br), and −16 ppm. The higher cyclic species detected by FAB mass spectrometry are listed in Table I, and the most intense ion found was that for [$N_4P_4(OCH_2CF_3)_6(O_2C_{12}H_8)$] ($m/z$ 959, MH^+). The GPC trace contained two peaks at elution volumes of 26.5 and 23 mL, in a ratio of 4:1.

Behavior of 1,1-[$N_3P_3(OCH_2CF_3)_4(O_2C_{10}H_6)$] (10) at 250 °C. (a) The molten trimer **10** remained clear, colorless, and fluid when heated for 2 weeks. Extraction of the tube contents with THF gave a colorless solution, the ^{31}P NMR spectrum of which contained resonances for cyclic trimer **10** [18.24 (d, *J* 94 Hz) and 5.17 (t, *J* 94 Hz) ppm] and minor peaks at −4.2 (m) and −17.0 (m) ppm. The most intense ion detected in the FAB mass spectrum was also that from **10** (m/z 716, MH^+), although weak signals for a number of higher cyclic species were also detected (see Table II). GPC analysis gave a single peak, at an elution volume of 28.1 mL. (b) When heated for 2 weeks in the presence of 1% $(NPCl_2)_3$ molten trimer **10** remained clear, colorless, and fluid. After extraction of the tube contents, a ^{31}P NMR spectrum of the THF solution showed an intense peak at −4.0 (m) and minor peaks at 15.0 (m), −9.3 (br), −16.7 (m), and −21.8 (br) ppm. The most intense ion detected in the FAB mass spectrum was that from the cyclic tetramer [$N_4P_4(OCH_2CF_3)_6(O_2C_{10}H_6)$] ($m/z$ 933, MH^+). The higher cyclic species detected are shown in Table II. One major peak was detected in the GPC trace, at an elution volume of 28 mL, with minor features found at 25.2 and 22.0 mL.

Behavior of 1,1-[$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}$] (11) at 200 °C. (a) The tube contents remained clear and colorless after heating for 3 days. After cooling to room temperature, the contents were extracted with THF. ^{31}P NMR spectroscopy, TLC, and GPC (shown in Figure 4) of the tube contents showed no reaction. The most intense peak in the FAB mass spectrum was identified as **11** (m/z 687, M^+), and weak signals for a number of higher cyclic species were also detected (see Table IV). (b) A slight increase in viscosity was detected after 3 days coupled with a discoloration of the tube contents. After cooling to room temperature, the tube was opened and the contents were extracted with THF. ^{31}P NMR spectroscopy showed numerous peaks between 0 and −10 ppm and between −17 and −22 ppm. The higher cyclic species detected by FAB mass spectrometry are shown in Table IV. The most intense peak was identified from the cyclic hexamer [$N_3P_3(OCH_2CF_3)_4\{(NH)_2C_{10}H_6\}]_2$ (m/z 1376, MH^+). Three peaks were found in the GPC trace at elution volumes of 27.2, 26.5, and 25.7 mL.

Acknowledgment. We thank the Dow Chemical Co. for financial support and L. M. Collins for recording the FAB mass spectra.

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Registry No. **5**, 143398-27-0; **6**, 143398-28-1; **6** (homopolymer), 144608-23-1; **7**, 143398-26-9; **7** (homopolymer), 144608-24-2; **8**, 143398-29-2; **8** (homopolymer), 144608-25-3; **9**, 143398-34-9; **10**, 143398-35-0; **11**, 143398-36-1; $(NPCl_2)_3$, 940-71-6.