according to literature[24] procedure (mp 208 °C (lit. 206 °C). 2,7,11,16-Tetra-*tert*-butylperylene (**7b**) was prepared in the usual Friedel-Crafts alkylation procedure, using *tert*-butychloride, $AlCl_3$, and chlorobenzene as solvent (mp 312 °C from toluene). For NMR properties (^1H, ^{13}C spectra) see text and tables.

General Procedure for the Metal Reduction Process. A wire of sodium or potassium was introduced to the upper part of a prolonged NMR tube containing 10^{-3} M of the hydrocarbon dissolved in 0.8 mL of THF-d_8 (Aldrich reagent). The frozen solution of the hydrocarbon was degassed and then the tube was sealed under vacuum. By turning the tube the solution is brought into contact with the metal wire for controlled periods of time.

The NMR spectra were obtained (5-mm samples) on a Bruker WH-300 pulsed FT spectrometer operating at 300.133, 75.46, and 79.53 MHz for ^1H, ^{13}C, and ^{23}Na, respectively. The field/frequency regulations were maintained by locking to the solvent deuterium. The free induction decay signals were digitized and accumulated on an Aspect-2000 computer (32K).

Quenching Experiments. (a) A solution of the hydrocarbon **1** (1 g) in 100 mL of dry THF was cooled to −78 °C and stirred under nitrogen. A wire of sodium was introduced into the reaction flask. The resulting purple solution was cautiously allowed to warm to room temperature. Samples of 1 mL were taken from the reaction mixture after 6, 12, and 24 h and 2, 3, 4, 5, 6, and 14 days, quenched with water, and titrated potentiometrically to follow the formation of base (a Beckman zeromatic pH meter instrument). The amount of sodium was followed by atomic absorption (atomic-absorption spectrophotometer, Perkin-Elmer 403). (b) Two milliliters of dry THF were treated with sodium under nitrogen. After 2 weeks the mixtures were poured into D_2O. The compounds which resulted in the usual workup were analyzed with chemical ionization and electron capture mass spectroscopies.

Chemical ionization and electron capture mass spectroscopies were obtained with a DuPont 21-490 B single focusing instrument equipped with a commercial dual CI/EI source. Reagent gas was isobutane and the source temperature was 160 °C.

(24) (a) Buu-Hoi, Ng. Ph.; Cagniant, P. *Ber.* **1944**, *2*, 111-126. (b) Berg, A.; Jakobsen, H. J.; Johansen, S. R. *Acta Chem. Scand.* **1960**, *23*, 567-575.

Acknowledgment. We thank Professor I. Agranat (Hebrew University of Jerusalem) for the generous gifts of 2,9-dimethylpyrene and 1,3,8,10-tetraphenylpyrene. We thank Dr. S. Zitrin, Mass Spectroscopy Unit, Criminal Identification Division, Police Headquarters (Jerusalem, Israel), for the mass spectroscopy measurements.

Registry No. 1, 129-00-0; **2A**, 80663-84-9; **2S**, 80663-85-0; **3a**, 15679-24-0; **3b**, 24300-91-2; **3b**$^{2-}$ K salt, 80664-63-7; **3b**$^{2-}$ Na salt, 80664-65-9; **4a-A** Na salt, 80663-86-1; **4a-S** Na salt, 80663-87-2; **4b-A** Na salt, 80663-88-3; **4b-S** Na salt, 80663-89-4; **4b-A** K salt, 80663-90-7; **4b-S** K salt, 80663-91-8; **5**, 13638-82-9; **6**, 80679-20-5; **7a**, 198-55-0; **7b**, 80663-92-9; **7b**$^{2-}$ Na salt, 80664-67-1; **8a**, 80663-93-0; **8b**, 80663-94-1.

Reactions of Bi(cyclophosphazenes) with Sodium Alkoxides or Aryl Oxides[1,2]

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Abstract: Bi(cyclophosphazenes) (**2**) react with nucleophiles such as sodium trifluoroethoxide or sodium phenoxide by two alternative pathways—(a) with cleavage of the P–P ring linkage unit and cleavage of P–Cl bonds to yield organocyclotriphosphazenes (**3**) or (b) by cleavage of P–Cl bonds without rupture of P–P bonds to give organobi(cyclophosphazenes) (**6**). These latter species eventually undergo P–P bond scission with alkoxides or aryl oxides under more forcing reaction conditions. Cleavage of the bi(cyclophosphazenes) **2** or **6** also yields phosphazene anions (**4**), which react with alcohols to form hydridocyclotriphosphazenes (**5**). Treatment of these with chlorine brings about the conversion of the P–H to P–Cl units. The phosphazene anions (**4**) also react with allyl bromide with attachment of the allyl residue to the ring and with carbon tetrachloride to abstract Cl^+ and generate neutral chloroorganocyclotriphosphazene species (**9**). These interconnected processes were monitored by both product isolation and NMR spectroscopy. Appendices A and B (supplementary material) outline the interpretation of the more complex ^1H and ^{31}P NMR coupling patterns observed.

The synthesis of new, small-molecule organocyclophosphazenes underlies much of the current interest in the synthesis of new inorganic backbone high polymers. Organocyclophosphazenes are used both as models for the reactions of the analogous high polymers[3] and as "monomers" for polymer synthesis.[4] Prominent among the problems in this area is the need to find new synthesis routes for both cyclic and high polymeric phosphazenes that contain alkyl or aryl groups bonded to the inorganic skeleton through P–C bonds. One route to accomplish this end is via the reactions of halocyclophosphazenes or halophosphazene high polymers with organometallic reagents.[5-12]

We have recently described[5] how hexachlorocyclotriphosphazene reacts with a number of Grignard reagents to yield two types of organophosphazenes—one in which alkyl groups are attached as substituents to a cyclophosphazene ring and the second in which phosphazene ring coupling occurs to yield bi(cyclophosphazenes) linked by P–P bonds, with each phosphorus at the linkage site bearing an alkyl or aryl group. Such bi(cyclophosphazenes) may be models for the cross-linked high polymers that are often formed when Grignard reagents react with high polymeric $(NPCl_2)_n$. It is speculated that the crosslinks may involve P–P bonds.

Phosphorus–phosphorus bonds can be cleaved by a variety of reagents. Hence, it seemed possible that bi(cyclophosphazenes)

(1) For a previous paper see: Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 716.
(2) See also: Allcock, H. R.; Fuller, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2250.
(3) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(4) Allcock, H. R. *Polymer* **1980**, *21*, 673.
(5) Harris, P. J.; Desorcie, J. L.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1981**, 852.
(6) Allcock, H. R.; Patterson, D. B.; Evans T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6095.
(7) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.*, **1981**, *103*, 2256.
(8) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
(9) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.
(10) Allen, C. W.; Toch, P. L. *Inorg. Chem.* **1981**, *20*, 8.
(11) Ranganathan, T. N.; Todd, S. M.; Paddock, N. L. *Inorg. Chem.* **1973**, *12*, 316.
(12) Biddlestone, M.; Shaw, R. A. *J. Chem. Soc. A* **1969**, 178; **1970**, 1750; **1971**, 2715.

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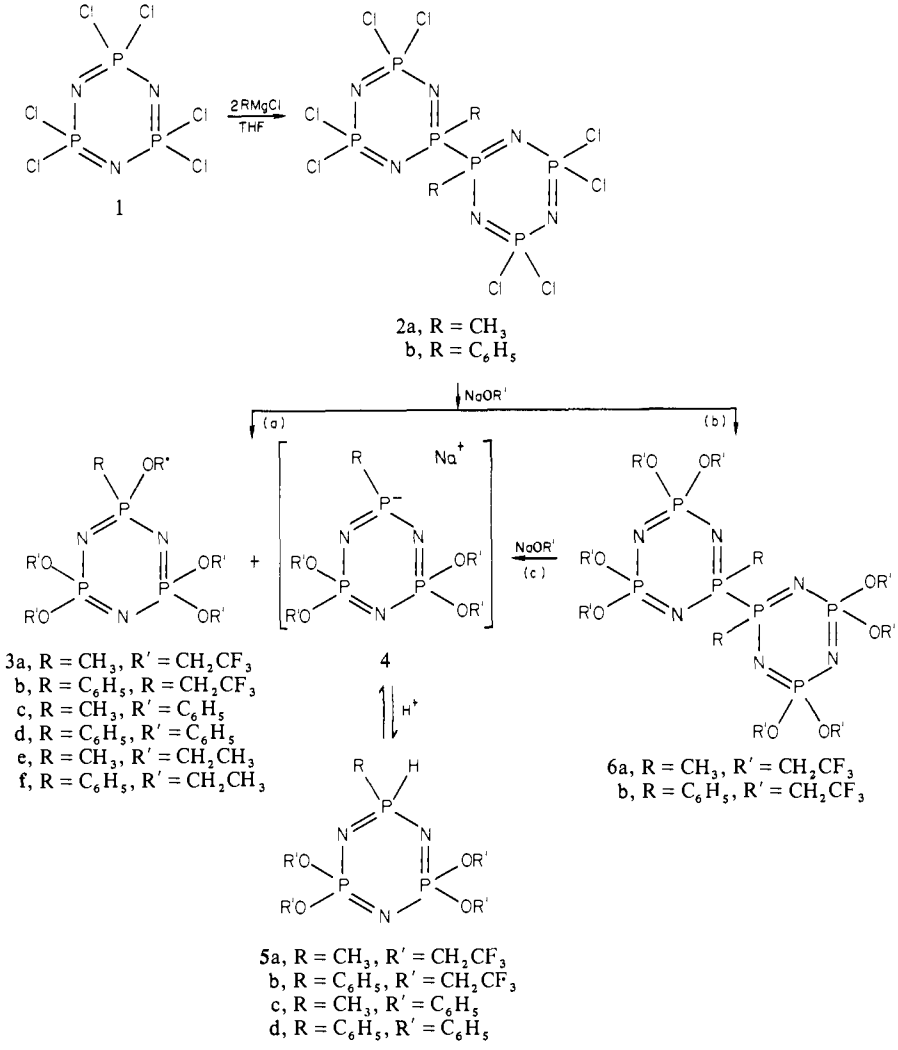
Scheme I



1

2a, R = CH_3
b, R = C_6H_5

3a, R = CH_3, R' = CH_2CF_3
b, R = C_6H_5, R = CH_2CF_3
c, R = CH_3, R' = C_6H_5
d, R = C_6H_5, R' = C_6H_5
e, R = CH_3, R' = CH_2CH_3
f, R = C_6H_5, R' = CH_2CH_3

4

6a, R = CH_3, R' = CH_2CF_3
b, R = C_6H_5, R' = CH_2CF_3

5a, R = CH_3, R' = CH_2CF_3
b, R = C_6H_5, R' = CH_2CF_3
c, R = CH_3, R' = C_6H_5
d, R = C_6H_5, R' = C_6H_5

might react with, for example, nucleophiles to yield hitherto inaccessible organocyclophosphazenes. At the same time such reactions could provide an insight into the mechanisms that occur when phosphazene high polymers such as $(NPCl_2)_n$ react sequentially with organometallic reagents and then with alkoxides or aryl oxides.[9,13,14]

In this study we have selected specific starting materials and reagents to yield the most useful information vis-à-vis the analogous macromolecular reactions. Thus, the cleavage of P–P bonds in bi(cyclophosphazenes) has been investigated with the use of sodium trifluoroethoxide, sodium phenoxide, and sodium ethoxide as cleavage reagents because these nucelophiles are used extensively in polymer substitution reactions. Moreover, two bi(cyclophosphazene) substrates were chosen, one with methyl groups attached to the two linked phosphorus atoms and the other with phenyl groups occupying the same sites. The opposing electronic characteristics and different steric factors of these two groups were expected to reveal mechanistic information.

Apart from these considerations, it was anticipated that the reactions of bi(cyclophosphazenes) with nucleophiles would supply important information about the nature of the P–P bond and its reactivity relative to P–Cl or P–N bonds. In particular, it was of interest to find out if such P–P bonds behave more like P^V–P^V bonds than the P^{III}–P^{III} bonds in diphosphines. And, in a practical sense, it was important to establish if the P–P cleavage reaction could be performed without the cleavage of P–Cl bonds also present. If so, it would provide a route to a valuable series of new polymerization "monomers".[4,15]

Results and Discussion

Overall Reactions. In this paper we will show that bi(cyclophosphazenes) such as **2** (Scheme I) react with alkoxides or aryl oxides to yield two main classes of product. In the first type of reaction, both P–P and P–Cl bonds are cleaved to form organocyclotriphosphazenes (**3**) and cyclotriphosphazene anions (**4**). These latter species react with proton sources to form hydridophosphazenes (**5**). In the second type of reaction, P–Cl bond cleavage occurs, but P–P bond cleavage does not. Thus, organobi(cyclophosphazenes) (**6**) are the main products. Which of these two pathways predominates depends on the type of nucleophile.

With excess trifluoroethoxide, both P–Cl and P–P bond cleavage occurred. Thus, **2a** and **2b** yielded **3a** and **3b**, respectively. Reaction conditions (**6**) summarized in Table I. No bi(cyclophosphazenes) **6** were recovered from these reactions. Sodium ethoxide behaved similarly. In the presence of an excess of this reagent, no species of type **6** were detected, and pathway a was followed exclusively. These reactions yielded **3e** and **3f**. Sodium phenoxide reacted with **2a** or **2b** to yield species of type **3c** or **3d** and bi(cyclophosphazene) derivatives (**6**). The relative predominance of pathway a or b (Scheme I) depended on the reaction times and stoichiometry and on the nature of the group R (see Table I). However, pathway b was favored strongly when R was CH_3. Apparently methyl groups adjacent to the site of ring linkage

(13) Evans, T. L.; Patterson, D. B.; Suszko, P. R.; Allcock, H. R. *Macromolcules* **1981**, *14*, 218.
(14) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201.
(15) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules* **1981**, *13*, 1332.

Table I. Reactions of Bi(cyclophosphazenes) with $NaOR'$[a]

bi(cyclic) precursor	reagent	equiv of reagent	reaction time,[d] h	% yields $N_3P_3(OR')_5R$	% yields $[N_3P_3(OR')_4(R)]_2$
$[N_3P_3Cl_4(CH_3)]_2$ (2a)	$NaOCH_2CF_3$	19		41[b] (3a)	
2a	$NaOC_6H_5$	12	12	11[b,c] (3c)	82[b,c] (6a)
2a	$NaOC_6H_5$	50	120	29[b] (3c)	30[b] (6a)
2a	$NaOCH_2CH_3$	20	48	36[b] (3e)	
$N_3P_3Cl_4(C_6H_5)]$ (2b)	$NaOCH_2CF_3$	19		46[b] (3b)	
2b	$NaOC_6H_5$	60	120	29[c] (3d)	15[c] (6b)
2b	$NaOCH_2CH_3$	20	48	38[b] (3f)	
$[N_3P_3(OC_6H_5)_4(CH_3)]_2$ (6a)	$NaOCH_2CF_3$	10	48	41[b] (7a)	
6a	$NaOC_6H_5$	20	48	20[b,c] (3c)	35[b,c] (6a)

[a] The % yield of each product was determined with the assumption that each bi(cyclophosphazene) species would react with $NaOR'$ to give 1 mol of the species $[N_3P_3(OR')_4(R)]_2$ and 2 mol of the species $[N_3P_3(OR')_5(R)]$. [b] % yield refers to the purified compound after isolation. [c] % yield refers to the % of that component in the mixture of reaction products as determined by ^{31}P NMR spectroscopy. These values were found to agree with the % yields of the purified compounds after isolation to within ±5% for representative cases. [d] Reactions were performed in THF (alkoxides) or 1,4-dioxane ($NaOC_6H_5$) at reflux.

protect the P–P bond against cleavage. Reasons for this will be discussed later.

Species **3** accounted for only half of the products derived from **2** by pathway a. The fate of the other half was presumed to be connected with the formation of a cyclophosphazene anion (**4**). Initially, the anion **4** contained unreacted P–Cl bonds, but these would be replaced by OR groups as the reaction progresses. However, although cyclophosphazene anions are known, they are generally unstable at temperatures above −60 °C.[7] Hence under the normal reaction conditions employed for the interaction of **2** with nucleophiles (66–101 °C), derivatives of **4** with P–Cl linkages would not be expected among the reaction products. However, hydridophosphazenes (**5**) were detected and these were presumed to be formed from **4**. Moreover, **5** could be isolated when species **6** was treated with sodium trifluoroethoxide and trifluoroethanol. This aspect is discussed in the next section.

Reactions of 6 with Sodium Trifluoroethoxide or Sodium Phenoxide. The formation of species such as **3** or **4** from **2** could take place by two alternative pathways. The most obvious route would be via pathway a, assuming that P–P bond cleavage is faster or concurrent with P–Cl bond cleavage. However, even if substitution (i.e., P–Cl bond cleavage) is fast compared to P–P cleavage, an alternative route exists for the formation of **3** and **4**. Substitution of **2** could occur to give **6**, and P–P cleavage of **6** could then take place to yield **3** and **4** (pathways b and c in Scheme I). An attempt was made, therefore, to find evidence for or against step c by the interaction of **6** with sodium trifluoroethoxide or phenoxide.

Reaction of **6a** or **6b** with an excess of sodium trifluoroethoxide gave 1-methyl- or 1-phenyl-1-(trifluoroethoxy)tetraphenoxycyclotriphosphazene (**7a** or **7b**) (Scheme II). Reaction of **6a** with an excess of sodium phenoxide gave 1-methylpentaphenoxycyclotriphosphazene (**3c**). Product **7a** was isolated in 41% yield (a maximum yield of 50% would be expected). However, unlike the reactions of **2a** with the bases, which took place at 25 °C, the reaction of **6** with base required the use of elevated temperatures. This effect was particularly evident when **6a** reacted with excess sodium phenoxide, probably a consequence of shielding of the P–P bond by bulky phenoxy groups. Hence, pathway c, while extremely useful from a synthetic viewpoint, appears to be only a minor contributor to the formation of **3** and **4** when **2** is the starting material. Few side reactions were evident in the conversion of **6a** to **7a** (Scheme II). Species **7a** appeared to be formed in more than 95% of the theoretical amount (based on ^{31}P NMR analysis of the reaction mixture), and mass spectral data indicated that only small amounts of phenoxy substituents had been displaced by trifluoroethoxy groups. This type of side group exchange is known from earlier work.[16]

The other half of the reaction product would be expected to be the cyclophosphazene anion (**4**). In fact, treatment of **6** with sodium trifluoroethoxide or phenoxide in the presence of excess trifluoroethanol or phenol yielded the hydridophosphazenes **5**. ^{31}P NMR analysis of the reaction mixture suggested that **5** was formed in roughly the same amounts as **7**.

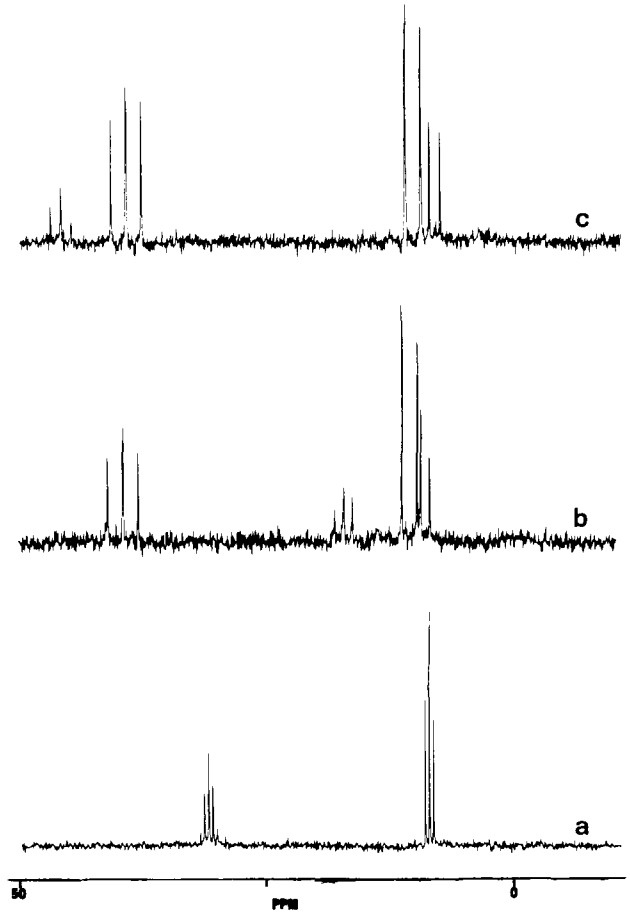


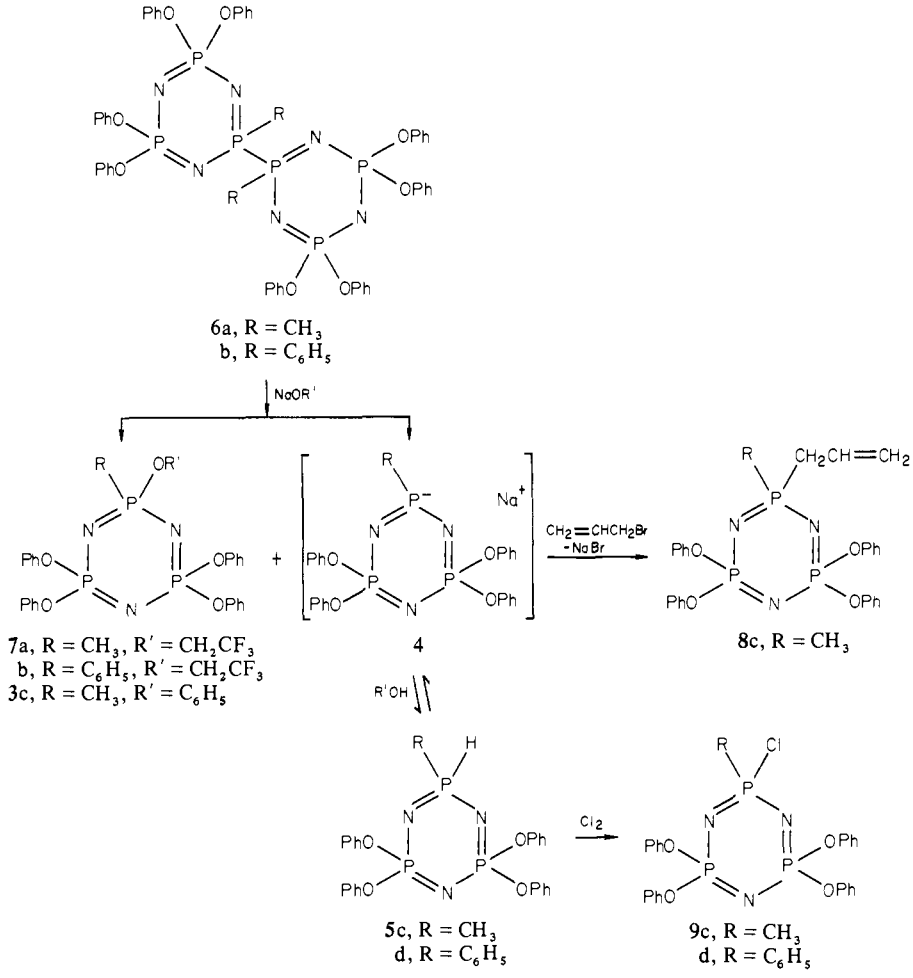
Figure 1. ^{31}P NMR spectral changes following the reaction sequence in Scheme II. Spectrum a is from the reaction mixture of **6a** in THF at 24 °C. Spectrum b was obtained after the addition of 12 equiv of sodium trifluoroethoxide and after 48 h in THF at reflux. Spectrum c was obtained after the mixture in CCl_4 was treated with excess chlorine.

Although the phosphazene hydrides could be detected directly, their presence was also confirmed indirectly by treatment of **5** with excess chlorine at 0 °C to yield **9**. These reactions were monitored readily by ^{31}P NMR analysis (see Experimental Section and Figure 1).

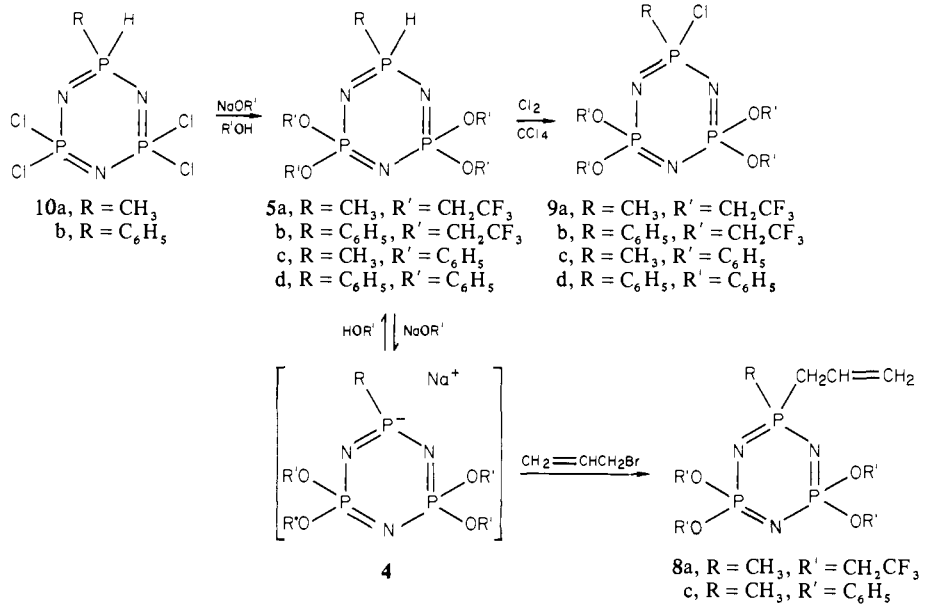
It should be noted that treatment of **2** with excess chlorine or bromine at 25 °C failed to cleave the P–P bond. Forcing reaction conditions (chlorination for 24 h in boiling carbon tetrachloride) were needed before **2a** could be converted to $N_3P_3Cl_5CH_3$, while **2b** was unreactive under the same conditions. Thus, it seems highly

(16) Allcock, H. R.; Smeltz, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 4143.

Scheme II



Scheme III



unlikely that **9** could be formed by direct chlorination of residual **6**, rather than via **4** and **5**. The addition of allyl bromide to the reaction mixture of **7** and **4** yielded a mixture of **7** and **8**. This also confirms that the anion **4** is a product of the reaction of **6** with base. Figure 1 illustrates the changes in the ^{31}P NMR spectra that accompany the reactions outlined in Scheme II.

Stability and Reactivity of the Cyclophosphazene Hydrides. Compounds of type **5** are unexpectedly stable, *even to water*. This constrasts with cyclophosphazene hydrides such as $N_3P_3Cl_4R(H)$ (**10**)[17] which decompose slowly in contact with the atmosphere. Apparently, if halogen atoms are not present elsewhere on the ring, one of the principal decomposition pathways is blocked. This is an important observation with respect to the extension of this work to high polymeric analogues. However, with species such as **10**, halogen replacement by nucleophiles can take place without

(17) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.

Table II. Reactions of Bi(cyclic) Compounds 2 with NaOR′ in the Presence of CCl_4[a]

starting material	reagent (NaOR′)	NaOR′, equiv	reaction time,[d] h	% yields $N_3P_3(OR')_5(R)$	% yields $[N_3P_3(OR')_4(R)]_2$
$[N_3P_3Cl_4(CH_3)]_2$ (2a)	$NaOCH_2CF_3$	24		89[b] (3a)	
2a	$NaOC_6H_5$	40	120	37[c] (3c)	51[c] (6a)
2a	$NaOC_6H_5$	80	96	28[c] (3c)	62[c] (6a)
$[N_3P_3Cl_4(C_6H_5)]_2$ (2b)	$NaOCH_2CF_3$	21		86[b] (3b)	
2b	$NaOC_6H_5$	40	120	64[c] (3d)	24[c] (6b)
2b	$NaOC_6H_5$	80	96	61[c] (3d)	25[c] (6b)

[a] The % yield of each product was determined with the assumption that each bi(cyclophosphazene) species would react with NaOR′ to give 1 mol of the species $[N_3P_3(OR')_4(R)]_2$ and 2 mol of the species $[N_3P_3(OR')_5(R)]$. [b] % yield refers to the purified compound after isolation. [c] % yield refers to the % of that component in the mixture of reaction products as determined by ^{31}P NMR spectroscopy. These values were found to agree with the % yields of the purified compounds after isolation to within ±5% for representative cases. [d] Reactions were performed in THF ($NaOCH_2CF_3$) or 1,4-dioxane ($NaOC_6H_5$) at reflux.

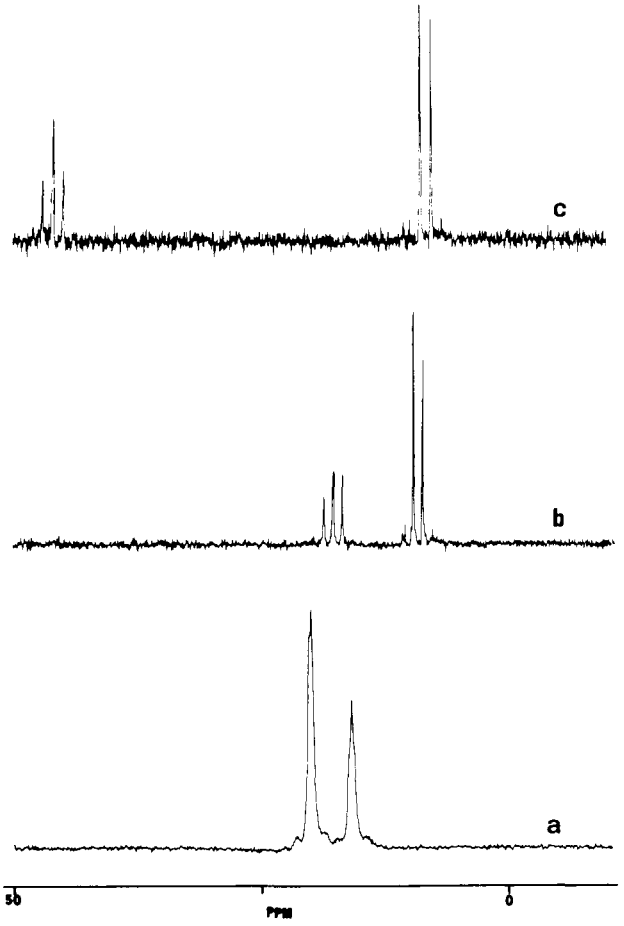
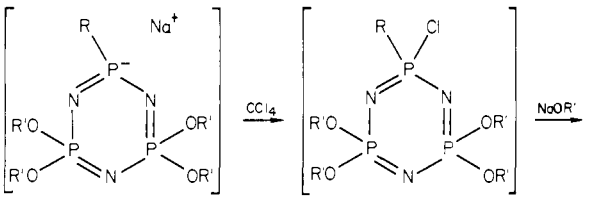


Figure 2. ^{31}P NMR spectral changes following the reaction sequence in Scheme III. Spectrum a is of **10a** in THF at 24 °C. Spectrum b is from the reaction mixture after the addition of 8 equiv of sodium phenoxide followed by 24 h in THF at reflux. Spectrum c is from the reaction mixture in CCl_4 after treatment with excess chlorine.

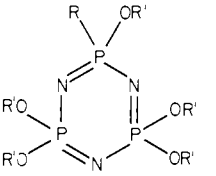
loss of the P–H bond (Scheme III). Thus, **10** reacts with sodium trifluoroethoxide or phenoxide in the presence of an excess of trifluoroethanol or phenol to yield **5**, which can be converted by reaction with chlorine to **9**, or (in the presence of base and alcohol) by interaction with allyl bromide to **8**. Compound **5c** was identical to the one formed by the reaction of **6a** with sodium trifluoroethoxide (Schemes I and II). The course of the reactions shown in Scheme III was monitored by ^{31}P NMR spectroscopy, and the results are shown in Figure 2. These spectroscopic changes are discussed in detail in the section on structure proof. Here it is sufficient to note that the data are compatible with the existence of an equilibrium between **4** and **5**. The presence of an equilibrium between **4** and **5** was suggested by allowing the P–D analogue of **10a** to react with sodium trifluoroethoxide or phenoxide in the presence of the appropriate alcohol. Each reaction led to a complete conversion to the P–H type species **5**.

Scheme IV



4

9a, R = CH_3, R′ = CH_2CF_3
b, R = C_6H_5, R′ = CH_2CF_3
c, R = CH_3, R′ = C_6H_5
d, R = C_6H_5, R′ = C_6H_5



3a, R = CH_3, R′ = CH_2CF_3
b, R = C_6H_5, R′ = CH_2CF_3
c, R = CH_3, R′ = C_6H_5
d, R = C_6H_5, R′ = C_6H_5

Reactions of 2 with NaOR and CCl_4. As illustrated earlier, the reaction of **2** with sodium trifluoroethoxide proceeds exclusively via pathway a (Scheme I) to yield, in principle, a 1:1 mixture of **3** and **4**. Of these two, only **3** can be isolated and characterized directly. However, the observation that species **4** could abstract H^+ to yield the hydridophosphazene suggested the possibility that **4** might be "captured" by reaction with other cation-releasing reagents, especially those that could liberate Cl^+. The P–Cl bond so formed would then undergo halogen replacement by the alkoxide nucleophile to generate additional quantities of **3**. A similar reaction is known when elemental phosphorus reacts with sodium alkoxide in the presence of carbon tetrachloride.[18]

When **2a** or **2b** was treated with excess sodium trifluoroethoxide in the presence of CCl_4, the yields of products **3a** or **3b** improved dramatically from <50% to >85% (Tables I and II). Furthermore, **2b** reacted with excess sodium phenoxide and CCl_4 to give a >60% yield of species **3d**. Although the use of sodium phenoxide and CCl_4 with **2a** did not increase the yield of **3c** significantly, the total yield of all phosphazene species was improved to >85%, presumably because decomposition of the anion **4** to irretrievable products (hydrides or ring-cleaved species) was reduced.

These results are compatible with a reaction sequence in which anion **4** abstracts a Cl^+ fragment from CCl_4 to give the transient species **9** (Scheme IV). This intermediate reacts rapidly with additional alkoxide to yield **3a–d**. This suggests that the P^V–P^V bond in bi(cyclophosphazenes) behaves in a similar manner to the P^{III}–P^{III} bonds in diphosphines or elemental phosphorus.

Other Aspects of the Mechanism. The overall mechanism outlined in Scheme I allows for two initial reaction pathways—

(18) Brown, H. C.; Hudson, R. F.; Wartew, G. A. *J. Chem. Soc., Chem. Commun.* **1978**, 7.

Table IV. NMR Data for Bi(cyclophosphazenes)

compd	^{31}P NMR, ppm		^{1}H NMR, δ		coupling const, Hz
	P(P)(R)	P(R′)$_2$			
$[N_3P_3Cl_4(CH_3)]_2$ (2a)	26.4	19.8	CH_3	1.9 (m)	$J_{PNP} < 2$ $\lvert J_{PCH} + J_{PPCH}\rvert = 8.8$ $J_{PNPCH} = 2.7$
$[N_3P_3Cl_4(C_6H_5)]_2$ (2b)	17.7	19.8	C_6H_5	7.7 (m)	$J_{PNP} < 2$
$[N_3P_3(OC_6H_5)_4(CH_3)]_2$ (6a)	29.9	6.8	CH_3 OC_6H_5	0.8 (m) 7.1 (m)	$\lvert J_{PNP} + J_{PPNP}\rvert = 26.5$ $\lvert J_{PCH} + J_{PPCH}\rvert = 9.6$ $J_{PNPCH} = 2.3$
$[N_3P_3(OC_6H_5)_4(C_6H_5)]_2$ (6b)	20.6	6.3	C_6H_5 OC_6H_5	7.0 (m) 7.0 (m)	$\lvert J_{PNP} + J_{PPNP}\rvert = 33.2$

pathways a and b. The relative ease of cleavage of P–Cl and P–P bonds by nucleophiles determined which pathway is followed. (No evidence was obtained that P–N bond cleavage occurs at this stage in the reaction.)

The course of the reaction was followed by ^{31}P NMR analysis. When **2b** reacted with sodium trifluoroethoxide at 25 °C, all of the bi(cyclophosphazene) was consumed by the time that 2 equiv of base had been added. The products at this stage possessed both P–Cl and P–OCH_2CF_3 units (detected by ^{31}P NMR spectroscopy). Product **3b** was identified in the mixture after 6 equiv of sodium trifluoroethoxide had been added, and the formation of **3b** was complete after the addition of 12 equiv. These results suggested that, *for this particular reaction*, P–P bond cleavage and P–Cl cleavage take place at comparable rates. However, the results do not distinguish between P–Cl or P–P cleavage as a *first* step. With sodium phenoxide used as a reagent, P–P bond cleavage can be slower than P–Cl cleavage, because reaction of **2a** or **2b** with excess sodium phenoxide yields **3c** and **3d**, together with the organo-substituted bi(cyclophosphazenes), **6a** or **6b**.

The cleavage of the P–P bond in compounds **2** was more facile when phenyl groups rather than methyl groups were present adjacent to the P–P bond (Tables I and II). Electron donation from methyl groups to the P–P bond could reduce the ease of nucleophilic attack at that site. A strong nucleophile such as trifluoroethoxide may overcome this influence and cause cleavage of the P–P bond, whereas a weaker nucleophile such as phenoxide may be less able to attack at this site. When phenyl groups are adjacent to the P–P bond, they may facilitate nucleophilic attack by withdrawing electrons from phosphorus. However, these are attacks on a nonpolar bond, and, therefore, nucleophilic attack by OR^- may not be the only rate-determining factor. Electrophilic attack by Na^+ may be important, yet we cannot differentiate between these two processes.

The reactivity of bi(cyclophosphazenes) **2** and **6** may also be rationalized through steric arguments. With phenyl groups adjacent to the P–P bond, strain is placed on the bond and it may be more prone to cleavage. In fact, Raman spectra[19] of the bi(cyclophosphazenes) **2** and **6** indicate that the strength of the P–P bond increases in the order: $[N_3P_3Cl_4Ph]_2 < [N_3P_3(OPh)_4Ph]_2 < [N_3P_3Cl_4Me]_2 < [N_3P_3(OPh)_4Me]_2$. Thus, the phenyl-substituted compounds have longer, weaker P–P bonds and are easier to cleave.

Proof of Structure. The two compounds of type **2** were identified by the presence of a strong parent ion at 580 or 704 amu, respectively, in the mass spectrum,[20] by strong absorbances in the 1100–1300-cm^{-1} region (P–N ring) of the infrared spectrum,[21,22]

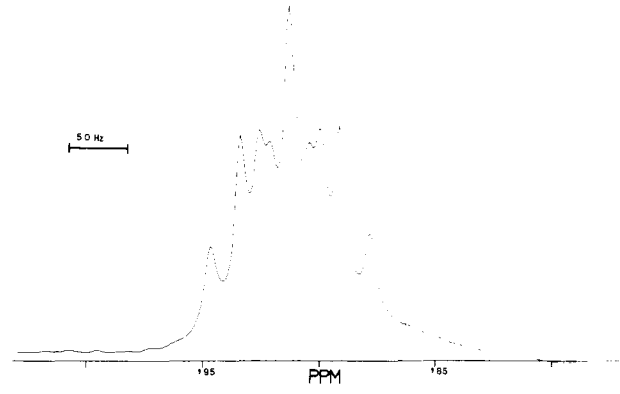


Figure 3. ^{1}H NMR spectrum at 200 MHz of $[N_3P_3Cl_4(CH_3)]_2$ (**2a**) in $CDCl_3$ at 24 °C.

by microanalysis,[23] and from the ^{31}P NMR spectra.[24] The ^{1}H NMR spectrum[25] of **2a** was interpreted as an $M_2X_3AA'X'_3M'_2$ spin system, with the CH_3 protons forming the X part of the spectrum[26] (Figure 3). An analysis of the coupling pattern is presented in Appendix A.

Organobi(cyclophosphazenes) of structure **6a** and **6b** showed a mass spectral parent ion at 1044 and 1168 amu, respectively. Strong infrared absorbances were evident at 1100–1300 cm^{-1} (P–N ring).[30] Microanalyses (Table III) were consistent with the two structures. The proton-decoupled ^{31}P NMR spectra (Table IV) were interpreted as $M_2AA'M_2$ spin systems and were classed as "deceptively simple" systems.[27-29] The ^{31}P resonance assigned to P(P)(R) units appeared as a multiplet downfield from the resonance for **1**. It broadened in the proton-undecoupled ^{31}P NMR spectrum due to unresolved P···H couplings. The position of resonance of the $P(OC_6H_5)_2$ units appeared as a multiplet upfield from **1** and remained virtually unchanged when proton decoupling was removed. An analysis of the couplings in this spin system is presented in Appendix B. The ^{1}H NMR spectrum of **6a** was interpreted as an $M_2X_3AA'X_3M'_2$ system, with the CH_3 protons forming the X component. An analysis of the couplings in this system is presented in Appendix A.

Cyclic trimers of types **3** and **7–9** were identified by the strong parent ions in the mass spectra (Table III), by strong infrared absorbances in the 1100–1300-cm^{-1} region (P–N ring),[30] by

(19) Raman spectra were recorded on a Jobin Yvon Raman HG2S spectrometer operating in the Fourier transform mode. The data were processed by using a Data General Nova III minicomputer. The laser source was a Spectra Physics argon-ion laser (Model 164). The Raman spectra of the bi(cyclotriphosphazenes) (**2**) and organobi(cyclotriphosphazenes) (**6**) showed absorbances as follows. **2a** (solid): 280 cm^{-1} (ν(PP)). **2b** (solid): 240 cm^{-1} (ν(PP)). **6a** (solid): 293 cm^{-1} (ν(PP)). **6b** (solid): 267 cm^{-1} (ν(PP)).

(20) Mass spectral data were obtained with the use of an AEI-MS-902 spectrometer.

(21) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972; Chapter 3.

(22) Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Samples were examined in the form of KBr disks or between NaCl plates.

(23) Microanalyses were obtained by Galbraith Laboratories.

(24) ^{31}P NMR spectra were recorded on a JEOL-PS-100 spectrometer operating at 40 MHz in the Fourier transform mode or were obtained with the use of a Varian CFT-20 spectrometer operating at 32 MHz in the Fourier transform mode. The data were processed by using a Nicolet 1080 computer or the computer contained within the CFT-20 spectrometer. Positive chemical shifts are downfield from external phosphoric acid.

(25) ^{1}H NMR spectra of **2**, **5**, **6**, **7**, and **9** were recorded on a Bruker WP-200 spectrometer operating at 200 MHz in the Fourier transform mode. The data were processed by using the computer contained within the WP-200 spectrometer. All other ^{1}H NMR spectra were recorded on a Varian EM-360 spectrometer operating at 60 MHz. Positive chemical shifts were downfield from tetramethylsilane at δ 0.

(26) Schmidpeter, A.; Hogel, J.; Ahmed, F. R. *Chem. Ber.* **1976**, *109*, 1911.

(27) Becker, E. D. "High Resolution NMR Theory and Chemical Applications"; Academic Press: New York, 1980.

(28) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

(29) Finer, E. G.; Harris, R. K. *Mol. Phys.* **1967**, *5*, 457.

Table V. NMR Data for Trimeric Phosphazenes

compd	^{31}P NMR, ppm A	^{31}P NMR, ppm B	^{1}H NMR, δ		coupling const, Hz
$N_3P_3(OCH_2CF_3)_5(CH_3)$ (3a)	39.8	15.6	CH_3	1.6 (d, t)	J_{PNP} = 47.9
			OCH_2CF_3	4.2 (m)	J_{PCH} = 17.0
					J_{PNPCH} = 2.1
$N_3P_3(OCH_2CF_3)_5(C_6H_5)$ (3b)	29.2	16.1	OCH_2CF_3	4.2 (m)	J_{PNP} = 53.0
			C_6H_5	7.6 (m)	other couplings unresolved
$N_3P_3(OC_6H_5)_5(CH_3)$ (3c)	35.0	7.9	CH_3	1.2 (d, t)	J_{PNP} = 49.4
			OC_6H_5	7.1 (m)	J_{PCH} = 17.1
					J_{PNPCH} = 1.2
$N_3P_3(OC_6H_5)_5(C_6H_5)$ (3d)	24.4	8.2	OC_6H_5	7.1 (m)	J_{PNP} = 53.9
			C_6H_5	7.1 (m)	
$N_3P_3(OCH_2CH_3)_5(CH_3)$ (3e)	35.3	15.9	CH_3	1.6 (d, t)	J_{PNP} = 44.2
			OCH_2CH_3	1.3 (t)	J_{PCH} = 16
			OCH_2CH_3	4.0 (m)	J_{HCCH} = 7
					J_{POCH} = 3
					J_{PNPCH} = 2
$N_3P_3(OCH_2CH_3)_5(C_6H_5)$ (3f)	25.8	16.5	OCH_2CH_3	1.2 (m)	J_{PNP} = 50.4
			OCH_2CH_3	4.0 (m)	J_{HCCH} = 7
			C_6H_5	7.6 (m)	J_{POCH} = 3
$N_3P_3(OCH_2CF_3)_4(CH_3)(H)$ (5a)	17.2	15.0	CH_3	1.59 (d, m)	J_{PH} = 542
			OCH_2CF_3	4.25 (m)	J_{PNP} = 30.6
			H	7.34 (d, m)	J_{PCH} = 15.5
					J_{HPCH} = 2.2
					other couplings unresolved
$N_3P_3(OCH_2CF_3)_4(C_6H_5)(H)$ (5b)	12.4	14.9	OCH_2CF_3	4.24 (m)	J_{PH} = 571
			C_6H_5	7.67 (m)	J_{PNP} = 32.2
			H	7.80 (d, m)	other couplings unresolved
$N_3P_3(OC_6H_5)_4(CH_3)(H)$ (5c)	16.2	7.3	CH_3	1.26 (d, m)	J_{PH} = 540
			H	7.20 (d, m)	J_{PNP} = 28.4
			OC_6H_5	7.26 (m)	J_{PCH} = 15.4
					J_{PNPH} = 11.0
					J_{PNPCH} = 5.0
					J_{HCPH} = 2.8
$N_3P_3(OC_6H_5)_4(C_6H_5)(H)$ (5d)	12.1	7.1	OC_6H_5	7.19 (m)	J_{PH} = 562
			C_6H_5	7.19 (m)	J_{PNP} = 30.3
			H	7.60 (d, m)	other couplings unresolved
$N_3P_3(OC_6H_5)_4(OCH_2CF_3)(CH_3)$ (7a)	38.5	8.7	CH_3	1.19 (d, t)	J_{PNP} = 49.2
			OCH_2CF_3	3.05 (m)	J_{PCH} = 17.7
			OC_6H_5	7.22 (m)	J_{FCCH} = 8.3
					J_{POCH} = 7.2
					J_{PNPCH} = 1.29
$N_3P_3(OC_6H_5)_4(OCH_2CF_3)(C_6H_5)$ (7b)	28.2	9.5	OCH_2CF_3	3.26 (m)	J_{PNP} = 53.2
			OC_6H_5	7.24 (m)	J_{FCCH} = 8.3
			C_6H_5	7.24 (m)	J_{POCH} = 7.0
$N_3P_3(OCH_2CF_3)_4(C_3H_5)(CH_3)$ (8a)	37.9	15.5	CH_3	1.6 (d, t)	J_{PNP} = 27.3
			$CH_2CH=CH_2$	2.6 (m)	J_{PCH} = 15
			OCH_2CF_3	4.2 (m)	J_{HCCH} = 7
			$CH_2CH=CH_2$	5.4 (m)	other couplings unresolved
$N_3P_3(OC_6H_5)_4(C_3H_5)(CH_3)$ (8c)	36.5	8.0	CH_3	1.1 (d, t)	J_{PNP} = 26.0
			$CH_2CH=CH_2$	2.1 (m)	J_{PCH} = 16
			$CH_2CH=CH_2$	5.1 (m)	J_{HCCH} = 7
			OC_6H_5	7.1 (m)	J_{PNPCH} = 2
$N_3P_3(OCH_2CF_3)_4(CH_3)(Cl)$ (9a)	47.6	14.7	CH_3	2.09 (d, t)	J_{PNP} = 32.4
			OCH_2CF_3	4.26 (m)	J_{PCH} = 17.7
					J_{PNPCH} = 2.2
					other couplings unresolved
$N_3P_3(OCH_2CF_3)_4(C_6H_5)(Cl)$ (9b)	37.7	14.8	OCH_2CF_3	4.3 (m)	J_{PNP} = 39.0
			C_6H_5	7.7 (m)	other couplings unresolved
$N_3P_3(OC_6H_5)_4(CH_3)(Cl)$ (9c)	45.7	6.4	CH_3	1.76 (d, t)	J_{PNP} = 33.0
			OC_6H_5	7.21 (m)	J_{PCH} = 17.7
					J_{PNPCH} = 2.1
$N_3P_3(OC_6H_5)_4(C_6H_5)(Cl)$ (9d)	36.4	6.5	OC_6H_5	7.4 (m)	J_{PNP} = 40.0
			C_6H_5	7.4 (m)	

microanalysis or high-resolution mass spectrometry (Table III), and from the ^{1}H and ^{31}P NMR spectra. The proton-decoupled ^{31}P NMR spectra (Table V) were interpreted as simple AB_2 spin systems. The A resonance appeared downfield from that of **1**, between 24.4 and 47.6 ppm, and was broadened in the proton-undecoupled spectra because of unresolved P···H couplings. The resonance position for the B-type phosphorus atoms was between 6.4 and 16.5 ppm (Table V). It was virtually unaffected when proton decoupling was removed.

Hydridocyclotriphosphazenes **5** were identified by the presence of strong parent ions in the mass spectra (Table III), by the presence of strong infrared absorbances in the 1100–1300-cm^{-1} region (P–N ring) and medium-intensity absorbances in the 2300–2450-cm^{-1} region (P–H stretch),[30] by microanalysis or high-resolution mass spectrometry (Table III), and from ^{1}H and ^{31}P NMR spectra (Table V). The proton-decoupled ^{31}P NMR spectra were interpreted as simple AB_2 spin systems, essentially similar to those of **3** and **7–9** (see Table V). The proton-undecoupled ^{31}P NMR spectra showed the A resonance split into a

(30) A summary of infrared data will be found in the supplementary material section, recorded in the microfilm edition.

doublet (J_{PH} = 531–549 Hz for **5a–d**), with additional fine structure from the PNP and PCH couplings. In the phosphorus-undecoupled ^1H NMR spectrum, the hydride resonance appeared as a doublet (J_{PH} = 540–571 Hz for **5a–d**), with additional fine structure from the PNPH and HCPH couplings. Additional proof of structure was obtained by the conversion of species **5** to compounds **9** by treatment with chlorine.

Identification of intermediates and products formed from the organobi(cyclophosphazene) derivatives, **6**, was accomplished by following the changes in ^{31}P NMR spectra. Thus, as shown in Figure 1, the reaction of **6a** with sodium trifluoroethoxide and subsequent treatment of the products with chlorine could be followed. Multiplets centered at 30.4 and 7.6 ppm (in Figure 1a) were assigned to P(P)(R) and $P(OR')_2$ resonances, respectively, in **6a**. Peaks at 39.4 and 9.7 ppm (Figure 1b) are characteristic of species **7a**, and those at 16.7 and 8.2 ppm indicate the presence of **5c**. After the reaction with chlorine, resonances at 45.6 and 7.2 ppm (Figure 1c) indicated the presence of **9c**. The spectra in Figure 1 demonstrate how clean these reactions are and that little or no ring cleavage takes place.

Similarly, the reaction of the hydridocyclotriphosphazene **10a** with sodium phenoxide, and the subsequent chlorination of the products, is illustrated in Figure 2. Peaks at 19.0 and 14.9 ppm (Figure 2a) were assigned to **10a**. Resonances at 16.7 and 8.2 ppm (Figure 2b) indicated the presence of **5c**. Treatment with chlorine was followed by the appearance of peaks at 45.5 and 7.3 ppm (Figure 2c) from **9c**. The spectra indicated that these transformations were virtually 100% complete.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was supplied by Ethyl Corp. and was purified by sublimation, followed by recrystallization from *n*-hexane to a final melting point of 111.5–112.5 °C. Trifluoroethanol (Halocarbon Products), phenol (Baker) and allyl bromide (Aldrich) were used as received. The Grignard reagents (Aldrich or Alfa-Ventron) and $LiBEt_3H$ (Aldrich) were used as received. Tetrahydrofuran (THF) was distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium benzophenone ketyl drying agent. Tetrachloromethane and 1,4-dioxane (Fisher Corp.) were distilled from phosphorus pentoxide or sodium metal, respectively. All reactions were performed under an atmosphere of dry nitrogen.

Preparation of 1,1′-Dimethyl and 1,1′-Diphenyl-3,3,3′,3′,5,5,5′,5′-octachlorobi(cyclotriphosphazene) (2a and 2b). The following is a typical procedure. Hexachlorotriphosphazene (10.0 g, 0.029 mol) was stirred in boiling THF (125 mL), and methylmagnesium chloride (19.5 mL of a 2.9 M solution in THF) was added dropwise over a period of 1 h. The reaction mixture was then stirred at reflux for an additional 1 h, and the solution was allowed to cool to room temperature. The solvent was removed at reduced pressure, and the product was purified by filtration of a solution in CH_2Cl_2 through silica gel. The solvent was removed under reduced pressure, and the crude product was washed with hot hexanes (2 × 100 mL) to remove any trimeric species. Evaporation of the solvent under reduced pressure left the product **2a** as a white solid (5.9 g, 70%). Characterization data for this compound are listed in Tables III and IV. Infrared peaks were detected (KBr) at 2970 (m), 2870 (m) (ν(CH)), 1280 (s), 1170 (vs), 1120 (s) (ν(PN)), and 590 (vs), 555 (vs) (ν(PCl)). Compound **2b** was recovered in 60% yield and was characterized fully by methods analogous to those used for **2a**.[5] The crude product was washed with hot hexanes (2 × 100 mL) to remove biphenyl. Infrared peaks were detected (KBr) at 3050 (vw) (ν(CH)), 1180 (vs), 1115 (s) (ν(PN)), and 575 (vs), 510 (vs), (ν(PCl)).[12]

Reactions of 2a and 2b with Sodium Trifluoroethoxide, Sodium Phenoxide, or Sodium Ethoxide. These reactions were all carried out in a similar manner. Specific reaction conditions are summarized in Table I. The following procedure is typical. A solution of sodium trifluoroethoxide was prepared from sodium (0.72 g, 0.031 mol) and trifluoroethanol (15.5 g, 0.155 mol) in THF (50 mL). To this was added slowly a solution of **2a** (1.5 g, 2.59 mol) in THF (50 mL). The solution was then stirred for 24 h at 24 °C. A ^{31}P NMR spectrum of the reaction mixture suggested that **2a** had been converted quantitatively to **3a** and **5a**. The reaction mixture was poured into water (200 mL) and was extracted with diethyl ether (2 × 100 mL). The extract was dried over magnesium sulfate, and the solvent was removed at reduced pressure to yield a mixture of the products (total yield, 75%). Purification of the product mixture by chromatography using silica gel or alumina gave exclusively **3**, with decomposition of the hydridocyclotriphosphazenes **5**. However, compounds **5** were identified unambiguously by comparison with authentic samples prepared by the reaction of **10** with excess sodium trifluoroethoxide or sodium phenoxide (see a later section). When **2a** or **2b** was allowed to react with sodium phenoxide, excess phenol was removed by sublimation at 50 °C (0.02 torr) during the purification process.

Preparation of 1,1′-Dimethyl-3,3,3′,3′,5,5,5′,5′-octaphenoxybi(cyclotriphosphazene) (6a). Compound **2a** was allowed to react with 12 equiv of sodium phenoxide in boiling dioxane for 12 h. Purification was effected by recrystallization from diethyl ether. Characterization data and yields of **6a** are listed in Tables I, III, and IV. Species **6b** could not be prepared in high yield by the same technique, and the products were $N_3P_3(OC_6H_5)_4(C_6H_5)Cl$ and **3c**.

Reactions of 6 with Sodium Trifluoroethoxide or Phenoxide. The following is a typical procedure. Specific reaction conditions for other examples are listed in Table I. A solution of **6a** (1.0 g, 0.96 mmol) in THF (25 mL) was added slowly to a solution of sodium trifluoroethoxide in THF (50 mL). The reaction mixture was then heated to reflux for 48 h, was cooled to room temperature, and was poured into water (200 mL). Extraction with diethyl ether (2 × 100 mL) and drying of the extract over $MgSO_4$, followed by removal of the ether at reduced pressure, yielded a mixture of **7a** (0.47 g, 41%) and **5c** (0.32 g, 27%). The ratio of products was deduced by ^{31}P NMR analysis of the mixture. When sodium phenoxide was used as a reagent, the excess phenol was removed by sublimation at 50 °C (0.02 torr) from the ether-extraction residue.

Reactions of 6 with Sodium Trifluoroethoxide or Phenoxide, Followed by Addition of Excess Chlorine. The same procedure was used as described in the preceding section. After the reaction was completed, the mixture was poured into water (200 mL) and was extracted with diethyl ether (2 × 100 mL). The extract was dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was dissolved in CCl_4 (25 mL). Excess chlorine was then bubbled through the extract at 0 °C for 5 min, and the solution was stirred for 12 h. A ^{31}P NMR analysis of the mixture showed that **5c** had been converted completely to **9c**. The ^{31}P NMR spectrum was identical with that of a sample prepared from $N_3P_3Cl_4(CH_3)H$, sodium phenoxide, and chlorine (see a later section).

Reactions of 6a with Sodium Trifluoroethoxide or Phenoxide, Followed by Addition of Excess Allyl Bromide. The same reaction conditions were used as described for the reaction of **6a** with alkoxide or aryl oxide. However, following cooling of the reaction mixture to room temperature, allyl bromide (5 mL) was added and the mixture was heated to reflux for 12 h. On the basis of ^{31}P NMR spectra, it was deduced that **5** had been transformed quantitatively to **8** via the anion **4**. This transformation could also be accomplished after several days reaction at 25 °C. Compounds **8** were identified by comparison with an authentic sample prepared by the reaction of $N_3P_3Cl_4(CH_3)(CH_2CH{=}CH_2)$ with excess sodium phenoxide or sodium trifluoroethoxide.

1-Hydrido- and 1-Deuterio-1-methyltetrachlorocyclotriphosphazene (10a). These compounds were prepared by a synthetic procedure reported previously.[17]

1-Hydrido-1-phenyltetrachlorocyclotriphosphazene (10b). This compound was prepared by the interaction of **2b** with $LiBEt_3H$ in THF at 0 °C, followed by filtration through silica gel.

Reactions of 10 with Sodium Trifluoroethoxide or Phenoxide. The following is a typical procedure. A solution of **10a** (1.1 g, 3.7 mmol) in THF (10 mL) was added slowly to a solution of sodium trifluoroethoxide, itself prepared from sodium (0.52 g, 0.023 mol) and trifluoroethanol (8.0 g, 0.08 mol) in THF (50 mL) at 0 °C. The reaction mixture was then stirred for 24 h at 0 °C. A ^{31}P NMR analysis of a sample from this mixture indicated that **10a** had been converted quantitatively to **5a**. The mixture was poured into water (100 mL) and was extracted with diethyl ether (2 × 100 mL). The extract was dried over $MgSO_4$, and the solvent was removed at reduced pressure to leave **5a** as an oil (1.36 g, 68%). Compound **10a** reacted with sodium phenoxide in boiling THF for 24 h. In this case, the excess phenol was removed by sublimation at 50 °C (0.02 torr), and the product was purified by filtration of a solution in CH_2Cl_2 through silica gel to give **5c** (1.69 g, 63%).

Reactions of 10a with Sodium Trifluoroethoxide or Phenoxide, Followed by Treatment with Excess Allyl Bromide. After the conversion of **10a** to **5** was complete (as described above), allyl bromide (5 mL) was added to the reaction mixture. After several days at 25 °C or several hours at reflux temperature, resonances corresponding to compounds **8** appeared in the ^{31}P NMR spectrum. The reaction solvent was removed at reduced pressure and the products in CH_2Cl_2 were purified by filtration through neutral alumina. (Products **8** were identified by comparison with authentic samples prepared from the reaction of $N_3P_3Cl_4(CH_3)(CH_2CH{=}CH_2)$[8] with sodium trifluoroethoxide or phenoxide. Typical yields were 93% and 91%, respectively.)

Reactions of the Deuterio Analogue of 10a with Sodium Trifluoroethoxide or Phenoxide. These reactions were carried out as described above

for **10a**. The deuterio derivative was prepared by treatment of the copper–phosphazene intermediate with DO-*i*-C_3H_7.[17] Incorporation of the deuterium was confirmed by ^{31}P NMR spectroscopy (J_{PD} = 87 Hz in THF) and electron-impact mass spectrometry (>86% D). After treatment with trifluoroethoxide or phenoxide, the product was nondeuterated **5**.

Reactions of 5 with Excess Chlorine. The following procedure is typical. Compound **5a** was dissolved in CCl_4 (25 mL), and chlorine was bubbled through the solution for 5 min at 0 °C. The ^{31}P NMR spectrum of the solution was compatible with a 100% conversion of **5** to **9** after this time. The mixture was stirred for 1 h, the solvent was removed, and the product was purified by filtration of a solution in CH_2Cl_2 through neutral alumina to give **9a** (53%). The yields of compounds **9b–d** were 70, 45, and 74%, respectively.

Reactions of 2a and 2b with Excess Chlorine. The following is a typical procedure. Excess chlorine was bubbled for 24 h through a solution of **2a** (3.0 g, 5.2 mmol) in CCl_4 (125 mL). A ^{31}P NMR spectrum at this stage was indicative of unreacted **2a** only. Similarly, no reaction was evident following ultraviolet irradiation. However, at reflux temperature in CCl_4, **2a** underwent chlorination to yield $N_3P_3Cl_5(CH_3)$ (1.0 g, 61%). This product was identified by comparison with an authentic sample prepared by another route.[31] Compound **2b** did not react under the same conditions. No reaction could be detected with excess bromine at 25 °C after 24 h.

Reactions of 2a or 2b with Sodium Trifluoroethoxide or Phenoxide in the Presence of CCl_4. All of these reactions were carried out in a similar manner. Table II contains a summary of specific reaction conditions. A solution of **2b** (4.0 g, 5.7 mmol) in 1:1 v/v THF/CCl_4 (100 mL) was added slowly to a solution of sodium trifluoroethoxide. The reaction mixture was then stirred for 24 h at 24 °C. The mixture was poured into water (200 mL) and was extracted with diethyl ether (2 × 250 mL). The extract was dried over $MgSO_4$, and the solvent was removed at reduced pressure to leave crude **3b**. This was purified by filtration of a solution in CH_2Cl_2 through neutral alumina to give **3b** as an oil (6.9 g, 86%). In the reactions of **2a** or **2b** with sodium phenoxide, excess phenol was removed by sublimation at 50 °C (0.02 torr) during the purification process and the products were separated by fractional recrystallization from diethyl ether.

Attempted Reactions of 6a with Sodium Trifluorethoxide or Phenoxide in the Presence of CCl_4. These reactions were incomplete because of the more facile reaction of the sodium alkoxide or aryl oxide with CCl_4 at the elevated temperatures needed for these interactions. After removal of unreacted material, small amounts of cyclic trimeric P–P cleavage products were detected.

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Registry No. 1, 940-71-6; **2a**, 80241-37-8; **2b**, 21229-71-0; **3a**, 75155-07-6; **3b**, 81098-36-4; **3c**, 75155-13-4; **3d**, 81098-37-5; **3e**, 81098-38-6; **3f**, 81098-39-7; **5a**, 81098-40-0; **5b**, 81098-41-1; **5c**, 81098-42-2; **5d**, 81098-43-3; **6a**, 81098-44-4; **6b**, 81120-75-4; **7a**, 81098-45-5; **7b**, 81098-46-6; **8a**, 81098-47-7; **8c**, 81098-48-8; **9a**, 81098-49-9; **9b**, 81098-50-2; **9c**, 81098-51-3; **9d**, 81098-52-4; **10a**, 68351-74-6; **10b**, 81098-53-5; $N_3P_3(OC_6H_5)_4(C_6H_5)Cl$, 81098-52-4; $[N_3P_3(OPh)_4(CH_3)][N_3P_3(OPh)_4(C_4H_9)]$, 81098-54-6; $[N_3P_3Cl_4(CH_3)][N_3P_3Cl_4(C_4H_9)]$, 81098-55-7; $NaOCH_2CF_3$, 420-87-1; $NaOC_6H_5$, 139-02-6; $NaOCH_2CH_3$, 141-52-6; allyl bromide, 106-95-6.

Supplementary Material Available: A compilation of infrared characterization data; Table III, characterization data including melting point, mass spectral, and elemental analysis data; Appendix A, an interpretation of the ^1H NMR couplings in the spectra of **2a** and **6a**, and Appendix B, an interpretation of the ^{31}P NMR couplings in the spectra of **6a** and **6b** (7 pages). Ordering information is given on any current masthead page.

(31) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.

(32) Letcher, J. H.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 247.

(33) For comparison, an asymmetric bi(cyclophosphazene) $[N_3P_3(OPh)_4(CH_3)][N_3P_3(OPh)_4(n\text{-}C_4H_9)]$ was prepared from $[N_3P_3Cl_4(CH_3)][N_3P_3Cl_4(n\text{-}C_4H_9)]$ by the method used to prepare **6a**. This compound showed a parent ion at 1086 amu in the mass spectrum and absorbances at 1200 (s), 1175 (sh), and 1160 cm^{-1} (ν(PN)) in the infrared spectrum. The 81.0-MHz ^{31}P NMR spectrum was not expected to exhibit such a high degree of "deceptive simplicity" due to asymmetry which would make the sets of P(P)R and $P(OPh)_2$ nuclei nonchemical shift equivalent. The spin system was interpreted as M_2ABN_2. The A and B resonances were multiplets centered at 31.81 and 32.38 ppm, respectively, while the M and N parts of the spin system were centered at 7.43 and 7.75 ppm (from the $[N_3P_3(OPh)_4(CH_3)]$ and $[N_3P_3(OPh)_4(n\text{-}C_4H_9)]$ fragments), respectively. Interestingly, the M part was a 1:2:1 triplet, while the N part was a 1:1:1:1 quartet and each part was "deceptively simple". The average coupling $N = |J_{PNP} + J_{PPNP}|$ was found to be 25.6 and 20.4 Hz for the M and N parts of the spin system. The value of N for the M part ($[N_3P_3(OPh)_4(CH_3)]$) of the spin system agrees closely to that found for **6a** (26.5 Hz). An analysis of this part of the spin system indicated that $J_{MB} = J_{PPNP} \simeq 7.4$ Hz and $|J_{PP}| > 168$ Hz. This is also consistent with the respective couplings determined for **6a**.

(34) No parent ion was observed in the high-resolution mass spectra of **9a** and **9b** due to the difficulty of resolution needed to separate it from fragment ions of perfluorokerosene at 580.9633 and 642.9601 amu, respectively. However, a parent ion was observed for ^{37}Cl-substituted **9b** at 644.9575 amu (calcd 644.9586 amu).

Decarbonylation of Tetrahydrofuran-2-carboxylic Acids and Tetrahydropyran-2-carboxylic Acids in Concentrated Sulfuric Acid: Formation of Oxonium Ions

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Abstract: Tetrahydrofuran-2-carboxylic acids **1**, **3**, and **5** readily decarbonylate in 96% sulfuric acid, generating stable oxonium ions **2**, **4**, and **6**, respectively. Analogously, tetrahydropyran-2-carboxylic acids **7**, **9**, **12**, and **14a** produce oxonium ions **8**, **10**, **13**, and **15**, respectively. These oxonium ions are quite stable, with the exception of **10**, which partially isomerizes to **11**, and **13**, which rearranges to ions **17** and **21**. Details in the transformation of oxonium ion **15** into lactone **23** by way of open chain acid **22a** were elucidated.

Unsaturated oxonium ions are important intermediates in numerous reactions and have been prepared by a variety of methods.[1] The synthetic utility of unsaturated oxonium ions resides in their reactivity with oxygen and carbon nuleophiles. It occurred to us

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