The calculation resulted in a ^1A_g ground state with a gap energy between the highest occupied and lowest unoccupied MO of 3.21 eV. The charge on the nickel atom was 0.16. The final electron configuration of the nickel atom was $(3d)^{9.61}$ $(4s)^{0.51}$ $(4p)^{-0.28}$. The −0.28 for 4p is physically impossible. It represents the sum of many antiboding interactions, primarily between the nickel 4p AO's and the boron 2s AO's. The orbital exponents were not altered here, however, since this effect could result from the nature of the Mulliken approximation in the partitioning of electron density.[33] One cannot say that the 4p AO's are not important in bonding since some occupied MO's have appreciable density in these orbitals. Some insight into the nature of the metal–ligand bonding is obtained on examining the overlap populations between the nickel atom and the eight borons to which it bonds. The overlap population subtotals for the nickel AO's are 0.23 for Ni (3d), 0.90 for Ni (4s), and 0.02 for Ni (4p). Clearly the bonding primarily involves the Ni (4s) orbital. Examination of individual overlaps shows that the primary nickel bonding to B(5) [B(10)] is between the 4s of Ni and the 2s, $2p_x$, and $2p_z$ of B(5) in decreasing order of importance. For B(6) [B(9)] it is between 4s of Ni and the 2s, $2p_y$, and $2p_z$ of B(6) in decreasing order of importance.

The highest occupied and lowest unoccupied MO's are both of B_u symmetry. Interestingly, the only metal AO's of the proper symmetry to contribute to these MO's are $4p_x$ and $4p_z$. The largest electron density in the highest occupied MO is in the metal p_x and p_z AO's and in the ligand p_x and p_z AO's of B(5) [B(10)]. This is reflected in the larger overlap population and shorter distance between Ni and B(5). The first unoccupied MO puts the electron density primarily in the metal p_x (and a smaller amount in p_z) and in the ligand p_z AO of B(6) [B(9)]. The calculations suggest that a two-electron oxidation of the anion would lead to more nearly equal Ni–B bond lengths at the Ni–B(6) distance, whereas a two-electron reduction might lead to more nearly equal lengths at the Ni–B(5) distance.

The ligand displacement in the *XZ* plane is a delicate balance between the nature of the metal (which influences the overlap strengths and the number of electrons available) and the nature of the ligand (both symmetry and electron availability are important). Here the symmetry of the molecule forces restrictions on the relative positions of the two fused polyhedra (the mirror plane prohibits movement along the *Y* axis). In general, maximizing the metal–ligand overlap (within the molecular symmetry contraints) can lead to slippage of the two polyhedra relative to the metal–ligand axis.[34]

The individual atoms charges are as follows: −0.05 for B(1), +0.09 for B(2), +0.10 for B(3), −0.02 for B(5), +0.20 for B(6), +0.17 for B(7), −0.16 for H(1), −0.24 for H(2), −0.18 for H(3), −0.21 for H(5), −0.22 for H(6), −0.19 for H(7), and +0.02 for H(67). The charges for the other atoms are related to these by the C_{2h} symmetry operations. The relative charge distribution should not change greatly with parameterization so that these values should be useful in predicting preferred sites of electrophilic or nucleophilic attack on the borane polyhedra.

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Phosphonitrilic Compounds. XII.[1] The Alkaline Hydrolysis of Fluoroalkoxycyclophosphazenes[2]

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Abstract: Product analysis studies of the hydrolysis of $[NP(OCH_2CF_3)_2]_3$ in basic aqueous methanol revealed a nongeminal pathway for the removal of trifluoroethoxy groups from phosphorus. Kinetic studies of the removal of the first fluoroalkoxy group from $[NP(OCH_2CF_3)_2]_3$, $[NP(OCH_2C_2F_5)_2]_3$, $[NP(OCH_2C_3F_7)_2]_3$, $[NP(OCH_2CF_3)_2]_4$, and $[NP(OCH_2C_3F_7)_2]_4$ in basic 25% aqueous diglyme showed that, for cyclic trimers, the ease of ligand displacement is in the order: $OCH_2C_2F_5 > OCH_2CF_3 > OCH_2C_3F_7$. Cyclic tetramers hydrolyzed two to four times faster than the appropriate trimers. The mechanistic implications of these results are discussed.

Although the hydrolytic behavior of organophosphazenes (organophosphonitriles) is of considerable fundamental and technological interest, very little prior work has been reported in this area. It is known that halocyclophosphazenes, such as $(NPF_2)_{3 \text{ or } 4}$, $(NPCl_2)_{3 \text{ or } 4}$, and $(NPBr_2)_{3 \text{ or } 4}$, hydrolyze quite rapidly in basic homogeneous media to yield hydroxyphosphazenes, $[NP(OH)_2]_{3 \text{ or } 4}$, and cyclophosphazanes, $[HNP(O)OH]_{3 \text{ or } 4}$, and eventually phosphates and ammonia.[3-9] When both organo and halogeno groups are present as ligands

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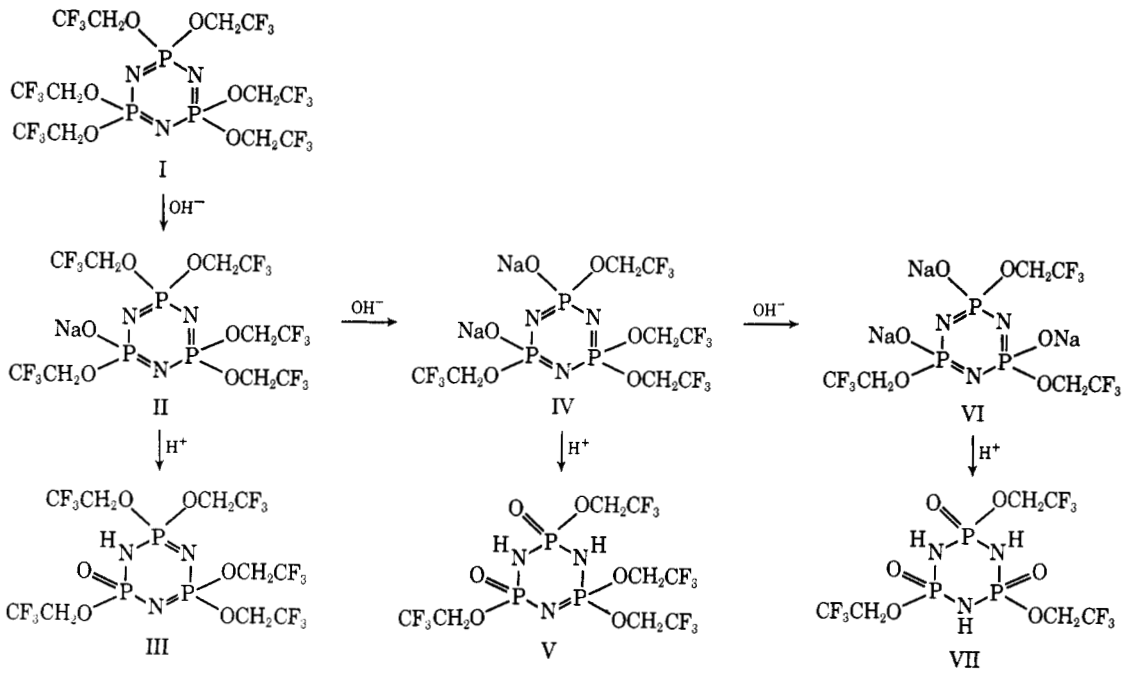

on the same ring, the halogeno group is removed first in basic media. For example, the cyclophosphazenes, $N_3P_3Cl(C_6H_5)_5$ and nongeminal $N_4P_4Cl_2(C_6H_5)_6$, are hydrolyzed in pyridine–water mixtures to yield the hydroxycyclophosphazenes, $N_3P_3(OH)(C_6H_5)_5$ and $N_4P_4(OH)_2(C_6H_5)_6$.[10,11]

Information about the hydrolytic cleavage of organic groups from phosphorus has been confined to brief, qualitative observations. The polymer $[NP(CF_3)_2]_n$, is unaffected by boiling acids but is partly hydrolyzed by aqueous sodium hydroxide solution;[12] the phenylcyclophosphazenes, $[NP(C_6H_5)_2]_{3 \text{ and } 4}$, are degraded to diphenylphosphinic acid and ammonia when heated with aqueous acid;[13] and methoxy-, ethoxy-, isopropoxy-, butoxy-, and benzyloxycyclophosphazenes are stable to water but are decomposed by hot acids.[14] The available information for fluoroalkoxyphosphazenes was restricted to the knowledge that, in heterogeneous media, the trimeric and tetrameric forms are stable to hot aqueous acid or base,[15,16] whereas degradation occurs in hot alcoholic base.[15,16] The high polymers, $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2C_2F_5)_2]_n$, and $[NP(OCH_2C_3F_7)_2]_n$, are unaffected after months in contact with concentrated sodium hydroxide solution in a heterophase system.[17] This present study was undertaken to compare the hydrolytic reactions of a number of fluoroalkoxycyclophosphazenes in homogeneous media with a view to understanding the hydrolytic behavior of biomedically or technologically important polymers which contain the same repeating units.

Results and Discussion

Hydrolysis Products. Hexakis(2,2,2-trifluoroethoxy)-cyclotriphosphazene (I) is hydrolyzed by boiling 50 vol % aqueous methanol containing 1 *M* sodium hydroxide solution during 50 hr to give the sodium salt of 1-hydroxy-1,3,3,5,5-pentakis(trifluoroethoxy)-cyclotriphosphazene (II). Treatment of this product with acid yields the appropriate phosphazadiene (III). The general structure of this material was confirmed by infrared spectra, proton nmr results, and mass spectrometry. Thus, a characteristic N–H infrared peak was observed at 2650 cm^{-1}, but no evidence for P–O–H units was detected from infrared or proton nmr spectra. A mass spectrometric parent peak was detected at 647–648 amu, which corresponded to the expected molecular weight of III. The phosphazadiene structure was indicated by the presence of a methylene proton nmr multiplet centered at δ 4.27 together with a broad N–H proton peak at δ 9.30. The integrated intensity ratio was 10:1.

Prolonged hydrolysis of I for 250 hr in the same medium yielded the disodium salt of the nongeminal dihydroxytetrakis(trifluoroethoxy) derivative IV and a trace of a trihydroxytris(trifluoroethoxy) compound VI. Derivative IV was converted to the cyclophosphazene V with acid, and the composition of V was confirmed by analysis and nmr and infrared spectra. Thus, the broad nmr peak at $\delta \sim 8.95$ was attributed to the N–H protons, but P–O–H protons could not be detected. An infrared peak at 2660 cm^{-1} was assigned to an NH mode, and this peak was correspondingly stronger than in III. Compound V could not be induced to form a silver salt, which constitutes further evidence against the presence of P–O–H units and against a geminal dihydroxy or geminal hydroxyoxo structure. The cyclophosphazane VII was formed from VI by treatment with acid, and its structure was confirmed by mass spectrometry. A parent multiplet centered at 383 mass units corresponded to the expected molecular weight (383) of VII.

Aqueous methanol (50 vol %) proved to be an unsuitable solvent for general kinetic studies because of the low solubility of several fluoroalkoxyphosphazenes in that medium. Accordingly, kinetic experiments were performed with the use of 25 vol % aqueous diglyme,

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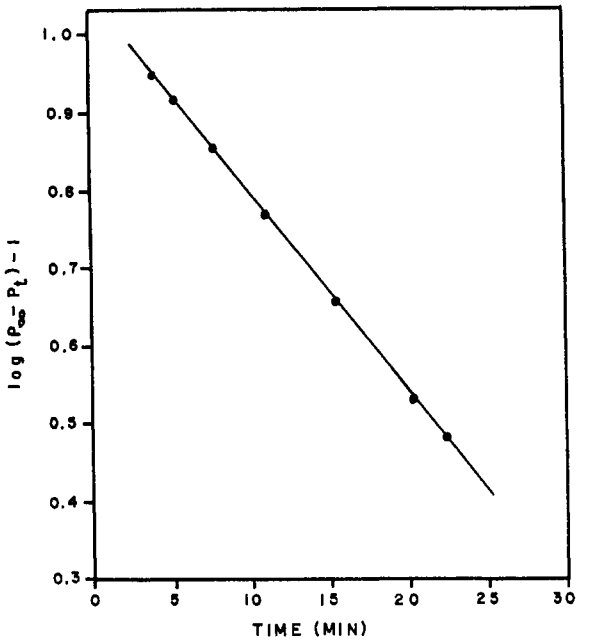


Figure 1. First-order plot for the hydrolysis of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (7.45×10^{-3} *M*) in 25 vol % aqueous diglyme with 1.0×10^{-2} *M* sodium hydroxide at 80.0°. *P* = peak height for trifluoroethanol from vapor phase chromatograms.

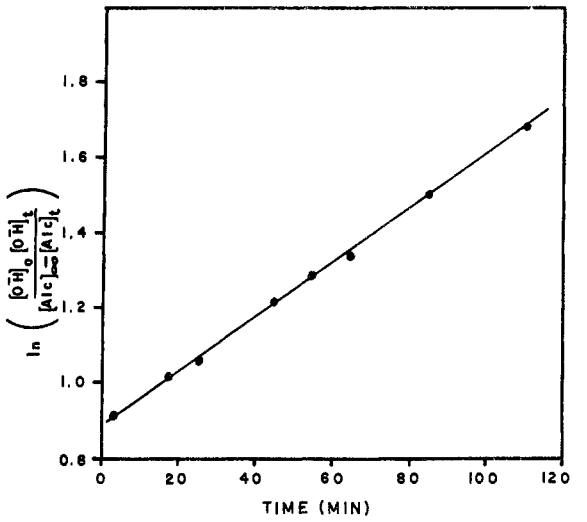
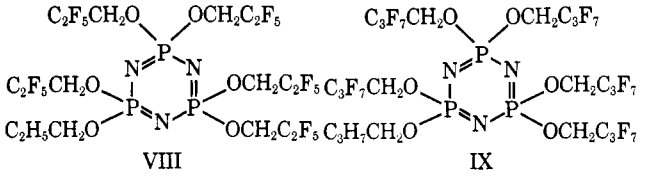
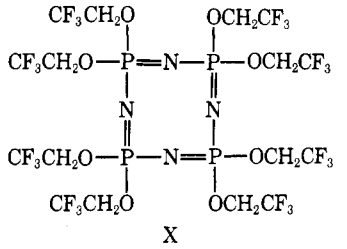


Figure 2. Second-order plot for the hydrolysis of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (1.95×10^{-3} *M*) in 25 vol % aqueous diglyme with 6.2×10^{-3} *M* sodium hydroxide at 80.0°. [Alc] = concentration of trifluoroethanol.

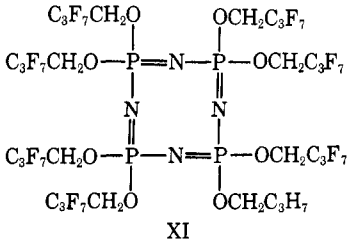
and the hydrolysis products formed in that medium were also examined. It was found that hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (I), hexakis(2,2,-3,3,3-pentafluoropropoxy)cyclotriphosphazene (VIII), and hexakis(2,2,3,3,5,5,5-heptafluorobutoxy)cyclotriphosphazene (IX) hydrolyzed in a solution of 2×10^{-2} *M* sodium hydroxide in 25 vol % aqueous diglyme at 80° to yield the sodium salts of the monohydroxypentakis-(fluoroalkoxy)cyclotriphosphazenes with structures comparable to II. No further hydrolysis products were



VIII IX

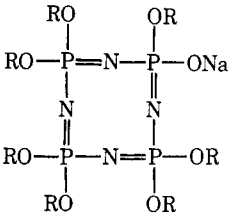


X



XI

detected. Cyclic tetramers such as octakis(2,2,2-trifluoroethoxy)cyclotetraphosphazene (X) and octakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotriphosphazene (XI) behaved similarly, and only one fluoroalkoxy group was removed under the reaction conditions employed to yield products with the general structure XII. In each case, the monohydroxy derivatives were



XII

isolated after treatment with acid followed by identification by microanalysis, infrared and mass spectrometry, and proton nmr methods (see Experimental Section). In each case, the phosphazane-type tautomer analogous to III appeared to form after acidification.

^{18}O Studies. Hydrolysis reactions were carried out with I and XI in 2.13×10^{-2} *M* sodium hydroxide in 25 vol % aqueous diglyme which contained 1% of $H_2{}^{18}O$. In each case, the displaced trifluoroethanol or heptafluorobutanol was collected and analyzed mass spectrometrically. In neither case was ^{18}O containing alcohol detected, a fact which strongly favors a phosphorus–oxygen cleavage mechanism rather than cleavage of a carbon–oxygen bond.

Kinetic Results. Cleavage of the first fluoroalkoxy group from I, VIII, IX, X, and XI was studied kinetically in 25% aqueous diglyme–sodium hydroxide media. Variations in base concentration, phosphazene concentration, and temperature were examined. With the conditions studied, the kinetics for all five compounds were found to obey the overall second-order rate expression, rate = k_2[OH⁻][phosphazene], with the reactions being first order in both hydroxide ion and phosphazene concentrations. A typical pseudo-first-order plot is shown in Figure 1 and a plot for second-order conditions is shown in Figure 2.

Table I. Hydrolysis Rate Constants for Fluoroalkoxyphosphazenes in 25 Vol % Aqueous Diglyme

Phosphazene	[Phosphazene] ($\times 10^3$)	[OH^-] ($\times 10^3$)	Temp, °C	k_2, M^{-1} sec^{-1} ($\times 10$)
I	1.95	6.25	80	1.00
I	1.95	3.12	80	1.00
I	1.99	10.00	80	0.98[a]
I	2.48	7.78	55	0.17
I	1.25	6.69	55	0.17
VIII	2.68	9.93	80	3.00
VIII	2.68	5.24	80	3.04
VIII	2.68	9.93	55	0.48
VIII	1.38	6.69	55	0.47
IX	1.32	9.93	80	0.41
IX	1.32	5.24	80	0.41
IX	1.72	4.96	55	0.06
IX	0.84	4.96	55	0.06
X	1.71	9.93	80	9.15
X	1.71	5.24	80	9.24
X	1.24	6.69	55	1.05
X	2.52	7.74	55	1.07
XI	1.30	2.67	80	1.27
XI	0.65	2.67	80	1.28
XI	0.39 (5)	3.35	55	0.15
XI	0.39 (5)	1.16	55	0.15

[a] Specific rate constant obtained from pseudo-first-order rate constant divided by base concentration.

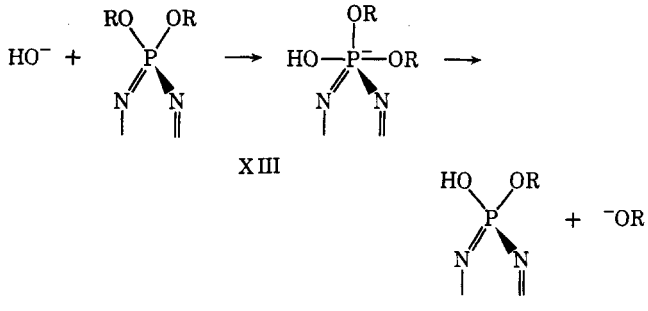
Table I lists the second-order rate constant data for the five cyclophosphazenes. It was found that, for cyclic trimers, $[NP(OR)_2]_3$, the hydrolysis rate decreased in the order: OR = $OCH_2C_2F_5$ > OCH_2CF_3 > $OCH_2C_3F_7$. For cyclic tetramers, $[NP(OR)_2]_4$, the rate decrease was in the order: OR = OCH_2CF_3 > $OCH_2C_3F_7$. The cyclic tetramers reacted two to four times as fast as the analogous cyclic trimers. Comparative rate data obtained at 80 and 55° were used to calculate activation energies and entropies, and these are shown in Table II.

Table II. Activation Energies and Entropies for the Hydrolysis of Fluoroalkoxyphosphazenes

Phosphazene		$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu[a]
$[NP(OCH_2CF_3)_2]_3$	(I)	16.6	−11.7
$[NP(OCH_2C_2F_5)_2]_3$	(VIII)	17.5	−12.5
$[NP(OCH_2C_3F_7)_2]_3$	(IX)	18.2	−8.3
$[NP(OCH_2CF_3)_2]_4$	(X)	20.5	−3.7
$[NP(OCH_2C_3F_7)_2]_4$	(XI)	20.5	−4.9

[a] Calculated from rate constants obtained at 80°.

Reaction Mechanism. The most plausible reaction mechanism is one which requires nucleophilic attack by hydroxide ion at phosphorus by an SN2-type mechanism (XIII). Such a mechanism allows retention of the 120° N–P–N ring angle during formation of a trigonal-bipyramidal transition state, and it is consistent with the reaction pathway deduced for the basic hydrolysis of other tetracoordinate phosphorus compounds.[18-22] Attack by hydroxide ion at the α-carbon atom appears to be precluded by the results of the $H_2{}^{18}O$ experiments described earlier.



XIII

The hydrolysis rates of all five fluoroalkoxyphosphazenes are quite rapid at 80°, and the rates are comparable to those reported earlier for hexakis(*p*-nitrophenoxy)cyclotriphosphazene.[23] This undoubtedly reflects the strong inductive electron-withdrawing characteristics of fluoroalkoxy groups, their ability to create an electron-deficient site at phosphorus to facilitate nucleophilic attack, and perhaps also their capacity to delocalize the negative charge and stabilize the pentacoordinate transition state. However, the relative activating influence of the different fluoroalkoxy ligands does not parallel the expected increase in electron-withdrawing power (OCH_3CF_3 < $OCH_2C_2F_5$ < $OCH_2C_3F_7$), and it seems clear that steric as well as inductive influences affect the reaction. Evidence in favor of this viewpoint is provided by the steady increase in activation energy for the trimers as the length of the fluoroalkoxy chain is increased (Table II). On the other hand, the activation entropies rise in the order: R = $OCH_2C_2F_5$ < OCH_2CF_3 < $OCH_2C_3F_7$, a sequence which parallels the *decreasing* rates of hydrolysis. Presumably, the observed order of reactivity reflects a delicate balance between the rate-enhancing inductive effect and the rate-retarding steric hindrance as the length of the side group is increased.

The faster hydrolysis rates of cyclic tetramers compared to cyclic trimers are consistent with the effects observed for other related reactions. Thus, the rate of exchange of chloride ion with $(NPCl_2)_3$ and $(NPCl_2)_4$ is faster for the tetramer.[24] Hydrolysis of $(NPCl_2)_4$ or $(NPF_2)_4$ proceeds faster than the hydrolysis of $(NPCl_2)_3$ or $(NPF_2)_3$.[3,4] Aminolysis of $(NPCl_2)_4$ takes place more rapidly than the reaction of $(NPCl_2)_3$,[25] and the degradation of cyclophosphazenes to phosphoranes in the presence of catechol or *o*-phenylenediamine occurs more readily with tetramers than with trimers.[26,27] These differences probably reflect the characteristic conformational freedom of the eight-membered ring system rather than the greater exposure of the phosphorus atoms to nucleophilic attack. The activation energies found for the hydrolysis of the two tetramers, X and XI, are higher than for the trimers, and the values appear to be unaffected by changes in the length of the ligand chain. However, the activation entropies are higher for the tetramers than for the trimers and this may result from the conformational freedom in the tetramer or from different solvation effects. It is un-

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fortunate that the linear high polymeric fluoroalkoxyphosphazenes, such as $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2C_2F_5)_2]_n$, and $[NP(OCH_2C_3F_7)_2]_n$, are exceedingly insoluble in suitable aqueous–organic media, and their hydrolysis rates under comparable conditions could not be measured.

The nongeminal reaction pathway observed for the hydrolysis of I is probably a consequence of salt formation in basic media. The product analysis work illustrates the fact that the sodium salt, II, exists as a stable entity. Presumably the presence of a P–O⁻ unit at one phosphorus atom serves to direct an attacking hydroxide ion to a nongeminal site. The apparent unreactivity of the monosubstituted cyclophosphazenes to further ligand cleavage is probably also a consequence of the general deactivating influence of the anionic charge.

Experimental Section[28]

Materials. Diglyme [bis(2-methoxy)diethyl ether] (Burdick and Jackson) was dried over calcium hydride for 12 hr and then vacuum distilled from a lithium aluminum hydride slurry. Exposure to air was minimized by the use of a nitrogen atmosphere, and the absence of peroxides was confirmed prior to each run by means of a potassium iodide test. Water was distilled twice in a nitrogen atmosphere and then used immediately. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (Hooker Chemical Co. or Millmaster Onyx), was recrystallized twice from *n*-heptane to yield material, mp 112–113°. Octachlorocyclotetraphosphazene, $(NPCl_2)_4$ (Alfa Inorganics), mp 121–123°, was used as received. 2,2,2-Trifluoroethanol (Halocarbon Products), 2,2,3,3,3-pentafluoro-1-propanol, and 2,2,3,3,4,4,4-heptafluoro-1-butanol (Pflatz and Bauer) were used as received. Diethyl ether (Fisher) was dried over sodium and then filtered before use.

Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (I). Sodium (23. 8 g, 1.05 g-atoms) was added to a cooled solution of 2,2,2-trifluoroethanol (103.3 g, 1.033 mol) in anhydrous ether (400 ml). To this solution was added dropwise a solution of hexachlorocyclotriphosphazene (59.6 g, 0.172 mol) in anhydrous ether (400 ml). The mixture was stirred at 25° for 8 hr and the white precipitate of sodium chloride was then filtered off. The filtrate was washed thoroughly with water to remove excess sodium trifluoroethoxide, and the ethereal layer was evaporated and then vacuum distilled. The product, bp 135° (3 mm), was a viscous oil which solidified on cooling. This solid was sublimed at 70° (2 mm) to give I (96.0 g, 77%), mp 49° (lit.[16] mp 48°), mol wt (by mass spectrometry) 729 (calcd mol wt 729). On several occasions explosions occurred during the distillation or sublimation step of this synthesis. These were tentatively traced to the presence of residual sodium trifluoroethoxide in the mixture. Thorough water washing prior to distillation or sublimation appeared to prevent this occurrence.

Octakis (2,2,2-trifluoroethoxy)cyclotetraphosphazene (X). Sodium 2,2,2-trifluoroethoxide was prepared by the slow addition of sodium (5.70 g, 0.248 g-atom) to a solution of 2,2,2-trifluoroethanol (24.95 g, 0.250 mol) in anhydrous ether (300 ml). A solution of octachlorocyclotetraphosphazene (14.25 g, 0.0305 mol) in dry ether (500 ml) was added dropwise to the alcoholate solution. The initial exotherm was sufficient to boil the solvent and refluxing was then maintained for 12 hr. The reaction mixture was cooled to 25° and filtered, and the filtrate was washed with distilled water (300 ml) and then dried for 12 hr over anhydrous sodium sulfate. Evaporation of the ether yielded a viscous oil which was crystallized from *n*-heptane to yield X (25.0 g, 85%), mp 65°. Sublimation at 80° (2 mm) yielded material, mp 65° (lit.[16] 65°). The infrared spectrum of this compound showed a characteristic P–N ring vibration band at 1280 cm^{-1}.

Hexakis(2,2,3,3,3-pentafluoro-1-propoxy)cyclotriphosphazene (VIII). Sodium 2,2,3,3,3-pentafluoro-1-propoxide was prepared by the slow addition of sodium hydride as a 50% dispersion in oil (6.50 g, 0.135 mol) to a solution of 2,2,3,3,3-pentafluoro-1-propanol (19.35 g, 0.130 mol) in anhydrous ether (300 ml). A solution of hexachlorocyclotriphosphazene (7.50 g, 0.022 mol) in dry toluene (300 ml) was added dropwise to the alkoxide solution at a rate sufficient to maintain steady boiling of the solvent. Thereafter, heating was applied to maintain boiling at reflux for 48 hr, after which time the mixture was cooled to 25° and filtered. The filtrate was washed twice with water (200 ml), then filtered through cotton, and dried over anhydrous sodium sulfate for 24 hr. Removal of the solvents *in vacuo* yielded a viscous oil. Vacuum distillation of this product provided VIII as an oil, bp 135–137° (6 mm) [lit.[16] bp 136.5° (6 mm)] (14.0 g, 60%). *Anal.* Calcd for $C_{18}H_{12}F_{30}N_3O_6P_3$: C, 21.00; H, 1.17; F, 55.39; N, 4.08. Found: C, 21.26; H, 1.30; F, 55.98; N, 4.05. A Beilstein test demonstrated the absence of chlorine. An infrared spectrum showed a characteristic P–N ring vibration frequency at 1200 cm^{-1}. A mass spectrum showed a parent peak at 1055–1065 amu (extrapolated calibration) (mol wt for VIII, 1061).

Hexakis(2,2,3,3,4,4,4-heptafluoro-1-butoxy)cyclotriphosphazene (IX). The sodium salt of 2,2,3,3,4,4,4-heptafluoro-1-butanol was prepared by the slow addition of sodium hydride (19.2 g, 0.40 mol), as a 50% dispersion in oil, to a solution of the alcohol (80.0 g, 0.40 mol) in diethyl ether (250 ml). The reaction was complete in 2 hr, and a solution of hexachlorocyclotriphosphazene (18.0 g, 0.052 mol) in dry ether (280 ml) was added dropwise. After the exothermic addition was complete, the reaction was boiled at reflux for 12 hr, then cooled to 25°, and filtered, and the solid was washed with dry ether (50 ml). Evaporation of solvent from the combined filtrates yielded a viscous liquid. This product was vacuum distilled to yield a fraction, bp 169–170° (5.5 mm) [lit.[16] bp 154° (3 mm)], and this was subsequently distilled at 199–200° (22 mm) to give clear liquid IX (29.5 g, 26%). *Anal.* Calcd for $C_{24}H_{12}F_{42}N_3O_6P_3$: C, 21.68; H, 0.91; F, 60.03; N, 3.46. Found: C, 21.85; H, 1.05; F, 59.38; N, 3.52. A Beilstein test demonstrated the absence of chlorine, and an infrared spectrum showed a trimeric P–N ring vibration band at 1210 cm^{-1}.

Octakis(2,2,3,3,4,4,4-heptafluoro-1-butoxy)cyclotetraphosphazene (XI). Sodium (2.62 g, 0.11 g-atom) was added to a solution of 2,2,3,3,4,4,4-heptafluoro-1-butanol (22.8 g, 0.11 mol) in dry ether (200 ml) and the mixture was boiled at reflux for 7 hr. The small amount of unreacted sodium (0.076 g, 0.003 g-atom) was removed and a solution of octachlorocyclotetraphosphazene (5.85 g, 0.0126 mol) in benzene (100 ml) was added dropwise. The mixture was boiled at reflux for 36 hr, cooled to 25°, and then washed with two 100-ml portions of water. The organic layer was filtered through cotton and dried over anhydrous sodium sulfate. Removal of the solvent yielded a white solid which was recrystallized from *n*-heptane to yield crystals of XI, mp 106–108° (lit.[16] mp 107°) (10.9 g, 49%). A Beilstein test indicated the absence of chlorine. *Anal.* Calcd for $C_{32}H_{16}F_{56}N_4O_8P_4$: F, 60.03. Found: F, 60.11.

Products from the Initial Hydrolysis of Hexakis(trifluoroethoxy)-cyclotriphosphazene in Aqueous Methanol. A solution of hexakis-(trifluoroethoxy)cyclotriphosphazene (I) (5.0 g, 6.87 × 10^{-3} mol) in 1 *M* sodium hydroxide in 50 vol % aqueous methanol (150 ml) was boiled at reflux for 50 hr. The methanol was then removed by distillation and the aqueous residue was cooled to 25° and then extracted twice with ether (100-ml portions). The combined ethereal layers were dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The white residue was recrystallized from benzene to yield **sodium 1,3,3,5,5-pentakis(trifluoroethoxy)-1-oxocyclotriphosphazenate (II).** *Anal.* Calcd for $C_{10}H_{10}F_{15}N_3O_5P_3Na$: C, 17.95; H, 1.49; F, 41.20. Found: C, 18.02; H, 1.51; F, 41.41. Compound II (0.20 g) was converted to the phosphazadiene (III) in absolute ethanol (25 ml) by the addition of hydrochloric acid (2.0 ml). Following the immediate formation of a precipitate, the solvent was removed *in vacuo* and the residue was dissolved in ether. Sodium chloride was removed from the ethereal mixture by filtration, and the filtrate was evaporated to dryness. The residue was sublimed at 135° (1 mm) during 10 hr to yield **1,3,3,5,5-pentakis(trifluoroethoxy)-1-oxo-2-hydrocyclotriphosphazadiene (III),** mp 56–57°. The structure was confirmed by mass spectrometry, infrared spectroscopy, and nuclear magnetic resonance spectroscopy as described earlier.

Products from the Extended Hydrolysis of Hexakis(trifluoroethoxy)cyclotriphosphazene in Aqueous Methanol. A solution of hexakis(trifluoroethoxy)cyclotriphosphazene (I) (5.0 g) in 1 *M* sodium hydroxide in 50 vol % aqueous methanol (150 ml) was boiled at reflux for 250 hr. Methanol was removed by distillation and the aqueous residue was cooled to 25° and then extracted with

(28) Mass spectrometric data were obtained with the use of an AEI MS 9 spectrometer, infrared spectra were measured on a Beckman IR5A spectrometer, and proton nmr spectra were recorded on a Varian A-60A instrument. Microanalyses were by Schwarzkopf Microanalytical Laboratory or Midwest Microlabs, Inc. Reagent transfers for kinetic experiments were effected within a nitrogen-filled glove bag.

two 100-ml portions of ether. The ethereal layers were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to yield the monosodium salt of the monohydroxycyclotriphosphazene (II) (0.06 g, 1.35%). The aqueous solution was acidified with 10% hydrochloric acid and then extracted with two 100-ml portions of ether. Evaporation of the dried ethereal layers yielded a solid residue. A mass spectrum of this material showed parent peaks which corresponded to the presence of a tetrakis(trifluoroethoxy)-dihydroxycyclotriphosphazene or its tautomer V plus a trace of a tris(trifluoroethoxy)trihydroxycyclotriphosphazene or its tautomer VII. Recrystallization of this residue from chloroform yielded **1,3,5,5-tetrakis(trifluoroethoxy)-1,3-oxo-2,4-dihydrocyclotriphosphazene (V)**, mp 173–174°. *Anal.* Calcd for $C_8H_{10}F_{12}N_3O_6P_3$: C, 17.00; H, 1.76; F, 40.40. Found: C, 17.12; H, 1.91; F, 40.72.

Product from the Hydrolysis of Hexakis(trifluoroethoxy)cyclotriphosphazene (I) in Aqueous Diglyme. A solution of I (0.22 g) in 2×10^{-2} *M* sodium hydroxide in 25 vol % aqueous diglyme (200 ml) was boiled at reflux for 24 hr. Removal of the solvents left a white residue which was dissolved in absolute ethanol and treated with 0.01 ml of concentrated hydrochloric acid. The ethanol was removed at reduced pressure and the residue was treated with anhydrous ether and filtered. Evaporation of the ether yielded **1,3,3,5,5-pentakis(trifluoroethoxy)-1-oxo-2-hydrocylcotriphosphazadiene.** A mass spectrum of this material showed a parent peak at mass 647 (calcd mol wt 647), and infrared and proton nmr spectra were consistent with structure III.

Product from the Hydrolysis of Hexakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotriphosphazene (IX). A solution of IX (1.0 g) in 2×10^{-2} *M* sodium hydroxide in 25 vol % aqueous diglyme (200 ml) was boiled at reflux for 48 hr. The solvents were then removed in a rotary evaporator, and the residue was dissolved in absolute ethanol. This solution was acidified with concentrated hydrochloric acid (0.2 ml), the ethanol was removed *in vacuo*, and the residue was dissolved in anhydrous ether and filtered. Evaporation of the filtrate yielded **1,3,3,5,5-pentakis(heptafluorobutoxy)-1-oxo-2-hydrocyclotriphosphazadiene.** *Anal.* Calcd for $C_{20}H_{11}F_{35}N_3O_6P_3$: C, 20.93; H, 0.96; F, 58.10. Found: C, 21.10; H, 1.08; F, 58.69. Infrared and proton nmr spectra were consistent with the proposed structure.

Product from the Hydrolysis of Octakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotetraphosphazene (XI). A solution of XI (1.0 g) in 25 vol % aqueous diglyme (300 ml) containing 2×10^{-2} *M* sodium hydroxide was boiled for 72 hr. Removal of the solvents on a rotary evaporator yielded a white residue, which was dissolved in absolute ethanol and acidified with concentrated hydrochloric acid (0.3 ml). Ethanol was then removed at reduced pressure, the white residue was dissolved in ether and filtered to remove sodium chloride, and the filtrate was evaporated to dryness. The white residue was then recrystallized from a chloroform–benzene mixture to yield **1,3,3,5,5,6,6-heptakis(heptafluorobutoxy)-1-oxo-2-hydrocyclotetraphosphazatriene.** *Anal.* Calcd for $C_{28}H_{15}F_{49}N_4O_8P_4$: C, 21.08; H, 0.94; F, 58.50. Found: C, 20.86; H, 1.06; F, 59.10. A similar reaction with the same amounts of reactants was boiled at reflux for 168 hr, and the same product only was isolated.

Hydrolysis of Hexakis(trifluoroethoxy)cyclotriphosphazene (I) in Diglyme–$H_2{}^{18}O$. A solution of I (0.02 g) in a solution of 2.13×10^{-2} *M* sodium hydroxide in 25 vol % aqueous diglyme (20 ml), which contained 1% $H_2{}^{18}O$, was boiled at reflux for 4 hr. The solvents were fractionally distilled, and the first 0.2 ml of distillate was collected. A mass spectrum of this material showed that the liquid was principally trifluoroethanol (100 amu). No peak at 102 amu, from $C_2H_2F_3{}^{18}OH$, could be detected. A reaction conducted with the use of trifluoroethanol in place of I, to test for hydroxide exchange, again showed no evidence of $C_2H_2F_3{}^{18}OH$ in the mass spectrum.

Hydrolysis of Octakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotetraphosphazene (XI) in Diglyme–$H_2{}^{18}O$. A solution of XI (0.02 g) in a solution of 2.13×10^{-2} *M* sodium hydroxide in 25 vol % aqueous diglyme, which contained 1% $H_2{}^{18}O$, was boiled at reflux for 6 hr. Fractional distillation of the mixture yielded 0.2 ml of the lowest boiling fraction. A mass spectrum of this material showed that it contained heptafluorobutanol (200 amu), but no $C_3F_7CH_2{}^{18}OH$ could be detected at 202 amu. No exchange occurred between heptafluorobutanol and $H_2{}^{18}O$ under the same conditions.

Kinetic Technique. Hydrolysis rates were followed by analysis of the fluoro alcohol concentration at different periods of time by means of vapor phase chromatography. A typical procedure was as follows. A 30.0-ml sample of a stock solution of the fluoroalkoxyphosphazene (5×10^{-3} *M*) in freshly distilled diglyme was pipetted in a nitrogen atmosphere into a 100-ml round-bottom flask, which was then stoppered. A 10.0-ml sample of 4×10^{-2} *M* sodium hydroxide solution in water was pipetted into a 25-ml volumetric flask in a nitrogen atmosphere, and the flask was stoppered. The two solutions were then allowed to reach the required temperature by partial immersion of the two flasks in a constant temperature bath for 20 min. The two solutions were then mixed rapidly by retransfer from flask to flask to least twice. The reaction solution was sealed in the 100-ml flask by means of a rubber septum. Each 1-ml sample was removed from the reaction mixture by syringe and was then frozen immediately by liquid nitrogen. The samples were stored at −5° until analyzed. All samples were analyzed within 10 hr of their removal from the reaction flask. Infinity values were measured at 24 and 36 hr or until no change occurred during successive 10-hr periods. Rate constants were obtained from a plot of $\ln [([OH^-]_0 - [OH^-]_t)/([alcohol]_\infty - [alcohol]_t)]$ against time. The slope of this line multipled by the reciprocal of the difference in concentrations of the reactants gave k_2 in M^{-1} sec^{-1}. A plot of $1/([alcohol]_\infty - [alcohol]_t)$ against time also gave the same rate constants. For I, both pseudo-first-order and second-order conditions were examined. The concentration variables for XI were limited by the low solubility of this compound in aqueous diglyme.

Vapor Phase Chromatography Technique. The fluoro alcohol concentration in each sample was determined by vapor phase chromatography with the use of a Perkin-Elmer 881 apparatus. A 15-ft, $^1/_8$-in. diameter, stainless steel column packed with Carbowax 20M on Chromosorb W was used, with a nitrogen flow rate maintained at 23 ml/min and with the column temperature maintained at 165°. Reaction mixture samples were injected into the apparatus without prior work-up. Control experiments showed no change in peak height for fluoro alcohol samples injected in neutral, basic, or acidic media, and this presumably reflects the pK_a values of 16–17 for these alcohols. A flame ionization detector was used to avoid interference by the water present. Under these conditions, a clear separation was achieved of the alcohol peak from those of other species present. The alcohol concentrations were determined from the peak heights. For each alcohol, a series of five standard solutions was prepared which covered the concentration range expected for each run. A plot of concentration *vs.* peak height was prepared daily, and each one was found to be linear for each set of solutions.

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