cm^{-1}. The value for the SCl wagging motion in SF$_5$Cl is reported to be 270 cm^{-1}.[19]

Recently several CF$_3$S-containing molecules have been studied, and the C–S stretching frequency was reported to be 475 cm^{-1} for CF$_3$SCF$_3$,[9] 468 cm^{-1} for CF$_3$S(O)CF$_3$,[9] and 446 cm^{-1} for CF$_3$SSCF$_3$.[9,20] Thus, we have assigned the C–S stretch in CF$_3$S(O)F and CF$_3$S(O)Cl to the bands of medium intensity at 480 and 463 cm^{-1}, respectively.

As mentioned previously, there should be nine bands associated with the CF$_3$X portion of the CF$_3$S(O)Cl and CF$_3$S(O)F molecules. Three of these should be stretching bands. These three vibrations should lie in the range 1100–1400 cm^{-1}.[21–23] There are four bands in this region in the infrared and Raman spectra of each of these compounds. One of these (the highest frequency band in each case) has been assigned to the SO stretching frequency. The others, very strong in the infrared spectra and weak in the Raman spectra, may be assigned to the three CF$_3$ stretching fundamentals. Although the values of the CF$_3$ stretching frequencies for CF$_3$S(O)F and CF$_3$S(O)Cl are quite different, the shift of the frequencies of the latter to lower energy causes the positions of the absorbance bands in this region of the spectrum to be nearly identical with that of (CF$_3$)$_2$SO[9] which is reasonable.

The three expected CF$_3$ deformation modes are observed and are easily assigned by comparison to assignments made for CF$_3$S(O)CF$_3$ (753, 591, and 558 cm^{-1})[9] and CF$_3$SSCF$_3$ (760, 573, and 545 cm^{-1}).[9] Thus, we have assigned the three bands at 757 (see discussion of S–F stretching mode), 587, and 550 cm^{-1} to the CF$_3$ deformation modes of CF$_3$S(O)F and those at 752, 574, and 553 cm^{-1} to analogous vibrations in CF$_3$S(O)Cl. By similar comparisons, the CF$_3$ rocking modes were assigned to the bands at 289 and 220 cm^{-1} for CF$_3$S(O)F and 301 and 211 cm^{-1} for CF$_3$S(O)Cl. CF$_3$ rocking modes had been assigned previously as high as 490[21] and as low as 149[24] cm^{-1}. According to Haas and coworkers,[25–27] an intense band around 300 cm^{-1} (289 and 301 cm^{-1}) is characteristic of CF$_3$ rocking motions.

Finally, the CF$_3$ torsional mode is not observed in either case and probably falls below 100 cm^{-1} in the Raman effect.[28,29] It has been observed at 75 cm^{-1} in the case of CF$_3$SCF$_3$ and CF$_3$S(O)CF$_3$.[9]

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Reaction of Sodium 2,2,2-Trifluoroethoxide with Hexachlorocyclotriphosphazene[1,2]

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The reaction between sodium 2,2,2-trifluoroethoxide and hexachlorocyclotriphosphazene (I) yielded nine cyclotriphosphazenes of the formula N$_3$P$_3$(OCH$_2$CF$_3$)$_n$Cl$_{6-n}$ where $n = 1$–6. Nuclear magnetic resonance analysis indicated that these products were compounds II–X. This constitutes the first isolation and identification of a complete series of alkoxychlorocyclophosphazenes. The reaction was found to follow almost exclusively a trans-nongeminal pathway, and a steric rather than an electronic "cis effect" is postulated to account for this pattern. Dipole moments were measured, but these were shown to be unsuitable for isomer identification, presumably because of the presence of the bulky, nonrigid trifluoroethoxy groups and a nonvanishing ring moment. The applicability of these results to related high molecular weight polyphosphazene systems is discussed.

Introduction

The syntheses of several fluoroalkoxycyclophosphazenes, including hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (X), were first reported in 1959 and 1962.[3,4] Later, the synthesis of tris-, tetrakis-, and pentakis(trifluoroethoxy)-chlorophosphazene trimers was reported,[5] and the NMR spectrum of trifluoroethoxypentachlorocyclotriphosphazene (II) was described.[6] Apparently no attempts were made to

identify the geometric isomers formed when alternative structures were possible.

The current interest in high molecular weight poly-organophosphazenes[7–15] has generated a need for new information about the replacement patterns that exist when alkoxy substituent groups replace chlorine atoms in phosphazene systems. The present study was undertaken in an effort to synthesize, separate, and identify the stereoisomers

of the series $N_3P_3(OCH_2CF_3)_nCl_{6-n}$ where n = 1–6 and, if possible, to identify the substitution mechanism. It was anticipated that this information would be valuable for an initial analysis of the related reactions that take place in the high polymeric systems.

Results and Discussion

General Reaction Products. The overall reaction studied was the nucleophilic replacement of chlorine atoms in hexachlorocyclotriphosphazene (I) by the trifluoroethoxide ion in organic media. The products obtained are depicted in structures II–X.
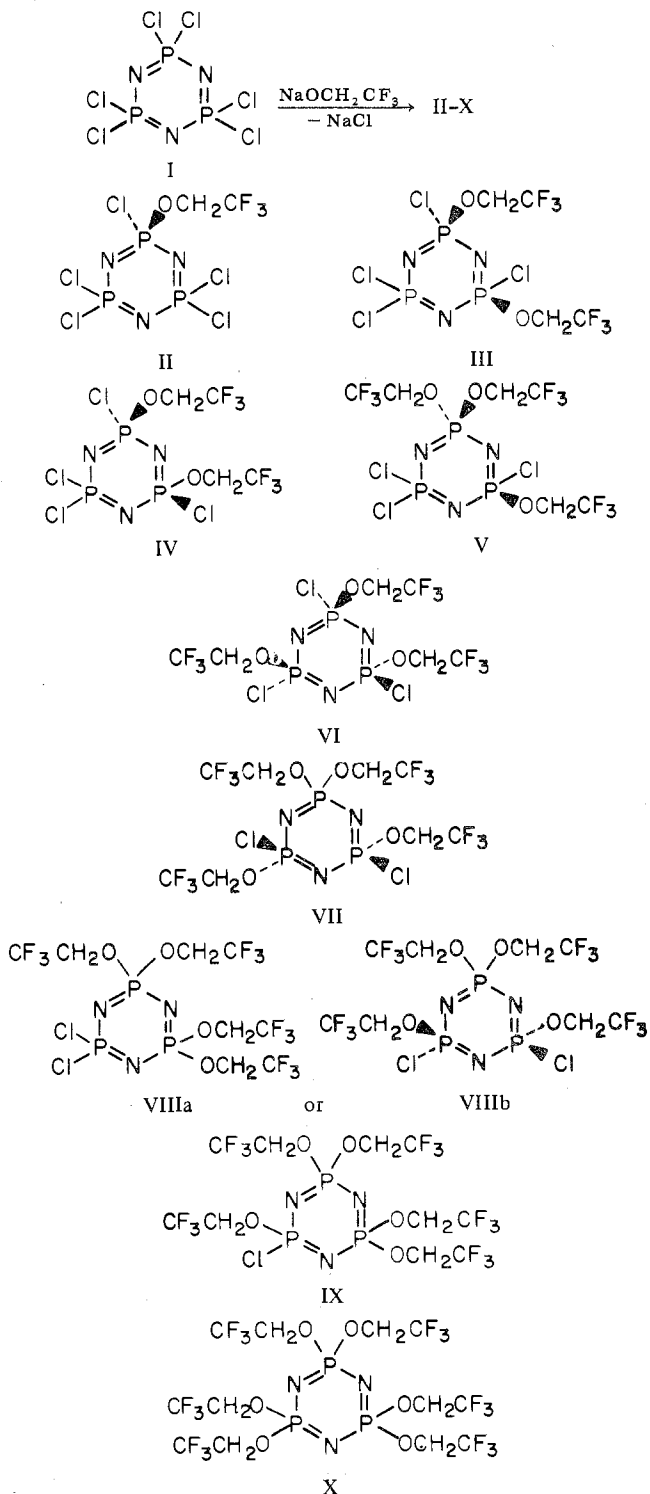
The rate of the reaction was markedly dependent on the polarity of the solvent, with rate increases observed in the order

Table I. Dipole Moments in Cyclohexane

Compd	Dipole moment, D
$(NPCl_2)_3$ (I)	1.00
$N_3P_3Cl_5(OCH_2CF_3)$ (II)	2.04
$N_3P_3Cl_4(OCH_2CF_3)_2$, trans nongeminal (IV)	2.72
$N_3P_3Cl_3(OCH_2CF_3)_3$, trans nongeminal (VI)	3.16
$N_3P_3Cl_3(OCH_2CF_3)_3$, geminal (V)	3.07
$N_3P_3Cl_2(OCH_2CF_3)_4$, cis nongeminal (VII)	3.64
$N_3P_3Cl(OCH_2CF_3)_5$ (IX)	3.85
$[NP(OCH_2CF_3)_2]_3$ (X)	3.73

diethyl ether < tetrahydrofuran < acetonitrile. This effect probably reflects an enhanced ionization of the sodium alkoxide in the more polar media.[16]

When diethyl ether was used as a solvent, the reaction was sufficiently slow to be monitored by vapor-phase chromatography (VPC). Using this technique it was found that introduction of the first three trifluoroethoxy groups was much more rapid than the introduction of the last three. Replacement of the first three chlorine atoms was complete in ether at 0° in less than 12 min, while the replacement of the last three required more than 4 hr for completion. This observation is consistent with a nongeminal substitution pattern.

Two isomers each of the bis-, tris-, and tetrakis(trifluoroethoxy)phosphazenes were detected from the VPC chromatograms. These, together with the mono-, pentakis-, and hexakis(trifluoroethoxy)derivatives (II, IX, and X), constituted the nine products detected in the system by VPC and VPC–mass spectrometry techniques. A minor VPC peak was detected which apparently represented VIIIa or b. Structure VIIIb was preferred, since this product was an expected derivative of VI and could also be formed from V.

In addition, most of these products were isolated from large-scale reaction mixtures and were purified by conventional column fractionation methods. Specifically, compounds II, III + IV, V, VI, VII, IX, and X were isolated. The relationship between the VPC peaks and the isolated compounds was established, and the compounds were subjected to dipole moment and NMR investigations in an attempt to identify the geminal or nongeminal and the cis or trans disposition of the substituent groups. No ring equilibration products, such as the cyclic tetramer, pentamer, etc., were detected.

Dipole Moments. Dipole moments are given in Table I. Koopman and coworkers[17] have shown that the dipole moments of mono-, bis-, and tris(dimethylamino)chlorocyclotriphosphazenes agree with the theoretical values obtained from the vector sum of vertical and horizontal components for each substituent on the ring. However, when trifluoroethoxy and chloro ring substituents are present, no such agreement can be discerned between the experimental data and the vector summation equations, a result that is ascribed to a large atomic polarizability[18] contribution. This is indicated by the 1.00-D dipole moment which should be nearly zero for $(NPCl_2)_3$. The discrepancy is probably due to ring polarizability. The very large (3.73 D) moment for $[NP(OCH_2CF_3)_2]_3$ can be attributed to a combination of ring and substituent polarizability. Equations which are similar to those of Koopman et al. but which allow for nonplanarity of the ring in an electric field showed better agreement than the other equations, but they too proved to be unsatisfactory for this system.

Identification by NMR Spectroscopy. All the ^{31}P NMR spectra were second order, with most $J/\Delta\nu$ values in the range from 0.2 to 0.3. The spectrum of trifluoroethoxypentachlorocyclotriphosphazene (II) shown in Figure 1 is typical of the AB_2 spectra observed. Both of the bis(trifluoroethoxy) isomers showed AB_2 spectra. The A-type phosphorus atoms showed no further splitting from the trifluoroethoxy protons. Thus these two isomers are the cis and trans nongeminal

Table II. NMR Data for Cyclotriphosphazenes

| | Phosphorus-31 | | | | | Proton |
| | Spectrum Type | Position,[a] ppm | | | $J_{P_A P_B}$,[e] Hz | Positions rel to TMS, ppm (rel intens) |
		A	B	C		
$N_3P_3Cl_6$	A_3	0.00				
$N_3P_3Cl_5(OCH_2CF_3)$	AB_2	3.68	-2.67		±66.0	3.91
$N_3P_3Cl_4(OCH_2CF_3)_2$	AB_2	-4.97	0.86		±69.6	3.93
$N_3P_3Cl_3(OCH_2CF_3)_3$, trans	AB_2	-2.06[b]	-1.91[b]			3.80 (2) 3.84 (1)
$N_3P_3Cl_3(OCH_2CF_3)_3$, geminal	ABC	11.4[c]	-1.2[c]	-6.7[c]		3.87 (1) 3.80 (1) ? (1)[d]
$N_3P_3Cl_2(OCH_2CF_3)_4$	AB_2	8.26	-4.52		±85.4	3.92 (2) 3.84 (1) 3.96 (1)
$N_3P_3Cl(OCH_2CF_3)_5$	AB_2	-6.50	5.59		±87.0	3.81 (2) 3.88 (2) 3.87 (1)
$N_3P_3(OCH_2CF_3)_6$	A_3	3.10				3.96

[a] Relative to $N_3P_3Cl_6$ internal; $N_3P_3Cl_6$ is −19.81 ppm from 85% H_3PO_4 external. [b] Because of the large $J/\Delta\nu$ value for this compound, ν_A and ν_B could not be determined. The positions of the two major distinguishable peaks are thus reported in this case. [c] Positions estimated by comparison with spectra for the ABC case of K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, New York, N.Y., 1962, spectra 3D-11, 3D-86, and 3E-11. [d] The position could not be determined because of peak overlap and the presence of VI as an impurity. [e] Other coupling constants: J_{FH} = 7.8–8.1 Hz; $J_{P_A H_A}$ = 9.3–10.3 Hz; $J_{P_A H_B} \cong 1$ Hz; $J_{PF} < 1$ Hz.
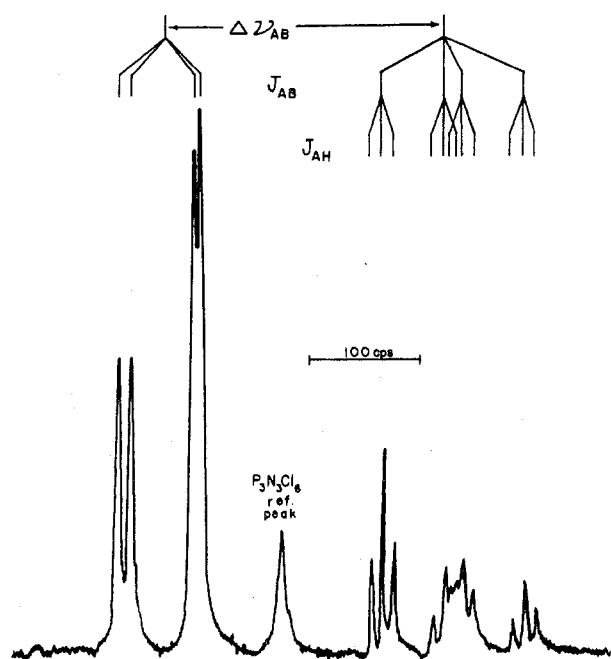

Figure 1. ^{31}P NMR spectrum of $N_3P_3Cl_5(OCH_2CF_3)$ measured at 40.5 MHz. The spectrum can be interpreted as an AB_2X_2 pattern.
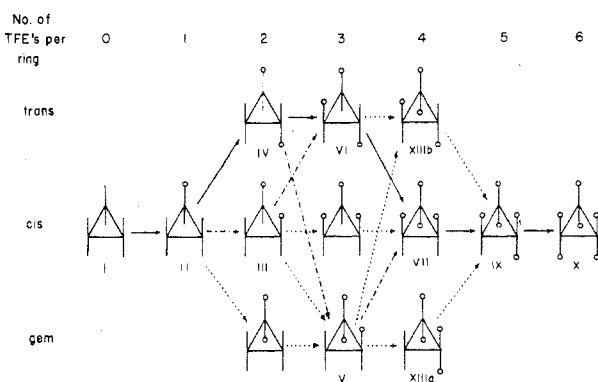

Figure 2. Possible reaction pathways for the replacement of chlorine in $(NPCl_2)_3$ by trifluoroethoxy groups. The circles represent trifluoroethoxy groups, and the solid arrows depict the principal pathway found in this work. The lines made up of dots and dashes represent the formation of the minor products. "TFE's per ring" refers to the number of trifluoroethoxy groups.

isomers III and IV. As discussed below, the trans bis(trifluoroethoxy) isomer IV predominates in the mixture.

The predominant tris component VI gave what appeared to be a singlet which was further split by the protons. However, following decoupling of the protons, the phosphorus peak proved to be a doublet. This apparent doublet could arise from the trans isomer VI since, in the limit of very large $J/\Delta\nu$ values, (expected for the trans isomer), the AB_2 spectra would tend toward the appearance of a doublet.[19] Alternatively, the doublet could result from ring conformational isomers of the cis geometric isomer in solution. The latter possibility was eliminated since no trend to coalesence appeared in spectra at temperatures up to 179°. Thus the major tris isomer was assigned a trans configuration (VI). The minor tris isomer (less than 20% of the total tris components) gave an ABC spectrum with two of the phosphorus atoms being further split by protons. This isomer is thus the tris geminal isomer V.

The reaction scheme shown in Figure 2 illustrates why the predominance of the trans tris(trifluoroethoxy) isomer VI provides a strong argument that the trans bis isomer IV is the principal bis(trifluoroethoxy) species formed. If the predominant bis(trifluoroethoxy) component were the cis isomer, all three tris(trifluoroethoxy) isomers could be formed, but a larger amount of the cis tris nongeminal isomer would be

expected if the main directing force during the second substitution was cis oriented. Furthermore, since geminal substitution is the least favored of any pattern,[20] more cis tris than geminal tris derivative would be expected if the cis bis isomer were the principal precursor. In fact, no cis nongeminal tris derivative was detected. Hence, the reaction pathway probably proceeds principally via the trans nongeminal bis component IV which can yield only the observed geminal tris (V) and trans nongeminal tris (VI) products.

The spectrum of the tetrakis(trifluoroethoxy)dichlorocyclotriphosphazene was an AB_2 spectrum with both types of phosphorus showing further splitting by protons. Thus the geminal structure can be eliminated. The cis nongeminal tetrakis-substituted product VII would have three different trifluoroethoxy proton environments, while the trans tetrakis product VIIIb would only have two. The ^{31}P-decoupled proton NMR spectra of the tetrakis product gave a spectrum consistent with three quartets (the quartets arise from ^{19}F splitting) in a 1:2:1 ratio. Thus cis-tetrakis(trifluoroethoxy)dichlorocyclotriphosphazene (VII) is the principal product at this stage of the substitution. This product would be expected if S_N2 attack on VI occurs from the least hindered side of the ring. In a competition reaction between a mixture of V (60%) and VI (40%) with sodium trifluoroethoxide, V reacted more rapidly than VI.

Figure 3 shows the ^{31}P chemical shifts of each of the products isolated. The introduction of a second trifluoroethoxy group onto a particular phosphorus atom causes an upfield (i.e., more shielded) ^{31}P shift. Table II summarizes the details of the NMR spectra.

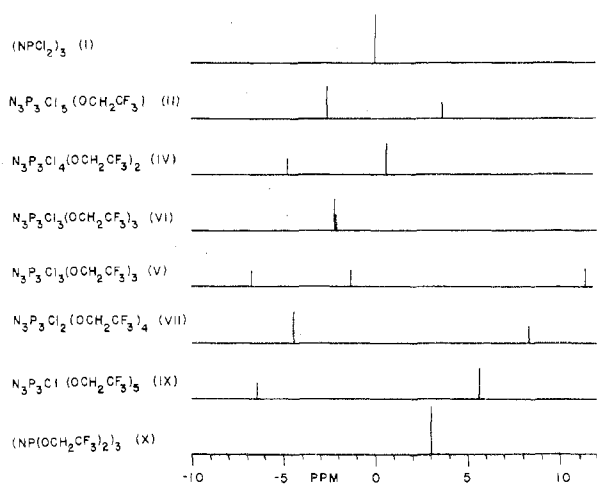**Mechanistic Pathway.** The evidence is consistent with an

Figure 3. ^{31}P chemical shifts of the cyclotriphosphazenes isolated during this study.

SN2-type mechanism in which inversion of configuration occurs during replacement of halogen by a trifluoroethoxy group. Other workers have postulated a "cis effect" to explain the substitution patterns observed when piperidine or other nucleophiles react with hexachlorocyclotriphosphazene.[21] Thus, piperidino[21] or dimethylamino[22] groups were assumed to supply electrons to the cis chlorine atoms thereby labilizing them and facilitating nongeminal nucleophilic attack with inversion from a direction trans to the amino group. If this mechanism were widely applicable, it would be expected that the opposite influence would be exerted by a strongly electron-withdrawing group such as trifluoroethoxy, namely, that cis nongeminal products should predominate. In fact, this is not observed, the cis:trans ratio for trifluoroethoxy being less than 0.2.

A second paradox found in the earlier work also appears to be inapplicable to our system. The forces proposed to be operative in the "cis effect" are said to cause higher electron density at a phosphorus atom to which one dimethylamino group and one chlorine atom are attached, yet the NMR suggested that this phosphorus was *less* shielded than one to which two chlorine atoms were attached.[23] We find the opposite to be true for trifluoroethoxy-substituted phosphazenes. The expected situation prevails, and the phosphorus atoms become progressively more shielded as additional chlorine atoms are replaced by trifluoroethoxy groups.

In the trifluoroethoxyphosphazene system, the results can be explained by the assumption that the substitution patterns are dominated by steric effects. The relatively bulky trifluoroethoxy substituent groups already present sterically direct the incoming nucleophile into a trans nongeminal attack pattern. Molecular models suggest that the steric hindrance between two trifluoroethoxy groups attached to the same ring decreases in the order geminal > cis nongeminal > trans nongeminal. This is true irrespective of whether the ring is planar or puckered in a chair or boat conformation. In fact, we suspect that steric factors will predominate over electronic effects for all substituent groups larger than NH$_2$, NHCH$_3$, or OCH$_3$.

Thus, in summary, the following mechanism is suggested. Nucleophilic attack by an SN2 process occurs at the least-hindered side of the ring. Steric hindrance in the final product is not nearly so important as the steric hindrance during the approach of the nucleophile. Thus, although nucleophilic attack takes place from the least hindered side of the *ring*, it may, in fact, require attack on the most hindered side of a particular phosphorus atom. For example, replacement of a chlorine atom in nongeminal tris(trifluoroethoxy)cyclotriphosphazene (VI) must proceed by an approach from the

side of the molecule that bears the two cis chlorine atoms, with attack on the phosphorus atom which bears a trifluoroethoxy group on that same side to give (following inversion of configuration) compound VII. The alternative process would have yielded preferentially the trans tetrakis product VIIIb. A similar mechanism was suggested by previous workers in connection with the introduction of phenoxy groups.[24]

Relationship to Polymer Synthesis. The synthesis of high molecular weight poly(fluoroalkoxyphosphazenes), [NP-(OR)$_2$]$_n$, by the interaction of sodium fluoroalkoxides with poly(dichlorophosphazene), (NPCl$_2$)$_n$, has been described previously.[9,10,12-15] Mixed-substituent polymers have also been prepared either by metathetical ligand exchange[12] or by cosubstitution with two or more different nucleophiles.[25-27] These latter products have a broad technological potential. It is important, therefore, to understand the pattern of alkoxide introduction in order that the disposition of two or more substituent groups along the chain can be predicted. The results obtained with phosphazene trimers cannot always be used to predict reaction patterns for phosphazene cyclic tetramers or high polymers because the conformational characteristics are different. Nevertheless, if the general reaction is dominated by steric effects, as appears to be the case in the trimer, two predictions can be made with respect to high polymer substitutions. First, nongeminal replacement of chlorine would be expected in solvents of low polarity and at moderate or low temperatures. Second, the trans-substitution pattern may not be retained in the polymer. Attack by the nucleophile is still expected to take place from the least hindered side of the molecule. However, the conformational mobility of the polyphosphazene chain is so high that either trans or cis products could be formed depending on whether the *chain* conformation is trans,trans (planar zigzag) or cis,trans planar[28,29] at the site of substitution. This suggests that the microcrystallinity detected in some mixed-substituent fluoroalkoxyphosphazene polymers may be due to homopolymer blocks rather than to the presence of genuine isotactic or syndiotactic sequences.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was obtained from El Monte Chemical Co., Pasadena, Calif., and was purified by sublimation and recrystallization from heptane to give material of mp 111.5–113.5°. Trifluoroethanol was obtained from Halocarbon Products Corp. and was used as received. Anhydrous diethyl ether and metallic sodium were obtained from Fisher Scientific Co. The diethyl ether was used as received from freshly opened containers. Sodium was purified with the use of an apparatus designed in this laboratory for separation of the molten metal from the impure crust. Deuterated solvents were from Mallinckrodt Chemical Co. Solvents for the dipole moment determinations were Fisher Spectroanalyzed reagents. These were dried with Linde molecular sieve, type 4A, by the method of Oehme and Wirth.[30]

Analyses and Instrumentation. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz. Vapor-phase chromatography was carried out with the use of a Hewlett-Packard Model 5750 with a Model 5795A preparative attachment. A $^1/_4$ in × 6 ft stainless steel column which contained 10% OV-17 silicone (50% phenyl, methyl) on 80–100 mesh Gas-Chrom Q (Applied Science Laboratories, Inc., State College, Pa.) was used for the preparative work. A similarly packed $^1/_8$ in. × 10 ft column was used for analytical experiments. Mass spectra were obtained on an AEI MS902 mass spectrometer at ionization potentials of 70 and 14 eV. Proton and phosphorus-31 NMR spectra were observed in deuterated acetone, benzene, or chloroform, on a Jeol PS-100 FT NMR or a Varian HA-100 spectrometer. Fractional distillations were performed with the use of a Todd column assembly which contained a 12-mm i.d. column packed with 4-mm glass helices. The reflux ratio was 50:1 and the temperatures were adjusted to give a takeoff rate of about 4 drops/min. For the final distillation of V, VII, and IX, the takeoff rate was reduced to about 1 drop/min. Refractive indices were obtained using a Bausch and Lomb Abbe-3L refractometer.

Table III. Relative Product Yields (%) for the Reactions of Sodium Trifluoroethoxide with Hexachlorocyclotriphosphazene[a,b]

Temp, °C	NaOCH$_2$CF$_3$: (NPCl$_2$)$_3$	I	II	III	IV	V	VI	VII	VIIIb[c]	IX	X
0	1.4:1	29	26		30	2	9	4			
	2.9:1		2	1	32	2	41	20		2	
	4.3:1						11	42	1	42	4
25	1.4:1	33	24		24	2	9	6		2	
	2.9:1		6	1	29	3	34	23		4	
	4.3:1					2	11	38	1	40	7
50	1.4:1	35	23	2	23	2	6	4	6		
	2.9:1		8	2	32	2	27	19	5	3	
	4.3:1					2	16	45	5	26	6

[a] In tetrahydrofuran solution. [b] These product ratios were obtained after dropwise addition of 0.3 M NaOCH$_2$CF$_3$ solution to 0.071 M (NPCl$_2$)$_3$ solution. [c] The identity of this product was inferred from the predominance of VI in the mixture. However, no definitive evidence could be obtained to confirm the structure.

Dipole moments were obtained with the use of a Model DM 01 dipolemeter with a Model DFL 1 cell, both from Kahl Scientific Instrument Co. The methods of Guggenheim and Smith[31,32] were used. The solvent used was cyclohexane. Benzene, carbon tetrachloride, air, and cyclohexane were used for instrument calibration. Temperature control of the dipolemeter was facilitated with a Model TE3 Tamson bath. Concentrations used ranged from 2.0 to 0.5 wt %.

Reaction of Trifluoroethanol with Sodium. A nitrogen-purged 5-l. reaction flask, equipped with a bottom drain, was fitted with an addition funnel and stirrer and was charged with purified sodium (200 g, 8.7 mol) and diethyl ether (1000 g). Trifluoroethanol (1500 g, 15 mol) was added slowly. Additional ether (about 500 g) was added during the course of the reaction to replace the ether lost in the nitrogen stream. *Caution!* Attempts to isolate solid sodium trifluoroethoxide gave only adducts which contained up to 2 mol of the alcohol and 1 mol of the sodium salt. *Attempts to remove all the alcohol by warming in vacuum resulted in explosions.*

Synthesis of Trifluoroethoxypentachlorocyclotriphosphazene, N$_3$P$_3$Cl$_5$(OCH$_2$CF$_3$), Bis(trifluoroethoxy)tetrachlorocyclotriphosphazene, N$_3$P$_3$Cl$_4$(OCH$_2$CF$_3$)$_2$, and Tris(trifluoroethoxy)trichlorocyclotriphosphazene, N$_3$P$_3$Cl$_3$(OCH$_2$CF$_3$)$_3$. To a slurry of (NPCl$_2$)$_3$ (1.5 kg, 4.3 mol) and ether (500 g) in a 12-l. flask cooled in an ice bath was added an etheric solution of sodium trifluoroethoxide as described above. The addition was carried out over 3–4 hr with stirring. When the addition was complete, the mixture was extracted with water to remove sodium chloride and sodium trifluoroethoxide and the etheric solution was dried overnight with anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and most of the ether was removed by distillation. A rapid vacuum distillation was then used to remove excess trifluoroethanol and the last traces of ether. An earlier attempt to incorporate this last step into the much slower Todd column fractionation resulted in the loss of about 50% of the product by polymerization. Apparently a rapid distillation serves to remove a polymerization catalyst from the product mixture fraction. The catalyst may be water. The product was then fractionated on the Todd column in 500–800-ml portions and each fraction (15 ml or less) was analyzed with the use of gas chromatography. All the fractions which contained primarily the same product were combined and each of these was again refractionated until a sample of sufficient purity of each of the products was obtained. The reaction was virtually quantitative. The amount and purity of each compound depended on the number of column fractionations performed. The final traces of other products were removed by preparative gas chromatography. The products included the following. N$_3$P$_3$Cl$_5$(OCH$_2$CF$_3$): bp 131° (16 mm), d = 1.72 g/ml, n^{20}D 1.4808, n^{25}D 1.4787. Anal. Calcd for C$_2$H$_2$OCl$_5$F$_3$N$_3$P$_3$: C, 5.84; H, 0.49; N, 10.22; mol wt 408.78. Found: C, 5.99; H, 0.39; N, 10.41; mol wt (by high-resolution mass spectrometry) 408.78. N$_3$P$_3$Cl$_4$-(OCH$_2$CF$_3$)$_2$: bp 137° (16 mm), d = 1.70 g/ml. Anal. Calcd for C$_4$H$_4$O$_2$Cl$_4$F$_6$N$_3$P$_3$: C, 10.12; H, 0.85; N, 8.85; mol wt 472.82. Found: C, 10.14; H, 1.02; N, 8.74; mol wt (by mass spectrometry) 472.82. *trans*-N$_3$P$_3$Cl$_3$(OCH$_2$CF$_3$)$_3$: bp 143° (16 mm), d = 1.67 g/ml, n^{20}D 1.4088, n^{25}D 1.4070. Anal. Calcd for C$_6$H$_6$O$_3$Cl$_3$F$_9$N$_3$P$_3$: C, 13.38; H, 1.12; N, 7.80; mol wt 536.85. Found: C, 13.32; H, 1.11; N, 7.79; mol wt (by mass spectrometry) 536.8554. *gem*-N$_3$P$_3$Cl$_3$-(OCH$_2$CF$_3$)$_3$: bp 141° (16 mm), mol wt (calcd) 536.85; mol wt found (by mass spectrometry) 536.86. The progress of the reaction was monitored directly by VPC analysis of the reaction mixtures during

a series of preliminary experiments. The relative percentage ratios of the products were estimated from both the VPC and the product isolation experiments.

Synthesis of Tetrakis(trifluoroethoxy)dichlorocyclotriphosphazene, N$_3$P$_3$Cl$_2$(OCH$_2$CF$_3$)$_4$, and Pentakis(trifluoroethoxy)chlorocyclotriphosphazene, N$_3$P$_3$Cl(OCH$_2$CF$_3$)$_5$. These two members of the series were synthesized using essentially the same procedure as described above, but with the following quantities of reactants. **Synthesis of NaOCH$_2$CF$_3$:** sodium (453 g), initially in ether (3000 g), with another 1000 g of ether added during the course of the reaction, was allowed to interact with trifluoroethanol (3000 g). **Substitution of (NPCl$_2$)$_3$:** hexachlorocyclotriphosphazene (1500 g) in ether (1000 g) was allowed to react with the above solution of sodium trifluoroethoxide. N$_3$P$_3$Cl$_2$(OCH$_2$CF$_3$)$_4$: bp 147° (16 mm), d = 1.67 g/ml, n^{20}D 1.3857, n^{25}D 1.3839. Anal. Calcd for C$_8$H$_8$O$_4$Cl$_2$F$_{12}$N$_3$P$_3$: C, 15.96; H, 1.34; N, 6.98; mol wt 600.89. Found: C, 16.10; H, 1.32; N, 6.92; mol wt (by mass spectrometry) 600.98. N$_3$P$_3$Cl(OCH$_2$CF$_3$)$_5$: bp 150° (16 mm), d = 1.63 g/ml,[5] n^{20}D 1.3674, n^{25}D 1.3653. Anal. Calcd for C$_{10}$H$_{10}$O$_5$ClF$_{15}$N$_3$P$_3$: C, 18.05; H, 1.51; N, 6.31. Found: C, 18.25; H, 1.28; N, 6.27.

Table III lists relative yields of the products formed by these reactions at various temperatures in tetrahydrofuran solvent.

Registry No. I, 940-71-6; II, 13053-90-2; III, 55975-47-8; IV, 55975-48-9; V, 55975-49-0; VI, 55975-50-3; VII, 55975-51-4; VIIIb, 55975-52-5; IX, 55975-53-6; X, 1065-05-0; NaOCH$_2$CF$_3$, 420-87-1.

References and Notes

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(18) In the usual method for obtaining dipole moments, the refractive index term, which contains the electronic polarizability, is subtracted from the dielectric constant term which contains the dipole moment, atomic polarizability, and the electronic polarizability. Thus the calculated dipole moment contains a contribution from the atomic polarizability. This is usually neglected since this contribution is small compared to the permanent dipole moment and electronic polarizability for *small rigid*

molecules. The compounds studied here apparently do not meet this criterion.

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Reactions of the Phosphorus Cage Molecule Tetraphosphorus Hexaoxide with Some Iron Carbonyls

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The phosphorus cage molecule P_4O_6 reacts with $Fe(CO)_5$ in diglyme solvent at 140° to produce $(CO)_4Fe(P_4O_6)$, *trans*-$(CO)_3Fe(P_4O_6)_2$, and P_4O_7, whereas the photochemical reaction in benzene or THF solvent yields the same two iron-containing compounds and another phosphorus oxide, presumably P_4O_9. The relative yield of $(CO)_4Fe(P_4O_6)$ to *trans*-$(CO)_3Fe(P_4O_6)_2$ during photochemical reactions is markedly solvent dependent. Under a carbon monoxide atmosphere, $Fe_2(CO)_9$ in THF reacts with P_4O_6 to produce the series of compounds $[(CO)_4Fe]_n(P_4O_6)$, where $n = 1-4$, where the products are essentially controlled by reaction stoichiometry. The reaction of P_4O_6 with $Fe_3(CO)_{12}$ parallels the reaction with $Fe_2(CO)_9$. Trends in ^{31}P chemical shifts and coupling constants are noted and discussed.

Introduction

Tetraphosphorus hexaoxide, P_4O_6, consists of tetrahedrally arranged phosphorus atoms with bridging oxygen atoms.[1] As such, the phosphorus atoms in one P_4O_6 molecule constitute, at least potentially, a nonchelating, tetrahedral, tetradentate ligand. Previous studies have shown that P_4O_6 does indeed behave as a tetradentate base toward $Ni(CO)_4$;[2] however toward B_2H_6, the phosphorus cage molecule exhibits only moderate basicity.[3] This indication of preferred basicity toward metal carbonyls has prompted the close investigation of P_4O_6 with the iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$. The results of this study are reported herein. A brief reference to the reaction of P_4O_6 with neat $Fe(CO)_5$ and $Fe_2(CO)_9$ has been reported previously.[2]

Experimental Section

All compound transfers and manipulations were carried out in a drybox, in a glove bag, or by use of Schlenk-type glassware using standard inert-atmosphere techniques.[4] All solvents were distilled from CaH_2 and collected and stored over Linde 4A molecular sieves. Solvents were degassed with a nitrogen purge for at least 5 min prior to use. The iron compounds iron pentacarbonyl, $Fe(CO)_5$, diiron enneacarbonyl, $Fe_2(CO)_9$, and triiron dodecacarbonyl, $Fe_3(CO)_{12}$, were purchased from Pressure Chemical Co. The compounds $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were used as received, and $Fe_2(CO)_9$ was dried in vacuo at 50° for 1 hr.[5] The compound P_4O_6 was prepared by controlled oxidation of white phosphorus with air, as previously described.[6] A Varian Associates NMR spectrometer Model XL-100-15 operating at 40.55 MHz was used to obtain ^{31}P spectra, employing either external or internal P_4O_6 as a reference. Ir spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer with sealed liquid cells equipped with KBr windows. Mass spectra were recorded on a Varian Matt Model 311 spectrometer. Photochemical reactions were carried out using a 100-W medium-pressure Hanovia lamp in Pyrex reaction vessels.

Reactions. (a) Thermal Reaction of P_4O_6 with $Fe(CO)_5$. One milliliter (9.7 mmol) of P_4O_6 was added to 15 ml of degassed diglyme in a 25-ml three-necked round-bottom flask under N_2 atmosphere.

To this was added 1.4 ml (10.0 mmol) of $Fe(CO)_5$. With the flask connected to an Hg bubbler, the reaction mixture was heated to 140° in an oil bath for 9 hr. The reaction mixture remained light yellow until a temperature of 110–120° was reached and then gradually darkened and became viscous. The reaction mixture was allowed to cool to room temperature and was filtered. The diglyme was removed from the filtrate at ambient temperature under dynamic vacuum. The residue was fractionally sublimed at 80°.[7] The sublimate consisted of about 3.0 mmol of P_4O_7[6] and 3.0 mmol of the less volatile, clear yellow crystals of $(CO)_4Fe(P_4O_6)$. The residue from the initial sublimation was transferred to a conventional sublimator and heated to 120° for 3 hr yielding crystals (ca. 1.5 mmol) of *trans*-$(CO)_3Fe(P_4O_6)_2$.

(b) Photochemical Reaction of P_4O_6 with $Fe(CO)_5$. One milliliter (9.7 mmol) of P_4O_6 and 1.3 ml (9.3 mmol) of $Fe(CO)_5$ were added to 50 ml of degassed benzene or tetrahydrofuran (THF) and irradiated under N_2 atmosphere for 10–16 hr. Some evidence of reaction was noted after ca. 1 hr of irradiation. The reaction mixture was filtered and the solvent was removed from the filtrate via vapor transfer. The remaining oil was washed five times with 10-ml portions of pentane. The residue showed no ^{31}P resonances. The pentane was removed by vapor transfer and the residue was sublimed under a dynamic vacuum at 80°. The sublimed material was identified as $(CO)_4Fe(P_4O_6)$. The unsublimed residue contained $(CO)_3Fe(P_4O_6)_2$ in addition to an unidentified contaminate (possibly P_4O_9, see Results). A separation of these compounds has not been achieved.

(c) Reaction of P_4O_6 with $Fe_2(CO)_9$. One milliliter (9.7 mmol) of P_4O_6 was added to 20 ml of THF which had been purged with CO. While under CO atmosphere, 12.8 g (36.0 mmol) of $Fe_2(CO)_9$ was added with vigorous stirring to the solution at 35°.[5] The reaction was then heated to 50° for 30 min. After cooling, the THF was removed to give $[(CO)_4Fe]_4(P_4O_6)$ with some $Fe_3(CO)_{12}$. By progressively lowering the mole ratio of $Fe_2(CO)_9$:P_4O_6 in the initial reaction stoichiometry from ca. 4:1 to 1:1, the entire series of compounds $[(CO)_4Fe]_n(P_4O_6)$, where $n = 1-4$, was observed (see Results).

(d) Reaction of P_4O_6 with $Fe_3(CO)_{12}$. One milliliter (9.7 mmol) of P_4O_6 was added to 30 ml of glyme or THF containing 2.0 g (4.0 mmol) of $Fe_3(CO)_{12}$. The mixture was heated to 70° for 1 hr, during which time the green color of $Fe_3(CO)_{12}$ disappeared. The solution