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Stereodirective Effects in Mixed Substituent Vinyloxycyclotriphosphazenes

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Reaction pathways leading to the new mixed substituent cyclophosphazenes, $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3)$ and $N_3P_3Cl_3(OCH{=}CH_2)(OCH_2CF_3)_2$, have been explored. Examination of the relative isomeric yields and the spectroscopic properties of these new derivatives gave insight into the mechanism of substitution of cyclophosphazenes with oxyanions. The syntheses of the mixtures of compounds were carried out by two different synthetic pathways. The nucleophilic substitution reaction involves either the vinyloxy ($^-OCH{=}CH_2$) or the trifluoroethoxy ($^-OCH_2CF_3$) ion. Either oxyanion could be reacted with the phosphazene first to be followed by the other oxyanion. A comparison of the observed pathways shows the stereoselectivity is controlled by the ring substituent with trifluoroethoxy species favoring trans substitution and the vinyloxy species favoring increased cis substitution. Density Functional Theory and NMR (^{13}C, ^{31}P) studies show the electronic relationships between the exocyclic group and the cyclophosphazenes including transmission of electronic information throughout the phosphazene ring.

Introduction

The cyclophosphazenes are known to undergo reactions with a variety of organic and organometallic reagents.[1−3] Of these many reactions, nucleophilic substitution reactions have been studied most extensively. Most investigations have focused on reactions of phosphazenes with amines, and the anions of alcohols and thiols. In many cases, reactions are performed on cyclophosphazenes as model reactions for reactions on the corresponding polymers.[4] There are a large number of studies dealing with the reactions of amines with hexachlorocyclotriphosphazene(**1**) and the mechanisms leading to the observed stereochemical pathways in these reactions.[2] Detailed studies of the reactions of alcohols and their anions are more limited and much is still unclear about the substitution patterns found in these reactions. It has been observed that a non-geminal pathway is preferred in these reactions. Depending upon the nature of the aryloxy or alkoxy ion, a cis or trans isomer substitution pattern may be favored. There are two oxyanions whose reaction pathways have been firmly established. We have shown that the enolate ion of acetaldehyde reacts with hexahalocyclotriphosphazenes $N_3P_3X_6$ [X = F,[5] Cl(**1**)[6]] and that these reactions are stereoselective showing a preference for the cis isomer in the reactions of **1**.[7] The cis isomer is also preferred in the reactions hexahalocyclophosphazenes with aryloxides.[8,9] The (vinyloxy)pentachlorocyclotriphosphazene, $N_3P_3X_5(OCH{=}CH_2)$ (**2**), has also been used as a monomer in free radical polymerization.[10] Allcock and Schmutz have previously explored the reaction of the sodium salt of trifluoroethanol with **1** and have shown that there is a strong preference for formation of the non-geminal trans isomer.[11] Although the reactions of **1** leading to a mixed substituent system involving amines and alkoxides have been reported[12] and one system was found to follow an unusual regiochemical pathway,[13] little interest has been shown in the reactions of hexachlorocyclotriphosphazene with two or more different oxyanions.

This paper involves the investigation of the substitutional pathways of hexachlorocyclotriphosphazene when reacted with both the enolate anion and sodium trifluoroethoxide. The products, $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3)$, **(5a,b)**, and

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$N_3P_3Cl_3(OCH{=}CH_2)(OCH_2CF_3)_2$, **(6)**, were found to contain various amounts of cis, trans, and geminal isomers. The relative amounts of isomers present in a reaction mixture were studied in relation to the order of addition of reagents in these reactions. The resulting mixed vinyloxy(trifluoroethoxy)cyclotriphosphazenes **(5a,b)** and **(6)** are also of interest as new monomers for polymer synthesis. A brief preliminary report of selected aspects of this work has appeared.[14]

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Nippon Soda Co., Ltd.) was used without further purification. Diethyl ether (EM) and tetrahydrofuran (THF) (Aldrich) were distilled from NaH or potassium before use and stored under nitrogen. All other solvents and reagents were purchased (Aldrich, Anachemia or EM) and were used without further purification unless otherwise noted.

Characterization. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Robertson Laboratory, Inc., Madison, NJ. Capillary gas chromatography (GC) was carried out with the use of a Varian Model 3700 equipped with a flame ionization detector. A Restek Corp. RTX-5 30 m 0.25 mm ID capillary column which contained crossbonded SE-54 (1.00 μm) was used for analytical GC experiments. Mass spectra were obtained on a Finnigan 4610 spectrometer operating at 80 eV. Gas chromatography−mass spectrometry (GC-MS) was carried out on the above spectrometer fitted with a Restek Corp. RTX-5 GC column. Proton (^{1}H) and carbon (^{13}C) NMR spectra were observed in deuterated chloroform on a Bruker WP-270SY spectrometer with an Aspect 2000 data station. Operating frequencies were 270.1 MHz (^{1}H) and 67.9 MHz (^{13}C). Phosphorus (^{31}P), fluorine (^{19}F), as well as additional proton (^{1}H) and carbon (^{13}C), NMR spectra were recorded on a Bruker WM-250 spectrometer with an Aspect 3000 data station. Operating frequencies were 101.2 MHz (^{31}P), 235.4 MHz (^{19}F), 250.1 MHz (^{1}H), and 62.9 MHz (^{13}C). Phosphorus (^{31}P) chemical shifts were reported in ppm with positive shifts being downfield relative to 85% H_3PO_4 at 0 ppm. Broad band ^{1}H decoupling was used for ^{13}C, ^{31}P, and ^{19}F spectra unless otherwise noted. NMR simulations were carried out with a locally modified version of DNMR-3.[15] Infrared (IR) spectra were recorded on either a Perkin-Elmer 1430 spectrophotometer or a Nicolet 6000SB Fourier transform spectrometer. Samples were either solid pressed KBr disks, thin films cast from CH_2Cl_2, or liquids on NaCl disks. All density functional theory (DFT) calculations were carried out as previously reported.[9,16]

Preparation of $N_3P_3Cl_5(OCH{=}CH_2)$ (2). This compound has been synthesized previously by a slightly different procedure.[6,17] A 250 mL round-bottom flask was equipped with a magnetic stirring bar, evacuated and backfilled with nitrogen using a Schlenk line, and kept under nitrogen pressure. The flask was filled with 150 mL of dry THF by Schlenk techniques, and 75 mL (0.19 mol) of an *n*-butyl lithium solution was added by syringe at 0 °C. The solution immediately turned a pale-green color. This mixture, the enolate solution, was allowed to warm to room temperature and stir for 12 h. The enolate solution was then added dropwise to a solution of 50 g (0.14 mol) of $N_3P_3Cl_6$ in 500 mL of dry THF at 0 °C in a nitrogen atmosphere. The mixture was allowed to react for 12 h while warming to room temperature. The solvent was removed from the resulting yellow solution under reduced pressure. The residue was dissolved in hexane and extracted with water. The organic layer was dried over magnesium sulfate and activated charcoal was added. The solution was filtered and solvent removed to give 36.5 g of crude **2**, as a yellow oily liquid. This liquid was purified by flash chromatography using petroleum ether (20−40°) as the eluent. Unreacted $N_3P_3Cl_6$ was eluted first, followed by the product. The fractions containing pure product (as determined by GC) were combined and the solvent removed. The product was then distilled in vacuo to give 23.36 g (0.069 mol, 45.6% yield) of a clear colorless liquid, bp 65−70 °C (0.1 mm Hg). Anal. Calcd for $N_3P_3Cl_5(OCH{=}CH_2)$: C, 6.76%; H, 0.84%; mol wt 356. Found: C, 6.74%; H, 0.80%; mol wt 356 (mass spectrum).

Preparation of $N_3P_3Cl_5(OCH_2CF_3)$ (3). This product has been synthesized and characterized previously by slightly different procedures.[11] All reactions were carried out in dry solvents and under a nitrogen atmosphere. A 250 mL round-bottom flask was equipped with a stirring bar and charged with 2.58 g (0.11 mol) Na metal and 100 mL of dry diethyl ether. To this mixture, 11.35 g (8.30 mL, 0.11 mol) of trifluoroethanol was slowly added by syringe at 0 °C. The sodium quickly disappeared, and the solution turned cloudy. This solution was transferred to an addition funnel by Schlenk line techniques and added to 30.0 g (0.087 mol) of $N_3P_3Cl_6$ in 250 mL of diethyl ether at 0 °C. The reaction mixture was allowed to come to room temperature and stir for 12 h. The mixture was then extracted with distilled water; the organic layer dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure. A gas chromatogram of the crude product revealed products of which **3** was shown to be the major portion. This mixture (32.0 g) was purified by flash chromatography using petroleum ether (20−40°) as the eluent. The order of elution of the products was $N_3P_3Cl_5(OCH_2CF_3) > N_3P_3Cl_4(OCH_2CF_3)_2 > N_3P_3Cl_3(OCH_2CF_3)_3 >$ and so forth. The fractions containing the desired product (as determined by GC) were combined and the solvent removed. The product was distilled in vacuo to give 10.09 g (0.025 mols, 28.4% yield) of a clear colorless liquid, bp 58−62 °C (0.1 mm Hg). The product was identified by its by mass spectrum and ^{31}P, ^{1}H, ^{19}F NMR spectra. Anal. Calcd for $N_3P_3Cl_5(OCH_2CF_3)$: mol wt 411 Found: mol wt 411 (mass spectrum). ^{1}H NMR: $\delta(\equiv POCH_2CF_3) = 4.6-4.3$ (complex multiplet). $^{31}P\{^1H\}$ NMR: $\delta(\equiv PCl_2) = 23.8$ *(d, 2P),* $\delta(\equiv PCl(OCH_2CF_3) = 17.3$ (t, 1P) ($^2J_{PP} = 65.3$). ^{19}F NMR: $\delta(\equiv POCH_2CF_3) = -61.7$ (t, 3F) ($^2J_{HF} = 7.7$).

Preparation of $N_3P_3Cl_4(OCH_2CF_3)_2$ (4). This product was obtained from the later fractions of flash chromatography in the preceding synthesis of **3**. The product was further purified by distillation in vacuo to give a clear colorless liquid, bp 72−73 °C (0.1 mm Hg). This material has been synthesized and characterized previously.[11] The product was identified by its mass spectrum and ^{31}P, ^{1}H NMR spectra. Anal. Calcd for $N_3P_3Cl_4(OCH_2CF_3)_2$: mol wt 474. Found: mol wt 474 (mass spectrum).

Preparation of $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3)$, Method A = (5a). All reactions were carried out in dry solvents and in nitrogen atmosphere. A 100 mL round-bottom flask was equipped with a stir bar and charged with 0.19 g Na metal and 50 mL of dry diethyl ether. To this mixture, 0.84 g (0.65 mL, 8.3 mmol) of trifluoroethanol were slowly added by syringe at 0 °C. The sodium quickly disappeared, and the solution turned cloudy. This solution was then transferred to an addition funnel and added to 2.0 g (5.6 mmol) of **2** in 100 mL of diethyl ether at 0 °C. The reaction was allowed to come to room temperature and stir for 12 h. The mixture was then extracted with distilled water; the organic layer dried over magnesium sulfate, filtered,

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and the solvent was removed at under reduced pressure. GC of the crude material revealed several products of which **5a** constituted the major portion. A 2.22 g sample of this mixture was purified by flash chromatography using petroleum ether (20−40°) as the solvent. The order of elution for this material was $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3) > N_3P_3Cl_3(OCH{=}CH_2)$-$(OCH_2CF_3)_2$ > and so forth. The fractions containing the pure product (as determined by GC) were combined, and the solvent removed. The product was then distilled in vacuo to give 0.54 g (1.3 mmol, 22.9% yield) of a clear colorless liquid, bp 60−65 °C (0.1 mm Hg). Anal. Calcd for $N_3P_3Cl_4(OCH{=}CH_2)$-(OCH_2CF_3): mol wt 418. Found: mol wt 418 (mass spectrum). Analysis of the ^{31}P NMR spectrum showed a mixture of isomers.

Preparation of $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3)$, Method B = (5b). All reactions were carried out in dry solvents and in nitrogen atmosphere. A 250 mL round-bottom flask was equipped with a stir bar, charged with 100 mL of dry THF and 11.73 mL of a 2.5 M *n*-butyllithium solution (0.03 mol) was slowly added by syringe at 0 °C. This solution was allowed to warm to room temperature and stir for 12 h. This solution was transferred to a 250 mL addition funnel and added dropwise to a 500 mL round-bottom flask containing a solution of 9.30 g (0.02 mol) of **3** in 200 mL of THF at 0 °C. This mixture was allowed to stir for 16 h, at which time the solvent was removed under reduced pressure, and the remaining slurry was extracted with hexane and water washes. The organic layer was dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure. This yielded 8.5 g of a pale-yellow oil. GC of this oil revealed a mixture of several products. The mixture was purified by flash chromatography using petroleum ether (20−40°) as the eluent. The order of elution for these materials was $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3) > N_3P_3Cl_3$-$(OCH{=}CH_2)_2(OCH_2CF_3)$ > higher degrees of substitution. Fractions after 450 mL of solvent had eluted were collected, checked by GC for purity, and combined. The product was then distilled in vacuo to give 7.31 g (0.018 mol, 75.8% yield) of a clear, colorless liquid, bp 51−53 °C (0.05 mm Hg). Anal. Calcd for $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3)$: mol wt 418. Found: mol wt 418 (mass spectrum). ^{1}H NMR: $\delta(\equiv POC\mathbf{H}=CH_2) = 6.5$ (center of a complex multiplet, 1H). $\delta(\equiv POCH{=}C\mathbf{H}_2(\text{trans})) = 5.1$ (center of a complex multiplet, 1H). $\delta(\equiv POCH{=}C\mathbf{H}_2(\text{cis})) =$ 4.9−4.8 (complex multiplet, 1H). $\delta(\equiv PO\mathbf{CH}_2CF_3) = 4.5-4.3$ (complex multiplet, 2H). $^{13}C\{^1H\}$ NMR: $\delta(\equiv PO\mathbf{C}H{=}CH_2) = 140.1$ (s), $\delta(\equiv PCl(OCH_2\mathbf{C}F_3) = 121.9$ (q) ($^2J_{CF} = 275.5$), $\delta(\equiv POCH=\mathbf{C}H_2) = 104.1$ (s), $\delta(\equiv PCl(O\mathbf{C}H_2CF_3) = 63.5$ (m). ^{31}P NMR: **trans isomer**; $\delta(\equiv \mathbf{P}_aCl_2) = 25.44$ (m, 1P), $\delta(\equiv \mathbf{P}_b\mathrm{Cl}(OCH_2CF_3) = 19.77$ (m, 1P), $\delta(\equiv \mathbf{P}_cCl(OCH{=}CH_2) = 15.61$ (m, 1P), ($^2J_{PaPb} = -78$), ($^2J_{PaPc} = 70$), ($^2J_{PbPc} = 69.5$). ***cis isomer***; $\delta(\equiv \mathbf{P}_a\mathrm{Cl}_2) = 25.42$ (m, 1P), $\delta(\equiv \mathbf{P}_bCl(OCH_2CF_3) = 19.88$ (m, 1P), $\delta(\equiv \mathbf{P}_c\mathrm{Cl}(OCH{=}CH_2) = 15.69$ (m, 1P), ($^2J_{PaPb} = 72$), ($^2J_{PaPc} = 69.5$), ($^2J_{PbPc} = 69.5$). **geminal isomer**; $\delta(\equiv \mathbf{P}Cl_2) = 24.80$ (d, 2P), $\delta(\equiv \mathbf{P}(OCH_2CF_3)(OCH{=}CH_2) = 2.69$ (t, 1P), ($^2J_{PP} = 72$). ^{19}F NMR: $\delta(\equiv POCH_2C\mathbf{F}_3) = -61.8$ (t, 3 F) ($^2J_{HF} = 7.7$). IR: 1645 (s, C=C), 1450 (m, PO str), 1416 (m, $-CH_2-$), 1290 (s, CF str), 1217 (s, PN str), 1174 (s, CF str), 1109 (s, PO str), 1085, 1036 (s), 959 (m, C=C), 864 (m, PCl str), 751 (m, PCl str), 662 (m, PCl str).

Preparation of $N_3P_3Cl_3(OCH{=}CH_2)(OCH_2CF_3)_2$ (6). Reactions were carried out in dry solvents and in a nitrogen atmosphere. A 250 mL round-bottom flask was equipped with a stir bar, charged with 100 mL of dry THF, and 16.4 mL of a 2.5 M *n*-butyllithium solution (0.04 mol) was slowly added by syringe at 0 °C. This solution was allowed to warm to room temperature and stir for 12 h. This solution was then transferred to a 250 mL addition funnel and added dropwise to a 500 mL round bottomed flask containing a solution of 9.30 g (0.02 mol) of $N_3P_3Cl_4(OCH_2CF_3)_2$, **(4)**, in 200 mL of THF at 0 °C. This mixture was allowed to stir for 16 h, at which time the solvent was removed under reduced pressure, and the remaining slurry was extracted from hexane and water washes. The organic layer was dried over magnesium sulfate, filtered, and the solvent removed under reduced pressure. This yielded 8.5 g of pale-yellow oil. The mixture was purified by flash chromatography using 1.5% diethyl ether/98.5% petroleum ether (20−40°) (v/v) as the eluent. Fractions after 200 mL of solvent had eluted were collected, checked by GC for purity, and combined. The product was then distilled in vacuo to give 5.02 g (0.01 mol, 45.3% yield) of a clear, colorless liquid, bp 72−73 °C (0.05 mm Hg). Anal. Calcd for $N_3P_3Cl_3(OCH{=}CH_2)(OCH_2CF_3)_2$: C, 14.94%; H, 1.45%; mol wt 482. Found: C, 15.21%; H, 1.41%; mol wt 482 (mass spectrum). ^{1}H NMR: $\delta(\equiv POC\mathbf{H}=CH_2) = 6.5$ (center of a complex multiplet, 1H). $\delta(\equiv POCH{=}C\mathbf{H}_2(\text{trans})) = 5.1$ (center of a complex multiplet, 1H). $\delta(\equiv POCH{=}C\mathbf{H}_2(\text{cis})) =$ 4.9−4.8 (complex multiplet, 1H). $\delta(\equiv PO\mathbf{CH}_2CF_3) = 4.5-4.3$ (complex multiplet, 4H). $^{13}C\{^1H\}$ NMR: $\delta(\equiv PO\mathbf{C}H{=}CH_2) =$ 140.4 (s), $\delta(\equiv PCl(OCH_2\mathbf{C}F_3) = 122.4$ (q) ($^2J_{CF} = 278.4$), $\delta(\equiv POCH=\mathbf{C}H_2) = 103.9$ (s), $\delta(\equiv PCl(O\mathbf{C}H_2CF_3) = 63.6$ (m). ^{31}P $\{^1H\}$ NMR **trans isomer** (major isomer; all trans): $\delta(\equiv \mathbf{P}Cl(OCH_2CF_3) = 23.5$ (d, 2 P) ($^2J_{PP} = 77.6$), $\delta(\equiv \mathbf{P}\mathrm{Cl}(OCH{=}CH_2) = 19.6$ (m, 1 P) ($^2J_{PP} = 78.5$). **geminal isomer**: $\delta(\equiv \mathbf{P}_aCl_2) = 27.6$ (m, 1P), $\delta(\equiv \mathbf{P}_b\mathrm{Cl}(OCH_2CF_3) =$ 23-21 (complex multiplet), $\delta(\equiv \mathbf{P}_c(OCH_2CF_3)(OCH{=}CH_2) = 6.2$ (m, 1P), ($^2J_{PaPc} = 73.2$), ($^2J_{PbPc} = 76.2$). IR: 1645 (s, C=C), 1453 (m, PO str), 1420 (m, $-CH_2-$), 1288 (s, CF str), 1224 (s, PN str) 1173 (s, CF str), 1086 (s, PO str), 963 (m,C=C), 845 (m, PCl str), 748 (m, PCl str).

Results and Discussion

The well characterized pathways followed in the reactions of the trifluoroethoxide[11] and enolate anions[6,7] with hexachlorocyclotriphosphazene (**1**) lead to predominance of the non-geminal *trans* and *cis* isomers, respectively. The strategy for the current investigation is to compare the stereochemical pathways observed in the formation of the mixed substituent isomers $N_3P_3Cl_4(OCH_2CF_3)(OCH{=}CH_2)$(**5a,b**) starting from either $N_3P_3Cl_5(OCH_2CF_3)$(**3**) or $N_3P_3Cl_5(OCH{=}CH_2)$(**2**) and the appropriate oxyanion. Similarly, the formation of $N_3P_3Cl_3(OCH_2CF_3)_2(OCH{=}CH_2)$(**6**) from N_3P_3-$Cl_4(OCH_2CF_3)_2$(**4**) was investigated. This approach will allow insight into the mechanism controlling the stereochemistry of the disubstituted cyclotriphosphazenes with oxyanion based substituents. Control by either the ring substituent[18] or the incoming group[19] has been demonstrated in the reactions of cyclophosphazenes with other nucleophiles.

The syntheses of **5a**, **5b**, and **6** are summarized in Scheme 1. These reactions are carried out under conditions similar to those reported for the preparation of **2** and **3**. The highest yields of products are isolated when the reactions are carried out in anhydrous polar solvents under an inert atmosphere. The displacement reactions involving the enolate ion were carried out in THF, and those involving trifluoroethoxide used diethyl ether. Diethyl ether is used in reactions involving trifluoroethoxide because the formation of the trifluoroethoxide anion involves the reaction of 1,1,1-trifluoroethanol with sodium metal. There was concern that the trifluoroethoxide anion might react with THF if that solvent were used as the reaction medium. Otherwise reaction conditions in either reaction were similar, that is, 0 °C for ∼12 h. The reactions were carried out at 0 °C to slow the rate of reaction thereby maximizing the displacement of a single chloride ion and reducing the possibility of side-reactions and polymerization.

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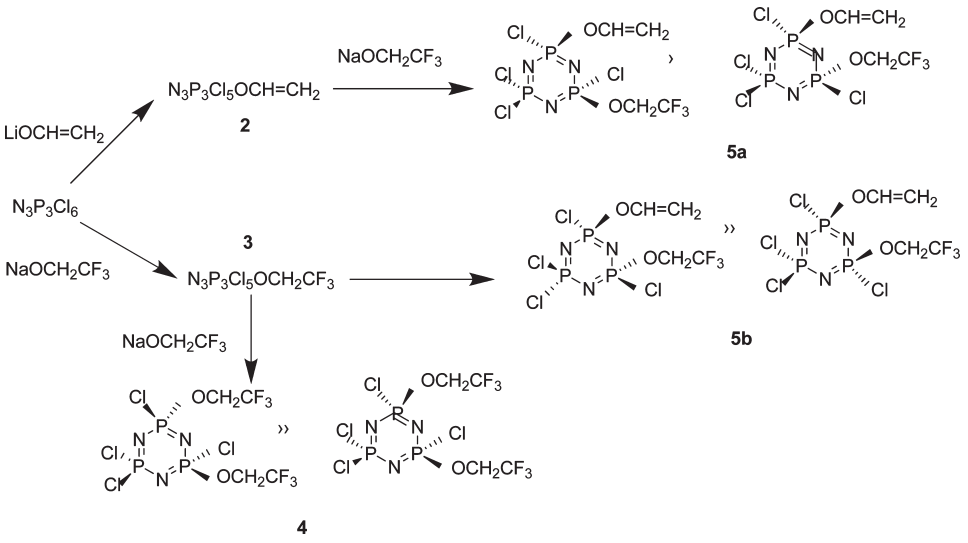
Scheme 1



In cases where monosubstitution was desired it was found that the use of a 30% mole excess of the oxyanion afforded the highest yield of the desired product with the main impurities being unreacted starting material and multisubstituted products.

The trifluoroethoxide anion is a more effective nucleophile toward $N_3P_3Cl_6$ than the enolate anion. This can be explained by the high negative charge on the oxygen atom of the trifluoroethoxide ion compared to the weaker dispersed charge of the oxyvinyl group. In the enolate ion, the negative charge is stabilized by resonance interactions. The facility of the reaction of trifluoroethoxide with halophosphazenes has been noted previously and partially explains why so many phosphazene syntheses rely on its use to remove residual halide groups.[4] More reactive nucleophiles such as trifluoroethoxide, give multiple substitution products in higher percentages than less reactive nucleophiles such as the enolate ion. This can be seen when comparing the yields of the two monosubstituted products, $N_3P_3Cl_5(OCH{=}CH_2)$, **(2)**, and $N_3P_3Cl_5(OCH_2CF_3)$, **(3)**. The product **3** can be isolated in 28% yield in contrast with **(2)**, which can be isolated in higher yield, 46%. Since stoichiometric control in the reaction of the enolate ion is superior to that of the corresponding reactions with trifluoroethoxide, mixed syntheses that use the addition the enolate last produce the desired product in greater yields. The synthesis of **5b** from the reaction of **3** with the enolate ion, affords a higher overall yield of **5b** with less formation of multisubstituted side products (e.g., $N_3P_3Cl_{5-n}(OCH{=}CH_2)_n(OCH_2CF_3)$ ($n=2-5$) than when **2** is reacted with trifluoroethoxide to yield **5a**. So in these syntheses, the yield of the desired product can be increased 2-fold simply by altering the order of addition of reagents. Similarly, the synthesis of **6** is carried out by first synthesizing **4**, followed by reaction with the enolate anion to give the desired product in 45% yield. Once isolated, the products **5a**, **5b**, and **6** are observed to be stable to both the atmosphere and moisture.

Unfortunately, all of the mixed substituent products, **5a**, **5b**, and **6** resisted attempts at chromatographic separation. The same problem was observed in the attempted separations of isomers of $N_3P_3Cl_4(OCH{=}CH_2)_2$ (**7**).[6] NMR has been shown to be a good spectroscopic probe for the determination of the relative amounts of isomers in substituted cyclophosphazenes.[6,7,9,20] While there is little observable difference in the ^1H, ^{13}C, and ^{19}F NMR spectra of these isomer mixtures, the ^{31}P NMR spectra contain a great deal of useful information since each isomer present in a product mixture can be observed as a slightly different subspectrum. We have previously shown that computer simulation of the spectra gives an excellent measurement of isomer ratios[6,7,20] in these products. In previous work, the differentiation of disubstituted isomers has been approached from arguments of the relative isomers in more highly substituted species,[11] relative chemical shifts,[6] and the unambiguous assignment of dimethylaminolysis products of **2**.[7] The consistency of these results allows for the use of relative chemical shifts for differentiation of cis and trans isomers. We further validated this approach in the present study by analyzing the ^{31}P NMR spectrum of the isomeric mixture contained in **4**. Our results (Table 1) are comparable to the published results[11] (reported using different techniques) for this system. However, we did detect a small amount of the geminal isomer (~3%) which was not previously reported. Geminal isomers are generally assumed to arise from a dissociative mechanism and are commonly found in reactions which follow a predominately non-geminal pathway.[2]

Table 1. Isomer Distributions for Substituted Phosphazenes[a]

compound	trans	cis	geminal
$N_3P_3Cl_4(OCH{=}CH_2)_2$ **(2)**	43%	53%	4%
$N_3P_3Cl_4(OCH_2CF_3)_2$ **(4)**	~78	~19	~3
$N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3)$ **(5a)**	57	38	5
$N_3P_3Cl_4(OCH{=}CH_2)(OCH_2CF_3)$ **(5b)**	75	20.5	4.5

[a]) Estimated from ^{31}P spectrum and computer simulations.

The ^{31}P NMR spectrum of **5a** clearly shows the existence of the cis, trans, and geminal isomers. Both of the predominant isomers in the mixture, cis and trans, would be expected to exhibit an ABX pattern but because of the similarity of all $^3J_{PP}$ values the doublet of doublets of each center collapses to a triplet. Some separation of the two doublets can be seen in the subspectrum. The geminal isomer is observed as a small A_2X subspectrum. The more abundant upfield PCl(OR) subspectrum was assigned to the trans isomer based on the

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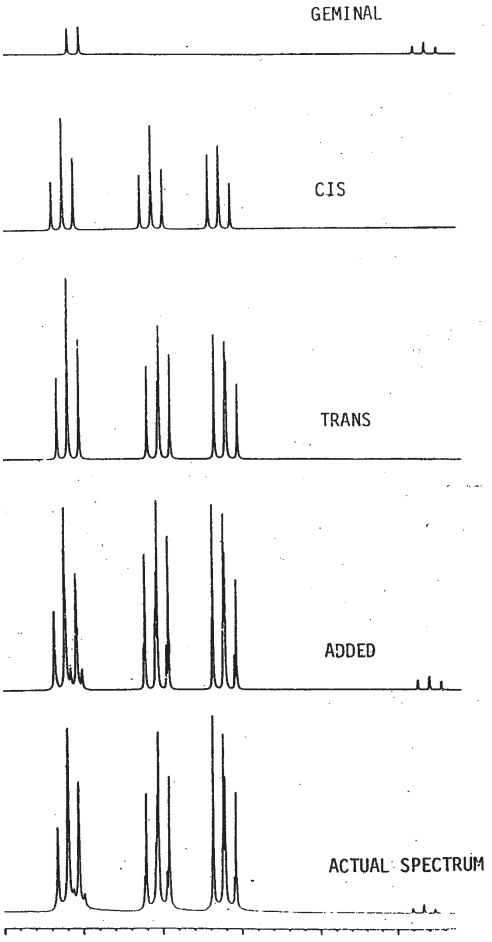

Figure 1. Simulation of the $N_3P_3Cl_4(OCH{=}CH_2)(OCH_2{=}CF_3)$ ^{31}P NMR spectrum.

relative chemical shifts of the cis and trans isomers of the closely related **4** and **7** systems . A similar analysis was applied to **5b**.

The ^{31}P NMR studies also gave valuable information as to the relative amounts of each isomer present. Since each isomer present gives rise to a slightly different subspectrum, computer simulation of these spectra gave an excellent measurement of isomer ratios present in these products. The NMR parameters for each isomer were estimated from the mixture spectrum and used to simulate the individual spectra. The mixture spectrum was matched to the composite of the individual spectra (Figure 1) by varying the contributions of each of the component, which allowed for the calculation of the relative concentration of each species. The results of the simulations are listed in Table 1. The relative amounts of trans and cis isomers in **5a** are 57 and 38% respectively. Using a similar approach, the respective amounts in **5b** are 75 and 20.5%, respectively, so there are clearly differing degrees of stereochemical control operative in these systems.

The product $N_3P_3Cl_3(OCH{=}CH_2)(OCH_2CF_3)_2$, **6**, consists of a variety of isomers of which the major isomer has a non-geminal configuration and thus would be expected to show an A_2X spectrum in ^{31}P NMR. The largest observable feature of this spectrum is a doublet and triplet (split by second order effects) which corresponds to the expected A_2X subspectrum. Other isomers are also observed in the NMR of

Table 2. Selected NBO Charges for Phosphazene Ring and Olefin Atoms in $N_3P_3F_5X$ (X = F, $OCH{=}CH_2$, $OCH_2CH{=}CH_2$)

X	P_2	$P_{4,6}$	$N_{1,3}$	N_5	C_1	C_2
F	2.5380	2.538O	*−1.4759*	*−1.4759*		
$OCH{=}CH_2$ (**8**)	2.5216	2.5375	*−1.4919*	*−1.4774*	*−0.0857*	*−0.4898*
$OCH_2CH{=}CH_2$ (**9**)	2.5291	2.5306	*−1.4841*	*−1.4760*	*−0.1531*	*−0.2624*

the product, the most notable being the isomer which has a trifluoroethoxy and vinyloxy group geminal to each other. This is observed as an AMX subspectrum with the $\equiv$PCl-(OCH_2CF_3) resonance being buried beneath the A_2X spectrum of the trans isomer. There appears to be greater than 80% of the trans isomer present by visual inspection of the spectra. This would be expected given the high percentage of the trans isomer in the precursor **4**.

To examine the role of the R group in this series of $P_3N_3Cl_{6-n}(OR)_x(OR')_y$, we have employed DFT calculations to examine electronic variations in the series of model compounds $N_3P_3F_5X$ [X = $OCH{=}CH_2$(**8**), $OCH_2CH{=}CH_2$(**9**)]. The previously reported data[16] for the parent compound, $N_3P_3F_6$, are included for comparison. We have previously found this approach of value in rationalizing the stereochemical pathways observed in chloro and flouro phenoxycyclotriphosphazenes.[9] The natural bond order (NBO) charges are reported in Table 2. The Wiberg bond indices of the olefin bonds and the phosphorus−oxygen bonds are 1.9592 and 0.7348 for **8** and 1.9716 and 0.7579 for **9**, respectively. The high NBO charges on the substituted phosphorus atoms coupled with the low Wiberg bond index for the phosphorus−oxygen bonds indicates high ionic character in these bonds. There is significant enolate anion character in the vinyloxy group as shown by the high NBO charge on the olefin C2 center in **8** versus **9**. This results in dispersion of the partial negative charge throughout the substituent. An additional, more subtle effect is noted in the slightly lower charge on the substituent bearing phosphorus atoms in **8** versus **9** and a concomitant higher negative charge on the adjacent nitrogen centers. The transfer of a small amount of negative charge from the vinyloxy substituent to the phosphorus center can be envisioned to occur through a hyperconjugative interaction with the electron rich carbon−oxygen bond.

Spectroscopic data can also provide insight into questions of the electronic structure of cyclophosphazenes. We have previously shown that there is a linear correlation of the ^{13}C and ^{31}P chemical shifts of C2 atom in the vinyloxy unit and the vinyloxy substituted phosphorus atom in the series $N_3P_3X_5(OCH{=}CH_2)$ (X = F, Cl, OCH_2CF_3, OCH_3, $N(CH_3)_2$)[7] which indicates cosubstituent control of the electron density in the olefin. A similar effect is seen for **1**, **5a**−**b**, and **6**, $N_3P_3Cl_5(OCH{=}CH_2)$, $N_3P_3Cl_4(OCH{=}CH_2)$ (OCH_2CF_3), and $N_3P_3Cl_3(OCH{=}CH_2)(OCH_2CF_3)_2$. The mechanism here is different; the withdrawal does not take place because of the group geminal to the vinyloxy group since in this series, all of these species have a $\equiv$P(Cl)-$(OCH{=}CH_2)$ local environment. As the number of trifluoroethoxy groups on the phosphazene ring increases, the ^{13}C NMR shift of the C2 vinyloxy carbon atom decreases indicating that as these groups are causing the phosphazene ring to become less electron withdrawing. The correlation between the ^{13}C NMR shift of the C2 vinyloxy carbon atom and the ^{31}P NMR shifts of the corresponding phosphorus atom is essentially linear (Figure 2) with a computed linear

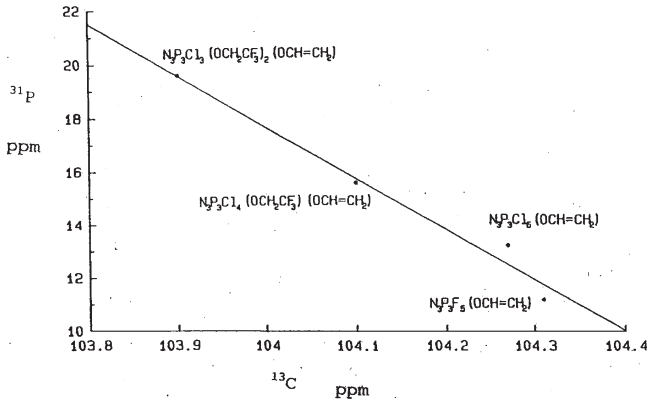

Figure 2. Correlation of the ^{13}C and ^{31}P chemical shifts for the C_2 atom in the vinyloxy unit and the phosphorus atom in the P(C1)OCH=CH_2 center.

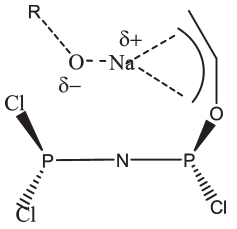

Figure 3. Substituent stabilization of the incoming alkali metal ion.

correlation coefficient $R = 0.978$. Therefore, the vinyloxy oxygen atom has more electron density which results in the vinyl group becoming more electron rich as compared to $N_3P_3Cl_5(OCH=CH_2)$. This shows the transmission of electronic effects from a distant phosphorus atom in the cyclophosphazene ring to an exocyclic group.

Non-geminal products predominate in the reactions of oxyanions with halocyclotriphosphazenes. The small amounts of the geminal isomer which have been observed are presumed to arise via a dissociative pathway (in contrast to the associative pathway leading to the non-geminal products).[2] In general (organic systems and in cyclophosphazenes) when steric effects dominate, the second nucleophile enters from the opposite side of the ring and the trans isomer is obtained. As noted by Allcock,[11] this effect is clearly demonstrated in the formation of **4** where nearly 80% trans preference is observed. In the case of **2**, where the nucleophile is the enolate anion, there is a slight predominance of cis product (43:53:4 - trans/cis/gem) indicating a driving force to cis attack since steric forces are trans directing. In the formation of the mixed substituent species **5a** in which the trifluoroethoxide ion attacks **2** (which has a vinyloxy group), the isomer distribution (57% trans, 38% cis) is similar to that found in **7** with a somewhat weaker cis preference. However, in the formation of **5b** which starts from **3** (which has a trifluoroethoxy substituent), the isomer distribution (75% trans, 20.5% cis) is nearly identical to that found in **4**. Thus in these systems, the stereochemical pathway is controlled by the substituent on the ring, and **5b** is the result of steric forces. In all of the previous cases, the oxyanions which have shown a cis preference have had π electron containing organic groups, and this cis preference occurs with relative small substituents such as the vinyloxy group and the much larger and more sterically demanding aryloxy groups. This led us to propose a π/π association of incoming and substituent groups as the origin of the cis orientation.[6,7,9] While this may indeed be correct for those systems, the enhanced cis preference in **5a** (where the incoming group is the trifluoroethoxide anion) over **5b** shows that an alternative rationale is required. An important insight comes from a study of the reactions of the sodium salts of alkoxy poly(ethylene glycols) with **1** in which, at the stage of tris substitution, gives exclusively the cis product.[21] The stabilization of the sodium salt by the polyether donors on the ring serve to orient the incoming reagent to the cis configuration. Other types of examples of exocyclic oxygen donor sites stabilizing an alkali metal cation have also been noted.[22,23] In the present system, the delocalization of the negative charge in the substituent in **2** provides an accessible donor site, relative to **3**, which can attract the incoming sodium oxyanion and lead to the cis product being competitive with the trans product (Figure 3).

Summary

The reaction pathways of oxyanions with hexachlorocyclotriphosphazene have been explored with an emphasis on a two systems. The starting material, $N_3P_3Cl_6$, was reacted with the lithium enolate of acetaldehyde and sodium trifluoroethoxide, to give the products, $N_3P_3Cl_4(OCH=CH_2)(OCH_2CF_3)$ and $N_3P_3Cl_3(OCH=CH_2)(OCH_2CF_3)_2$. These materials were purified, and the isomer mixtures present were analyzed by ^{31}P NMR so that relative ratios of trans, cis, and geminal products could be determined. We found that the mechanism of nucleophilic substitution, a non-geminal pathway, is influenced predominately by electronic and steric forces, mainly dictated by the nature of the ring substituent. By evaluating the ^{13}C NMR shift of the C2 vinyloxy carbon atom of the vinyl groups, we are able to probe the perturbations of electronic structure of the phosphazene ring as a function of the nature of the substituents. These new materials are also potential monomers in radically initiated polymerization.

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