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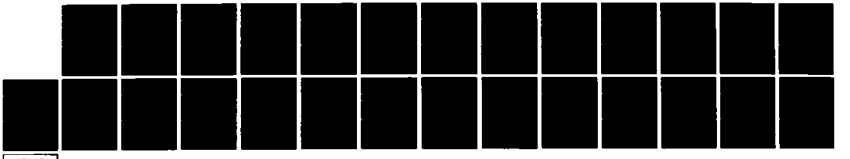

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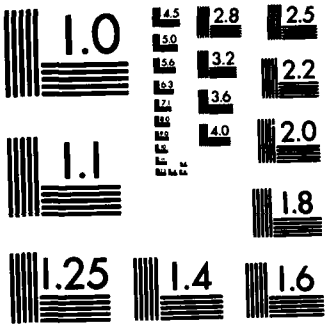

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The reactions of 1-lithioalkoxyethylenes with hexafluorocyclotriphosphazene ($N_3P_3F_6$) have been examined. In contrast to similar reactions of propenyl lithium with $N_3P_3F_6$, no evidence for degradation reactions via anionic attack on the olefinic center was observed and the reaction proceeds smoothly to yield $N_3P_3F_{6-n}[C(OR)=CH_2]_n$ (n=1,2; R=$CH_3$, $C_2H_5$). The reaction follows a geminal pathway at the stage of disubstitution. The mixed phenyl/ethoxyvinyl derivative, 2,2-$N_3P_3F_4(C_6H_5)$ $C(OC_2H_5)=CH_2$, and dimethylamino/ethoxyvinyl derivatives,



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# Organophosphazenes. 16. The Synthesis and Reactions of 1-Alkoxyvinylfluorocyclotriphosphazenes.

by

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University of Vermont
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# Organophosphazenes.16. The Synthesis and Reactions of 1-Alkoxyvinylfluorocyclotriphosphazenes.[1]

Christopher W. Allen* and Randall P. Bright

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405.

Abstract: The reactions of 1-lithioalkoxyethylenes with hexafluorocyclotriphosphazene ($N_3P_3F_6$) have been examined. In contrast to similar reactions of propenyl lithium with $N_3P_3F_6$, no evidence for degradation reactions via anionic attack on the olefinic center was observed and the reaction proceeds smoothly to yield $N_3P_3F_{6-n}[C(OR)=CH_2]_n$ (n=1,2; R=$CH_3$, $C_2H_5$). The reaction follows a geminal pathway at the stage of disubstitution. The mixed phenyl/ethoxyvinyl derivative, 2,2-$N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2$, and dimethylamino/ethoxyvinyl derivatives, 2,4-$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$, have been prepared. Evidence for both incoming group and ring substituent control of product stereochemistry has been observed. A model for ring substituent control is presented. The new alkoxyvinyl phosphazenes are characterized by mass spectrometry and NMR ($^1H$, $^{13}C$, $^{19}F$, $^{31}P$) spectroscopy. Examination of the $^{13}C$ NMR spectra show that the electron withdrawing effect of the phosphazene results in a significant reduction of the electron rich nature of the parent olefins.

In recent years there have been a number of investigations involving organophosphazenes.[2] Factors such as the complexities of reactions leading to these materials[3,4], electronic structure,[5] and thermal stability[6,7] all contribute to the interest in this class of compounds. We have been interested in the preparation and synthetic transformations of phosphazenes with organofunctional substituents.[8] These studies have lead to new and interesting organophosphazenes and organophosphazene polymers.[9] One such species 2-propenylpentafluorocyclotriphosphazene, $N_3P_3F_5C(CH_3)=CH_2$ is prepared by the reaction of the appropriate lithium reagent with hexafluorocyclotriphosphazene ($N_3P_3F_6$).[10] In addition, one also obtains considerable amounts of materials which apparently arise from the attack of the anionic lithium reagent on the olefinic center.[11] It has been shown by a variety of techniques that the $P_3N_3F_5$ moiety exhibits a strong electron withdrawing effect when attached to organic substituents.[5,9] The olefinic center in $N_3P_3F_5C(CH_3)=CH_2$ would thus be highly polar and susceptible to anionic attack. In order to avoid these undesirable side reactions, we decided to prepare alkenylphosphazenes with strong electron donating substituents on the olefinic center, thus counterbalancing the electron withdrawing effect of the phosphazene. Due to their electron rich nature, the vinyl ethers were considered to be favorable substituents for this study. A preliminary account of this work has appeared.[11]

## Experimental Section

Materials and methods. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, (Ethyl Corp.) was converted to hexafluorocyclotriphosphazene, $N_3P_3F_6$,[12] which in turn was converted to phenylpentafluorocyclotriphosphazene, $N_3P_3F_5C_6H_5$,[13] and dimethylaminopentafluorocyclotriphosphazene[14] by previously reported procedures. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Ethyl vinyl ether (Aldrich), methyl vinyl ether (Pfaltz and Bauer), tert-butyl lithium (2.0m in pentane, Aldrich), bromobenzene (Fisher), lithium metal (Alfa) and anhydrous dimethylamine (Eastman) were used without further purification. NMR spectra (in $CDCl_3$) were recorded on a Brucker WM250 spectrometer operating at 250.1 MHz($^1H$), 62.9 MHz ($^{13}C$), 235.2 MHz ($^{19}F$) and 101.2 MHz ($^{31}P$). Tetramethylsilane, TMS, (for $^1H$ and $^{13}C$) and fluorotrichloromethane, $CFCl_3$, (for $^{19}F$) were used as internal references. For $^{31}P$ NMR, 85% $H_3PO_4$ was used as an external reference. Chemical shifts upfield to the reference are assigned a negative sign. $^{13}C$, $^{19}F$ and $^{31}P$ NMR spectra were recorded under conditions of broad band decoupling. Infrared (IR) spectra were obtained as their films (NaCl discs) or KBr pellets on a Beckman IR 20 A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Gas chromatography was performed on a Hewlett-Packard 5700A instrument equipped with a chromasorb W(SE-30) column. NMR simultations were carried out using a locally modified version of the DNMR3 computer program.[15] Elemental analyses were performed by Integral Microanalytical Laboratories.

All reactions were carried out under anhydrous conditions in a three necked round bottomed flask fitted with a reflux condenser and a pressure-equalizing dropping funnel. The system was stirred magnetically and flushed with nitrogen which exited through a mercury bubbler. Lithium reagents were transferred using syringe techniques.

Preparation of $N_3P_3F_5C(OC_2H_5)=CH_2$. A previously described [16] vessel for the preparation and transfer of air sensitive reagents was charged with ethyl vinyl ether (6mL; 0.063 mol) and 100 ml of tetrahydrofuran (THF) flushed with $N_2$ and cooled to -78°. tert-Butyllithium (27 ml; 0.054 mol) was added over a half hour period. The solution was allowed to stir for an hour while warming to 0° and stirring was continued for an additional hour. The lithiated vinyl ether was transferred[16] over a half hour period to a solution of $N_3P_3F_6$ (15g; 0.06 mol) in 75ml THF at -78°. The solution was allowed to come to room temperature and proceeded for 18 hours. The solvent was removed; the mixture was dissolved in petroleum ether and the salts removed by filtration. After treatment with activated carbon, the solvent was removed and the resulting oil was distilled to yield 5.4g (33.2% theory) of a water white liquid (b.p. 25-30° at 0.02 mm Hg). Anal. Calcd. for $N_3P_3F_5C_4H_7O$ (1): C, 15.95; H, 2.33; mol wt 301. Found: C, 15.71; H, 2.44; mol wt 301 (mass spectrum[17]).

$^1H$ NMR[18]: $\delta_{H_c}$ = 5.23 (d of d, 1H), $^2J_{H_cH_t}$ = 3.66, $^3J_{H_cP}$ = 17.09; $\delta_{H_t}$ = 4.96 (d of t, 1 H), $^2J_{H_tH_c}$ = 3.66, $^3J_{H_tP}$ = 47.61, $^4J_{H_tF}$; $\delta_{OCH_2}$ = 3.91 (q, 2 H), $^3J_{HH}$ = 6.71; $\delta_{OCH_2\underline{CH_3}}$ = 1.38 (t,3 H), $^3J_{HH}$ = 6.71. $^{13}C$ NMR[19]: $\delta_{C_1}$ = 152.71, $^1J_{C_1P}$ = 246.28, $^2J_{C_1F}$ = 36.20; $\delta_{C_2}$ = 99.03, $^2J_{C_2P}$ = 29.81; $\delta_{C_3}$ = 65.66, $^3J_{C_3P}$ = 12.77; $\delta_{C_4}$ = 14.08. $^{31}P$ NMR: $\delta_{\equiv PF(C_4H_7O)}$ = 25.18, $^1J_{PF}$ = 1001.8; $\delta_{\equiv PF_2}$ = 9.45, $^1J_{PF}$ = 919.7. $^{19}F$ NMR: $\delta_{\equiv PF(C_4H_7O)}$ = -68.25; $\delta_{\equiv P\underline{F}F}$ = -68.11; $\delta_{\equiv PF\underline{F}}$ = -69.20. IR[20]: 2970 (w, $\nu_{CH}$), 1620 (s, $\nu_{C=C}$), 1450(w), 1385 (m), 1360 (m), 1270 (vs, $\nu_{P=N}$) 1110 (w, COC asym.), 1045 (s, COC, sym.), 1010 (m), 940 (vs, PF asym.), 855 (vs, PF sym), 760 (s, = $CH_2$ wag).

Preparation of 2,2-$N_3P_3F_4[C(OC_2H_5)=CH_2]_2$ (2). This preparation was allowed to proceed as above except that the following quantities of reagents were used: ethyl vinylether (9 mL; 0.095 mol), tert-butyl lithium (42.5 mL; 0.088 mol). An aliquot of the lithiated vinylether was quenched with distilled water and titrated with a standard HCl solution. The solution was found to contain 0.066 mol of the reagent and consequently required 8.2 g (0.033 mol) of $N_3P_3F_6$ (in 100 mL THF). The resulting product was recrystallized twice from hexane to afford 2.37g (20.4% of theory) of a milk white solid m.p. 51.52°. Anal. Calcd. for $N_3P_3F_4C_8H_{14}O_2$: C, 27.20; H, 3.97; N = 11.90; mol wt 353. Found: C, 27.02; H, 4.08; N = 11.78; mol wt 353 (mass spectrum[17]). $^1H$ NMR[18]: $\delta_{H_c}$ = 5.17 (d of d, 2H), $^2J_{H_cH_t}$ = 3.42, $^3J_{H_cP}$ = 14.16; $\delta_{H_t}$ = 4.92 (d of d, 2H), $^2J_{H_tH_c}$ = 3.42, $^3J_{H_tP}$ = 38.57; $\delta_{OCH_2}$ = 3.90 (q, 4H), $^3J_{HH}$ = 6.84; $\delta_{OCH_2CH_3}$ = 1.35 (t, 6H), $^3J_{HH}$ = 6.84. $^{13}C$ NMR[19]: $\delta_{C_1}$ = 155.29, $^1J_{C_1P}$ = 174.59; $\delta_{C_2}$ = 97.94, $^2J_{C_2P}$ = 25.55; $\delta_{C_3}$ = 65.25, $^3J_{C_3P}$ = 9.94; $\delta_{C_4}$ =14.06. $^{31}P$ NMR: $\delta_{=P(C_4H_7O)_2}$ = 15.03; $\delta_{=PF_2}$ = 8.95, $^1J_{PF}$ = 895.03. $^{19}F$ NMR: $\delta_{PF_2}$ = -68.16. IR[20]: 2990 (s, ν CH), 2950 (m, ν CH), 1630 (m, ν C=C), 1610 (s, ν C=C), 1485 (m), 1465 (m), 1450 (m, $CH_3$ asym). 1390 (s, $CH_3$ sym), 1365 (m), 1255 (vs, ν P=N), 1155 (m,COC asym), 1045 (s, COC sym), 975 (s, $=CH_2$ wag), 950 (m), 920 (vs, PF asym), 855 (s), 810 (vs, PF sym), 760 (s), 745 (s, $=CH_2$ wag).

Preparation of $N_3P_3F_5C(OCH_3)=CH_2$ (3) and $N_3P_3F_5[C(OCH_3)=CH_2]_2$ (4). The procedure used was identical to that described above except that the methyl vinylether was condensed at -78° and subsequently transferred to the reaction vessel. In a typical experiment, the following quantities of reagents were used: 8 mL (0.107 mol) methyl vinylether, 45 mL (0.09 mol ) tert-butyl lithium and 23g (0.092 mol) $N_3P_3F_6$. The resulting oil was distilled to yield 3.38g (13% of theory) of a water white liquid b.p. 25° at 0.02 mm Hg. Anal. Calcd for $N_3P_3F_5C_3H_5O$: C, 12.45; H, 1.74; mol. wt 287. Found: C, 13.06; H, 1.54; mol wt 287 (mass spectrum).[17]

$^{1}H$ NMR[18]: $\delta_{H_c}$ = 5.27 ( d of d, 1H), $^{2}J_{H_cH_t}$ = 3.97, $^{3}J_{H_cP}$ = 16.48; $\delta_{H_t}$ = 5.00 ( d of t, 1H), $^{2}J_{H_tH_t}$ = 3.97, $^{3}J_{H_tP}$ = 46.35, $^{4}J_{H_tF}$ = 3.66; $\delta_{OC\underline{H}_3}$ = 3.73 (s, 3H). $^{13}C$ NMR[19]: $\delta_{C_1}$ = 152.75, $^{1}J_{C_1P}$ = 250.09, $^{2}J_{C_1F}$ = 36.47; $\delta_{C_2}$ = 98.77, $^{2}J_{C_2P}$ = 29.77; $\delta_{C_3}$ = 53.68, $^{3}J_{C_3P}$ = 12.65. $^{31}P$ NMR: $\delta_{\equiv PF(C_3H_5O)}$ = 25.49, $^{1}J_{PF}$ = 1003.65; $\delta_{\equiv PF_2}$ = 9.09, $^{1}J_{PF}$ = 933.46, $^{2}J_{PF}$ = 82.00, $^{3}J_{PF}$ = 18.75, $^{4}J_{PF}'$ = 5.15. $^{19}F$ NMR: $\delta_{\equiv PF(C_3H_5O)}$ = -66.85, $^{1}J_{PF}$ = 989.87; $\delta_{PF\underline{F}}$ = -67.85; $\delta_{P\underline{F}F}$ = -69.23. IR[20]: 2970 (w,$\nu$ $CH_3$), 1620 (m, $\nu$ C=C), 1460 (w), 1380 (w), 1280 (vs, $\nu$ P=N), 1195 (w), 1045 (s, COC sym), 1015 (m, $=CH_2$ wag),945 (s, PF asym), 910 (m), 865 (s), 840 (s, PF sym), 760 (s, $=CH_2$ wag), 720 (w).

The residue from the distillation was subjected to column chromatography using hexanes as the eluting solvent. A small amount of 2,2-$N_3P_3F_4[C(OCH_3)=CH_2]_2$, as identified by the mass spectrum and NMR spectroscopy,was isolated.

$^{1}H$ NMR[18]: $\delta_{H_c}$ = 5.22 (d of d, 2H), $^{2}J_{H_cH_t}$ = 3.66, $^{3}J_{H_cP}$ = 13.67; $\delta_{H_t}$ = 4.97 (d of d, 2H), $^{2}J_{H_tH_c}$ = 3.66, $^{3}J_{H_tP}$ = 37.60; $\delta_{OC\underline{H}_3}$ = 3.70 (s, 3H), $^{13}C$ NMR[19]: $\delta_{C_1}$ = 156.26, $^{1}J_{C_1P}$ = 176.41; $\delta_{C_2}$ = 97.78, $^{2}J_{C_2P}$ = 25.31; $\delta_{C_3}$ = 56.63, $^{3}J_{C_3P}$ = 10.42. $^{31}P$ NMR: $\delta_{\equiv P(C_3H_5O)_2}$ = 13.88; $\delta_{\equiv PF_2}$ = 8.32, $^{1}J_{PF}$ = 892.89. $^{19}F$ NMR: $\delta_{\equiv PF_2}$ = -67.86. IR[20]: 2950 (m, $\nu$CH), 2860 (w, $\nu$CH), 1620 (s, $\nu$C=C), 1460 (m, $CH_3$ asym.), 1375 (m, $CH_3$ sym), 1255 (vs, $\nu$ P=N), 1190 (w), 1000 (m, $=CH_2$ wag), 960 (m), 925 (s, PF asym), 895 (m), 855 (m), 820 (s, PF sym), 740 (s, $=CH_2$ wag).

Preparation of 2,2-$N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2$ (5) from $N_3P_3F_5C_6H_5$. The procedure used was identical to that described above except that $N_3P_3F_5C_6H_5$ was used in place of $N_3P_3F_6$. In a typical experiment, the following quantities of reagents were used: 4.5 mL (0.047 mol) ethyl vinylether, 23 mL (0.046 mol) tert- butyl lithium and 14.2g (0.046 mol) of $N_3P_3F_5C_6H_5$. The resulting oil was distilled to yield 2.80g (17% theory) of a water white liquid (b.p. 80-90° at 0.02 mm Hg). Anal. Calcd. for $N_3P_3F_4C_{10}H_{12}O$: C, 33.43; H, 3.34; mol wt 359. Found: C, 32.92; H, 3.07; mol wt 359 (mass spectrum[17]).

$^1$H NMR[18]: $\delta_{H\ (Ar)}$ = 7.54 (m, 5H), $\delta_{H_c}$ = 4.86 (d of d, 1H), $^2J_{H_cH_t}$ = 3.43, $^3J_{H_cP}$ = 14.23; $\delta_{H_t}$ = 4.78, (d of d, 1H), $^2J_{H_tH_c}$ = 3.43, $^3J_{H_tP}$ = 38.40; $\delta_{OCH_2}$ = 3.82 q, 2H), $^3J_{HH}$ = 6.86; $\delta_{OCH_2CH_3}$ = 1.27 (t, 3H), $^{13}$C NMR[19]: $\delta_{C_1}$ = 157.74, $^1J_{C_1P}$ = 168.65; $\delta_{C_2}$ = 96.60, $^2J_{C_2P}$ = 25.70; $\delta_{C_3}$ = 65.18, $^3J_{C_3P}$ = 8.03; $\delta_{C_4}$ = 13.99; $\delta_{C_o}$ = 128.61, $^2J_{C_oP}$ = 14.46; $\delta_{C_m}$ = 131.11, $^3J_{C_mP}$ = 11.24; $\delta_{C_p}$ = 133.07. $^{31}$P NMR: $\delta_{\equiv P(C_6H_5)(C_4H_7O)}$ = 21.11; $\delta_{\equiv PF_2}$ = 9.03, $^1J_{PF}$ = 923.6. $^{19}$F NMR: $\delta_{\equiv PF\underline{F}}$ = -68.98; $\delta_{\equiv P\underline{F}F}$ = -67.30. IR[20]: 3080 (w, ν CH), 2950 (2, ν CH), 1620 (s, ν C=C), 1450 (m), 1250 (vs, ν P=N), 1190 (m), 1130 (m, COC asym), 1050 (m, CH bend), 1000 (w, $=CH_2$ wag), 980 (w), 925 (s, PF asym), 860 (m), 820 (s, PF sym), 740 (s, $=CH_2$ wag), 690 (m, CH bend).

Preparation of 2,2-$N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2$ (5) from $N_3P_3F_5C(OC_2H_5)=CH_2$. A solution of phenyl lithium was prepared[13] from bromobenzene (2 mL, 0.019 mol) and lithium (0.35g, 0.05 mol) in the air sensitive reagent transfer vessel[16] using diethyl ether as the solvent. The lithium reagent was added to a solution of 5.75g (0.019 mol) of $N_3P_3F_5C(OC_2H_5)=CH_2$ in 50 mL of diethyl ether at 0°. Work up was as described as above with the addition of a column chromatography step using petroleum ether as the eluent. The resulting oil was distilled (80 - 90°, 0.02 mm Hg) to give 1.44 g (21% of theory) of a product which was shown NMR spectroscopy to be equivalent to that obtained in the preceeding preparation.

Preparation of 2,4-$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$ (6) from $N_3P_3F_5N(CH_3)_2$. The procedure was identical to that described for the preparation of 1 except that $N_3P_3F_5N(CH_3)_2$ was used in place of $N_3P_3F_6$. In a typical experiment the following quantities of reagents were used: 4.75 mL (0.05 mol) ethyl vinylether, 20 mL, (0.04 mol) tert-butyl lithium and 11.0g (0.04 mol) of $N_3P_3F_5N(CH_3)_2$. The resulting oil was distilled to yield 0.99g (7.6% of theory) of a water white liquid (b.p. 32-37° at 0.02 mm Hg).

Anal. Calcd. for $N_4P_3F_4C_6H_{13}O$: C, 22.09; H, 3.99; N, 17.17; mol wt 326. Found: C, 22.01; H, 3.90; N, 17.17; mol wt 326 (mass spectrum[17]).

$^1H$ NMR[18]: $\delta_{H_c}$ = 5.19 (d of d, 1H), $^2J_{H_cH_t}$ = 3.36, $^3J_{H_cP}$ = 16.18; $\delta_{H_t}$ = 4.87 (d of t, 1H), $^2J_{H_tH_t}$ = 3.36, $^3J_{H_tP}$ = 46.08, $^4J_{H_tF}$ = 3.97; $\delta_{OCH_2}$ = 3.88 (q, 2H), $^3J_{HH}$ = 7.02; $\delta_{NCH_3}$ = 2.74 (d, 6H), $^3J_{HP}$ =12.51; $\delta_{CH_2CH_3}$ = 1.37 (t, 3 H), $^3J_{HH}$ = 7.02. $^{13}C$ NMR[19]: $\delta_{C_1}$ = 153.82, $^1J_{C_1P}$ = 269.64, $^2J_{C_1F}$ = 36.54; $\delta_{C_2}$ =97.41, $^2J_{C_2P}$ = 28.11; $\delta_{C_3}$ = 64.99, $^3J_{C_3P}$ = 11.24; $\delta_{C_4}$ = 14.10; $\delta_{NCH_3}$ = 35.85, $^2J_{CP}$ = 4.82. $^{31}P$ NMR: $\delta_{\equiv PF(C_2H_6N)}$ = 23.75; $^1J_{PF}$ = 908.69; $\delta_{\equiv PF(C_4H_7O)}$ = 23.75, $^1J_{PF}$ = 993.20; $\delta_{\equiv PF_2}$ = 8.12, $^1J_{PF}$ = 922.00. $^{19}F$ NMR: $\delta_{\equiv PF(C_2H_6N)}$ = -61.72; $\delta_{\equiv PF(C_2H_6N)}$ = -62.53; $\delta_{\equiv PFC_4H_7O}$ = -65.76; $\delta_{\equiv PFC_4H_7O}$ = -66.56; $\delta_{\equiv PF_2}$ = -67.56; $\delta_{\equiv PF_2}$ = -69.12. IR[20]: 2950 (m, $\nu$ CH), 1620 (s, $\nu$ C=C), 1490 (m, $CH_3$ sym), 1465 (m, $CH_3$ sym), 1450 (m), 1385 (m), 1365 (m), 1260 (vs, $\nu$P=N), 1170 (m, $\nu$ CN), 1115 (w, COC asym), 1050 (s, CH bend), 1015 (s, $=CH_2$ wag), 980 (s), 920 (vs, PF asym), 845 (vs, PF sym), 770 (s 730 (s, $=CH_2$ wag), 710 (s).

Preparation of 2,4-$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$ (6) from $N_3P_3F_5C(OC_2H_5)=CH_2$. A dropping funnel equipped with a cold jacket was maintained at 0° and charged with 2.0 mL (0.03 mol) of anhydrous dimethylamine in 30 mL of diethylether. The resulting solution was added dropwise to a solution of 4.0g (0.013 mol) $N_3P_3F_5C(OC_2H_5)=CH_2$ in 50 mL of diethyl ether at 0°. The reaction mixture was allowed to come to room temperature and continued to react, with stirring, for 24 hours. The salts were separated and the solvent was removed. Distillation (32-37° at 0.02 mm Hg) of the crude material yielded 1.15g (26.5% of theory) of a product which was shown, by NMR spectroscopy, to be identical to that obtained in the preceeding preparation.

## Results and Discussion

The reactions of lithiated methyl or ethyl vinylether with hexafluorocyclotriphosphazene, $N_3P_3F_6$, proceed to give moderate yields of the appropriate monosubstituted phosphazenes. In addition to the expected products, trace amounts

$$N_3P_3F_6 + LiC(OR) = CH_2 \longrightarrow N_3P_3F_5C(OR) = CH_2 + LiF$$

$$R = C_2H_5\ (1),\ CH_3\ (3)$$

of the compound derived from metalation of ethyl vinylether at the β position, i.e. $N_3P_3F_5CH{=}CHOC_2H_5$, were detected in the $^1H$ NMR spectrum of the crude product. The desired material, 1, could be obtained in the pure state by distillation. Significantly, one does not obtain any of the degradation products arising from anionic attack on the olefinic center in 1 or 3. This is contrast to the results obtained in the 2-propenyl lithium system where such degradative processes play a dominant role in the reaction.[11] This observation confirms, at the synthetic level, our postulation of the reduction of olefin polarity in 1 and 3 by the incorporation of a strong electron donating substituent on the olefin which counter balances the strong electron withdrawing effect[5] of the phosphazene. The new compounds were characterized by elemental analyses, mass and NMR ($^1H$, $^{13}C$, $^{19}F$, $^{31}P$) spectra.

The $^1H$ NMR spectrum of 1 shows multiplets in the β-hydrogen region but none in the region assigned to the α-hydrogen atoms in ethyl vinylether. A complex multiplet in the α-hydrogen region does appear in the spectrum of the trace by product described above. Simulation of the $^1H$ NMR spectrum of 1 requires, in addition to the expected interactions, fluorine coupling with the β-hydrogen atom trans to the phosphazene. The $^{13}C$ NMR spectrum also confirms the position of attachment of the phosphazene. The α carbon resonance is of very low intensity with large one bond phosphonus-carbon coupling along with two bond fluorine-carbon coupling and some possible addition long range phosphorus coupling. The $^{31}P$ and $^{19}F$ NMR spectra confirm a monosubstituted phosphazene by showing two $\equiv PF_2$ centers and one $\equiv PF$ [$C(OR){=}CH_2$] center.

Certain features of the NMR parameters require additional discussion. The phosphorus atom chemical shifts are relatively constant on going from $\underset{\sim}{1}$ to $\underset{\sim}{3}$ thus implying no significant bond angle changes at the phosphorus center. The chemical shift of the fluorine atom in a $\equiv PF[C(OR)=CH_2]$ environment varies with the nature of the alkyl group. The magnitude of this variation (1.4 ppm) is such that it could be ascribed to solvent or related effects. There is no long range fluorine coupling to the alkyl group. The β-carbon chemical shifts of olefins can be correlated to substituent electron donor/acceptor effects.[21] The β- carbon chemical shift goes from 84.6 ppm in ethyl vinylether to 99.0 ppm in $\underset{\sim}{1}$. This latter value is in the general range of olefins with weak electron withdrawing substituents (e.g. vinyl acetate). Thus the effect of the phosphazene has been to significantly reduce the electron rich nature of the vinylether. The net result is a slightly electron deficient olefin which may be contrasted to the very polarized propenylphosphazene.[9,11] The qualitative difference in polarity between $\underset{\sim}{1}$ and the corresponding propenyl derivative is in agreement with the differences observed in their reactivity towards lithium reagents.

The addition of two molar equivalents of $Li(COR)=CH_2$ to $N_3P_3F_6$ produces the geminally substituted derivatives, 2,2-$N_3P_3F_4[C(OR)=CH_2]_2$, $\underset{\sim}{2}$ and $\underset{\sim}{4}$. The corresponding reaction using 2-propenyl lithium yielded only degradation products,[10] presumably from anionic attack on the electron deficient olefin.[11] These observations further demonstrate the validity of the reduction of polarity hypothesis in the synthetic chemistry of alkyl vinylether-phosphazene derivatives. The geminal configurations were unambiguously deduced from the NMR spectroscopic data. The absence of fluorine coupling in both the $^1H$ and $^{13}C$ NMR spectra of $\underset{\sim}{2}$ and $\underset{\sim}{4}$ suggests a geminal configuration since such coupling was observed for a $\equiv PFC(OR)=CH_2$ center in $\underset{\sim}{1}$ and $\underset{\sim}{3}$. The phosphorus-carbon ($^1J_{PC}$) and phosphorus-hydrogen ($^3J_{PCCH}$) coupling constants all decrease ongoing

from the mono to the disubstituted derivatives. Similar trends have been observed in the $^{1}H$ [5c,22] and $^{13}C$ [5b,e] NMR spectra of a wide variety of geminal organo and aminophosphazenes. The geminal assignment can be confirmed by $^{19}F$ and $^{31}P$ NMR spectroscopy. The complex $^{19}F$ NMR spectra observed for 1 and 3 reduce to a doublet in 2 and 4 indicating a single fluorine environment. The second-order fine structure is of the type expected for an $ABB'X_2X_2'$ system. The $^{31}P$ NMR spectra of 2 and 4 show a large triplet due to $\equiv PF_2$ centers and a small triplet due to a phosphorus atom in a $\equiv P[C(OR)=CH_2]_2$ center coupling with two equivalent phosphorus atoms. The fine structure on the $\equiv P[C(OR)=CH_2]_2$ resonance is clarified by broad band proton decoupling and results (in the decoupled spectra) from long range phosphorus-fluorine coupling. The chemical shift of the β olefinic carbon undergoes a small (∿ 1 ppm) shift on going from the mono to the disubstituted derivatives. The direction of the shift[21] is consistent with a small decrease in electron withdrawing ability as a fluorine atom is replaced by a less electronegative organic group[5a]. A substantive shift (∿ 10 ppm) is observed for the organosubstituted phosphorus resonance on going from the mono to the disubstituted derivatives. The origins of this variation are complex but the major contributions would be expected to be electron release from the olefin and change in bond angle at the phosphorus atom.

Attempts to introduce additional ethyl vinylether substituents on to the phosphazene ring have proved unsuccessful. The NMR and mass spectra of the small amounts of product mixtures obtained suggest that these materials arise from displacement of the ethoxy function from the olefin in 2.

The fact that the reduced polarity of the olefinic centers in 1 and 3 allows for further ring substitution reactions by $LiC(OR)=CH_2$ without exocyclic group attack has lead us to examine the synthesis of mixed substituent derivatives of 1. These reactions are summarized below.

$$N_3P_3F_5C(OC_2H_5)=CH_2\ (1) + LiC_6H_5 \longrightarrow 2,2\text{-}N_3P_3F_4(C_6H_5)C(OC_2H_5) = CH_2\ (5)$$

$$N_3P_3F_5C_6H_5 + LiC(OC_2H_5)=CH_2 \longrightarrow 5$$

$$\underset{\sim}{1} + HN(CH_3)_2 \longrightarrow 2,4\text{-}N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2 \quad (\underset{\sim}{6})$$

$$N_3P_3F_5N(CH_3)_2 + LiC(OC_2H_5)=CH_2 \longrightarrow \underset{\sim}{6}$$

The same mixed phenyl/ethoxylvinyl derivative ($\underset{\sim}{5}$) is formed independent of the order of introduction of the substituents. The geminal configuratio for $\underset{\sim}{5}$ is established by NMR spectroscopy. The $^{1}H$ and $^{13}C$ NMR spectra show the same characteristic shifts and absence of fluorine coupling as was observed in the preceeding geminal derivatives $\underset{\sim}{2}$ and $\underset{\sim}{4}$. The $^{19}F$ NMR spectrum is complicated since even in a geminal configuration the fluorine atoms in a $\equiv PF_2$ center are inequivalent hence one observes two sets of complex doublets. The structure is unambiguously confirmed by the $^{31}P$ NMR spectrum which is very similar to those of the other geminal derivatives except for a substantive shift in the organosubstituted phosphorus atom over the divinylether derivatives. One would expect that the size difference between a phenyl and a vinylether substituent would effect bond angle changes at the phosphorus atom and hence be reflected in $^{31}P$ chemical shifts. The olefinic β-carbon $^{13}C$ NMR shift in $\underset{\sim}{5}$ suggests a slightly more electron rich olefinic environment in $\underset{\sim}{5}$ than in $\underset{\sim}{2}$.

The same mixed dimethylamino/ethoxyvinyl derivative ($\underset{\sim}{6}$) is also obtained independent of the order of introduction of substituents. Examination of $\underset{\sim}{6}$ by gas chromatography shows the existance of two components in similar (but not exactly equivalent) amounts. The relative amounts of each component do not vary significantly with the order of introduction of the substituent. The $^{1}H$ and $^{13}C$ NMR data are suggestive of a non-geminal configuration in that the coupling constants resemble $\underset{\sim}{1}$ and $\underset{\sim}{3}$ and fluorine coupling is observed. The $^{19}F$ and $^{31}P$ NMR spectra are complex due to the presence of the isomeric mixture however in each case the expected features of $\equiv PF_2$ and $\equiv PFR$ environments are observed. Thus, it can be concluded that sample $\underset{\sim}{6}$ is a mixture of cis and trans $2,4\text{-}N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$.

The results presented above are of interest in the continuing question of the basis of the stereoregulation effects observed in the substitution reactions of the cyclophosphazenes. In recent years, careful studies of the cross reactions of various

amines with $N_3P_3Cl_6$ have clearly demonstrated the importance of incoming group control over the stereochemistry of phosphazene derivatives.[23] Evidence for incoming group control is also noted in this investigation. If one considers various reactions of the same monosubstituted phosphazene (1), one observes geminal isomer formation when the incoming moiety is an organolithium reagent and non-geminal isomer formation when the incoming group is dimethylamine. By using the same lithium reagent and changing the phosphazene one also observes evidence for phosphazene substituent control over the stereochemistry of the product. Thus the reaction of $LiC(OC_2H_5)=CH_2$ with 1 and $N_3P_3F_5C_6H_5$ leads to geminal products while the comparable reaction with $N_3P_3F_5N(CH_3)_2$ yields non-geminal products.

The reactions examined this investigation bridge the balance point between incoming reagent and substituent control. While many of the mechanistic features of incoming reagent control in the reactions of amines with $N_3P_3Cl_6$ are understood,[23d] similar details for the reactions of organolithium reagents with $N_3P_3F_6$ are lacking. However, a consistent model for ring substituent control is beginning to emerge. The clear predilection for geminal isomer formation for organophosphazenes[2] can be related to the $\sigma$ electron releasing ability[5a] of the organic group. The preferential shift of ring nitrogen lone pair electron density to the $\equiv PF_2$ center [24] results in occupation of phosphorus acceptor orbitals at that center, which otherwise would serve as sites for an incoming reagent in a bimolecular reaction. This leaves more acceptor orbitals for an incoming reagent at the $\equiv PFR$ center and consequently geminal substitution is formed. In the case of aminophosphazenes, such as $N_3P_3F_5N(CH_3)_2$, the substituent is a $\pi$ donor[22], hence acceptor orbitals at the $\equiv PFN(CH_3)_2$ center are occupied and attack occurs at the $\equiv PF_2$ site giving non-geminal products.

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Supplementary Material Available: A listing of major mass spectral fragments and their relative intensities (Table 1). Ordering information is given on any current masthead page.

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(18) All NMR ( $^{1}H$, $^{13}C$, $^{31}P$, $^{19}F$) chemical shifts in ppm and coupling constants in Hz. Hc is the olefinic hydrogen atom cis to the phosphazene and $H_t$ is trans to the phosphazene.

(19) Numbers refer to: $\equiv PF\ C^{1}(OC^{3}H_2C^{4}H_3)=C^{2}H_3$

(20) In $cm^{-1}$

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Material to be placed in microfilm edition

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# Organophosphazenes. 16. The Synthesis and Reactions of 1-Alkoxyvinylfluorocyclotriphosphazenes.

Table 1. Selected Mass Spectra for Alkoxyvinylfluorocyclotriphosphazenes.

$N_3P_3F_5C(OC_2H_5) = CH_2$ (1)

| | | | |
|---|---|---|---|
| 301 | (31%, $N_3P_3F_5C_4H_7O^+$), | 300 | (10%, $N_3P_3F_5C_4H_6O^+$) |
| 287 | (19%, $N_3P_3F_5C_3H_5O^+$), | 286 | (100%, $N_3P_3F_5C_3H_4O^+$) |
| 282 | (7%, $N_3P_3F_4C_4H_7O^+$), | 275 | (4%, $N_3P_3F_5C_2H_5O^+$) |
| 274 | (6%, $N_3P_3F_5C_2H_4O^+$), | 273 | (33%, $N_3P_3F_5C_2H_3O^+$) |
| 272 | (5%, $N_3P_3F_5C_2H_2O^+$), | 259 | (19%, $N_3P_3F_5C_2H_5^+$) |
| 258 | (23%, $N_3P_3F_5C_2H_4^+$), | 257 | (44%, $N_3P_3F_5C_2H_3^+$) |
| 256 | (90%, $N_3P_3F_5C_2H_2^+$), | 255 | (65%, $N_3P_3F_5C_2H^+$) |
| 254 | (4%, $N_3P_3F_4C_2H_3O^+$), | 253 | (9%, $N_3P_3F_4C_2H_2O^+$) |
| 247 | (87%, $N_3P_3F_5OH^+$), | 246 | (64%, $N_3P_3F_5O^+$) |
| 245 | (14%, $N_3P_3F_5CH_3^+$), | 244 | (91%, $N_3P_3F_5CH_2^+$) |
| 243 | (78%, $N_3P_3F_5CH^+$), | 232 | (41%, $N_3P_3F_5H_2^+$) |
| 231 | (96%, $N_3P_3F_5H^+$), | 230 | (93%, $N_3P_3F_5^+$) |
| 229 | (6%, $N_3P_3F_4OH_2^+$), | 228 | (30%, $N_3P_3F_4OH^+$) |
| 227 | (8%, $N_3P_3F_4O^+$) | | |

$N_3P_3F_4[C(OC_2H_5)=CH_2]_2$ (2)

354 (25%, $N_3P_3F_4C_8H_{15}O_2^+$), 353 (100%, $N_3P_3F_4C_8H_{14}O_2^+$)

338 (34%, $N_3P_3F_4C_7H_{11}O_2^+$), 325 (23%, $N_3P_3F_4C_6H_{10}O_2^+$)

324 (88%, $N_3P_3F_4C_6H_9O_2^+$), 308 (10%, $N_3P_3F_4C_6H_9O^+$)

307 ( 6%, $N_3P_3F_4C_6H_8O^+$), 297 (10%, $N_3P_3F_4C_5H_{10}O^+$)

296 (72%, $N_3P_3F_4C_5H_9O^+$), 294 (39%, $N_3P_3F_4C_5H_7O^+$)

284 ( 9%, $N_3P_3F_4C_4H_9O^+$), 283 (18%, $N_3P_3F_4C_4H_8O^+$)

282 (66%, $N_3P_3F_4C_4H_7O^+$), 280 (.0%, $N_3P_3F_4C_4H_5O^+$)

278 (11%, $N_3P_3F_4C_4H_3O^+$), 276 ( 6%, $N_3P_3F_4C_4H\ O^+$ and/or $N_3P_3F_3C_5H_8O^+$)

279 (15%, $N_3P_3F_4C_3H_7O^+$), 269 (15%, $N_3P_3F_4C_3H_6O^+$)

268 (70%, $N_3P_3F_4C_3H_5O^+$), 267 (11%, $N_3P_3F_4C_3H_4O^+$)

266 ( 7%, $N_3P_3F_4C_3H_3O^+$), 205 (37%, $N_3P_3F_4C_3H_2O^+$ and/or $N_3P_3F_3C_4H_9O^+$)

264 (19%, $N_3P_3F_4C_3H\ O^+$ and/or $N_3P_3F_3C_4H_8O^+$), 256 (8%, $N_3P_3F_4C_2H_5O^+$)

254 (16%, $N_3P_3F_4C_2H_3O^+$), 252 ( 7%, $N_3P_3F_4C_2H\ O^+$)

240 (58%, $N_3P_3F_4C_2H_5^+$), 239 (67%, $N_3P_3F_4C_2H_4^+$)

238 (40%, $N_3P_3F_4C_2H_3^+$), 228 (64%, $N_3P_3F_4C\ H_4^+$ and/or $N_3P_3F_4\ OH^+$)

225 (14%, $N_3P_3F_4\ CH^+$), 215 (54%, ?)

213 (68%, $N_3P_3F_4H_2^+$), 212 (91%, $N_3P_3F_4H^+$)

211 (49%, $N_3P_3F_4^+$),

$N_3P_3F_5C(OCH_3)=CH_2$ (3)

288 ( 6%, $N_3P_3F_5C_3H_6O^+$), 287 (83%, $N_3P_3F_5C_3H_5O^+$)

286 (87%, $N_3P_3F_5C_3H_4O^+$), 272 ( 9%, $N_3P_3F_5C_2H_2O^+$)

268 (11%, $N_3P_3F_4C_3H_5O^+$), 259 ( 6%, $N_3P_3F_5C_2H_5^+$)

258 (84%, $N_3P_3F_5C_2H_4^+$), 247 (100%, $N_3P_3F_5C_2H_3^+$)

256 (87%, $N_3P_3F_5C_2H_2^+$), 255 (12%, $N_3P_3F_5C_2H^+$)

252 ( 7%, $N_3P_3F_4C_3H_5^+$), 248 (20%, $N_3P_3F_5O\ H_2^+$)

245 (22%, $N_3P_3F_5CH_3^+$), 244 (68%, $N_3P_3F_5CH_2^+$)

242 (20%, $N_3P_3F_5C^+$), 232 (29%, $N_3P_3F_5H_2^+$)

231 (81%, $N_3P_3F_5H^+$), 232 (84%, $N_3P_3F_5^+$)

210 (68%, $N_2P_3F_5^+$)

$N_3P_3F_4[C(OCH_3)=CH_2]_2$ (4)

326 ( 4%, $N_3P_3F_4C_6H_{11}O_2^+$), 325 (44%, $N_3P_3F_4C_6H_{10}O_2^+$)

324 (75%, $N_3P_3F_4C_6H_9O_2^+$), 323 (15%, $N_3P_3F_4C_6H_8O_2^+$)

310 ( 7%, $N_3P_3F_4C_5H_7O_2^+$), 309 (29%, $N_3P_3F_4C_5H_6O_2^+$)

299 (22%, $N_3P_3F_4C_4H_8O_2^+$), 298 (10%, $N_3P_3F_4C_4H_7O_2^+$)

297 (25%, $N_3P_3F_4C_4H_6O_2^+$), 294 ( 7%, $N_3P_3F_4C_5H_7O^+$)

293 (13%, $N_3P_3F_4C_5H_6O^+$), 285 (26%, $N_3P_3F_4C_3H_6O_2^+$)

284 (16%, $N_3P_3F_4C_3H_5O_2^+$), 283 (82%, $N_3P_3F_4C_3H_4O_2^+$ and/or $N_3P_3F_4C_4H_8O^+$)

282 ( 6%, $N_3P_3F_4C_4H_7O^+$), 281 (14%, $N_3P_3F_4C_4H_6O^+$)

269 (21%, $N_3P_3F_4C_3H_6O^+$), 268 (21%, $N_3P_3F_4C_3H_5O^+$)

267 (64%, $N_3P_3F_4C_3H_4O^+$), 256 (17%, $N_3P_3F_4C_2H_5O^+$)

255 (29%, $N_3P_3F_4C_2H_4O^+$), 254 (12%, $N_3P_3F_4C_2H_3O^+$)

253 (38%, $N_3P_3F_4C_2O^+$, and/or $N_3P_3F_4C_3H_6^+$), 252 ( 8%, $N_3P_3F_4C_2H\ O^+$, and/or $N_3P_3F_4C_3H_5^+$)

251 (56%, $N_3P_3F_4C_2O^+$, and/or $N_3P_3F_4C_3H_4^+$), 250 ( 7%, $N_3P_3F_4C_3H_3^+$)

243 (44%, $N_3P_3F_4CH_4O^+$), 242 (15%, $N_3P_3F_4CH_3O^+$)

241 (95%, $N_3P_3F_4CH_2O^+$), 239 ( 7%, $N_3P_3F_4C_2H_4^+$ and/or $N_3P_3F_4CO^+$)

238 (18%, $N_3P_3F_4C_2H_3^+$), 237 (14%, $N_3P_3F_4C_2H_2^+$)

229 ( 6%, $N_3P_3F_4OH_2^+$), 228 ( 7%, $N_3P_3F_4OH^+$)

227 (40%, $N_3P_3F_4O^+$ and/or $N_3P_3F_4CH_4^+$), 226 (15%, $N_3P_3F_4CH_3^+$)

225 (24%, $N_3P_3F_4CH_2^+$), 224 (24%, $N_3P_3F_4CH^+$)

223 ( 9%, $N_3P_3F_4C^+$), 212 (32%, $N_3P_3F_4H^+$)

211 (100%, $N_3P_3F_4^+$)

$N_3P_3F_4(C_6H_5)C(OC_2H_5)=CH_2$ (5)

360 ( 6%, $N_3P_3F_4C_{10}H_{13}O^+$), 359 (38%, $N_3P_3F_4C_{10}H_{11}O^+$)

358 (14%, $N_3P_3F_4C_{10}H_{11}O^+$), 345 ( 6%, $N_3P_3F_4C_9H_{10}O^+$)

344 (100%, $N_3P_3F_4C_9H_9O^+$), 341 ( 5%, $N_3P_3F_3C_{10}H_{12}O^+$)

330 (14%, $N_3P_3F_4C_8H_9O^+$), 316 (34%, $N_3P_3F_4C_8H_9^+$)

315 (85%, $N_3P_3F_4C_8H_8^+$), 314 (86%, $N_3P_3F_4C_8H_7^+$)

313 (21%, $N_3P_3F_4C_8H_6^+$), 312 (10%, $N_3P_3F_4C_8H_5^+$)

302 (27%, $N_3P_3F_4C_7H_7^+$), 290 (11%, $N_3P_2F_2C_{10}H_{12}O^+$)

289 (12%, $N_3P_3F_4C_6H_7^+$ and/or $N_3P_2F_2C_{10}H_{11}O^+$), 288 (83%, $N_3P_3F_4C_6H_6^+$)

287 ( 3%, $N_3P_3F_4C_6H_5^+$) 286 ( 8%, $N_3P_3F_4C_6H_4^+$)

274 ( 6%, $N_3P_3F_3C_5H_6O^+$), 266 ( 8%, $N_3P_3F_4C_2H_3O^+$)

245 ( 7%, $N_3P_2F_2C_8H_7^+$), 243 (11%, $N_3P_3F_4O\ H_2CH_2^+$ and/or $N_3P_2F_2C_8H_5^+$)

240 (11%, $N_3P_3F_4C_2H_5^+$ and/or $N_3P_3F_4COH^+$), 231 ( 8%, $N_3P_2F_2C_7H_5^+$)

229 ( 9%, $N_3P_3F_4OH_2^+$), 228 ( 8%, $N_3P_3F_4OH^+$)

214 ( 7%, $N_3P_3F_4H_3^+$), 213 (12%, $N_3P_3F_4H_2^+$)

212 (68%, $N_3P_3F_4H^+$), 211 ($N_3P_3F_4^+$)

$N_3P_3F_4[N(CH_3)_2]C(OC_2H_5)=CH_2$ (6)

326 (45%, $N_3P_3F_4N\ C_6H_{13}O^+$), 325 (17%, $N_3P_3F_4N\ C_6H_{12}O^+$)

312 (23%, $N_3P_3F_4N\ C_5H_{11}O^+$), 311 (100%, $N_3P_3F_4N\ C_5H_{10}O^+$)

307 ( 6%, $N_3P_3F_3N\ C_6H_3O^+$) , 298 ( 8%, $N_3P_3F_4N\ C_4H_9O^+$)

297 (82%, $N_3P_3F_4N\ C_4H_8O^+$), 291 (11%, $N_3P_3F_3N\ C_5H_{10}O^+$)

284 ( 5%, $N_3P_3F_4C_4H_9O^+$), 283 (25%, $N_3P_3F_4C_4H_8O^+$)

282 (84%, $N_3P_3F_4C_4H_7O^+$ and/or $N_3P_3F_4N\ C_4H_9$), 281 (72%, $N_3P_3F_4C_4H_6O^+$ and/or $N_3P_3F_4NC_4H_8$)

280 ( 7%, $N_3P_3F_4N\ C_4H_7^+$), 270 (16%, $N_3P_3F_4NC_3H_9^+$)

269 (54%, $N_3P_3F_4\ N\ C_3H_8^+$), 268 (12%, $N_3P_3F_4NC_3H_7^+$ and/or $N_3P_3F_4OC_3H_5^+$)

267 (12%, $N_3P_3F_4NC_3H_6^+$ and/or $N_3P_3F_4OC_3H_4^+$), 264 ( 6%, $N_3P_3F_3C_4H_8O^+$)

257 ( 5%, $N_3P_3F_4\ N\ C_2H_8^+$ and/or $N_3P_3F_4OC_2H_6^+$), 256 (36%, $N_3P_3F_4NC_2H_7^+$ and/or $N_3P_3F_4OC_2H_5^+$)

255 (37%, $N_3P_3F_4NC_2H_6^+$ and/or $N_3P_3F_4OC_2H_4^+$), 254 (22%, $N_3P_3F_4NC_2H_5^+$ and/or $N_3P_3F_4OC_2H_3^+$)

253 ( 6%, $N_3P_3F_4NC_2H_4^+$ and/or $N_3P_3F_4OC_2H_2^+$), 241 (26%, $N_3P_3F_4C_2H_6^+$ and/or $N_3P_3F_4NC\ H_4$)

240 ( 8%, $N_3P_3F_4C_2H_5^+$ and/or $N_3P_2F_4NCH_3$), 239 (46%, $N_3P_3F_4C_2H_4^+$ and/or $N_3P_3F_4NCH_2$)

238 (14%, $N_3P_3F_4C_2H_3^+$ and/or $N_3P_3F_4MCH$), 237 ( 6%, $N_3P_3F_4C_2H_2^+$ and/or $N_3P_3F_4NC^+$)

236 (10%, $N_3P_3F_4C_2H^+$), 235 ( 8%, $N_3P_3F_4C_2^+$)

228 (14%, $N_3P_3F_4CH_5^+$ and/or $N_3P_3F_4OH^+$) 227 (19%, $N_3P_3F_4CH_4^+$ and/or $N_3P_3F_4O^+$)

226 (12%, $N_3P_3F_4CH_3^+$), 214 (30%, $N_3P_3F_4H_3^+$)

213 (75%, $N_3P_3F_4H_2^+$), 212 (53%, $N_3P_3F_4H^+$)

211 (10%, $N_3P_3F_4^+$)

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