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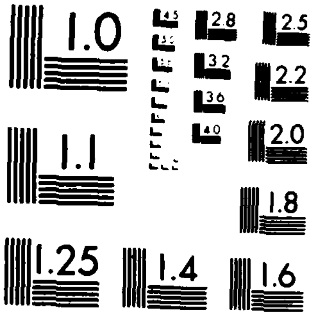
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# Organophosphazenes. 17. The Synthesis of Trimethysilylacetylene and Terminal Acetylene Derivatives of Hexafluorocyclotriphosphazene.

by

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# Organophosphazenes. 17. The Synthesis of Trimethylsilyacetylene and Terminal Acetylene Derivatives of Hexafluorocyclotriphosphazene.[1†]

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The reactions of lithio trimethylsilylacetylene, $LiC{\equiv}CSiMe_3$, with hexafluorocyclotriphosphazene, $N_3P_3F_6$, lead to the new alkynphosphazenes $N_3P_3F_{6-n}(C{\equiv}CSiMe_3)_n$ (n=1,2). Both the geminal and non-geminal isomers are observed in the $^{31}P$ and $^{19}F$ n.m.r. spectra. A reinvestigation of the reaction of lithio phenylacetylene, $LiC{\equiv}CPh$, with $N_3P_3F_6$ showed that, at the stage of bis substitution, in addition to the previously reported major product, gem-$N_3P_3F_4(C{\equiv}CPh)_2$, small amounts of the non-geminal $N_3P_3F_4(C{\equiv}CPh)_2$ isomers are formed. The reactions of $N_3P_3F_{6-n}(C{\equiv}CSiMe_3)_n$ (n=1,2) with potassium fluoride in anhydrous ethanol leads to the terminal acetylene derivatives, $N_3P_3F_{4-n}(OC_2H_5)_2(C{\equiv}CH)_n$ (n=1,2).

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†Non-S.I. unit employed: mm Hg ≈ 13.6 x 9.8 Pa.

The reactions of organolithium and Grignard reagents with halophosphazenes have been shown to be valuable routes to organophosphazenes.[2] Much of the effort in this area has been devoted to aryl[2-4] and alkyl[2,4-6] substituted species with alkenyl[1,2,6-8] and especially alkynl[2,9,10] derivatives being less common. We are particularly interested in alkenyl and alkynl phosphazenes because of the potential, as shown in our work on propenyl phosphazenes, for further synthetic transformations into new organophosphazenes[2,7,12] and organophosphazene polymers.[2,11,12] A previous study by Chivers involving phosphazene derivatives of phenylacetylene, $N_3P_3F_{6-n}(C{\equiv}CC_6H_5)_n$ (n=1,2)[9] demonstrated the viability of synthesis of alkynlphosphazenes. Alkynlphosphazenes have also been observed in the reactions of copper or lithiophosphazene anions with prop-2-ynyl bromide leading to materials of the type $N_3P_3Cl_4(R)CH_2C{\equiv}CH$ (R=alkyl., allyl).[10] Rearrangement from the prop-2-ynyl derivative to the prop-1-ynyl derivative, $N_3P_3Cl_4(R)C{\equiv}CCH_3$ was also observed.[10] A prop-1-ynyl derivative, $N_3P_3F_5C{\equiv}CCH_3$, was previously reported as a byproduct in the reaction of the lithiopropene $LiCH{=}CHCH_3$ with $N_3P_3F_6$.[7] In this paper we describe the synthesis of phosphazenes with trimethylsilylacetylene and terminal acetylene substituents.

## Experimental

**Materials and Methods.** Hexafluorocyclotriphosphazene, $N_3P_3F_6$, was prepared from $N_3P_3Cl_6$ (Ethyl Corp.) by a previously reported procedure.[13] Phenylacetylene and n-butyl lithium (1.55 M solution in hexane) were obtained from Aldrich Corp.. Trimethylsilylacetylene was obtained from Petrarch systems. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Petroleum ether (b.p. 35-55°C) was distilled over sodium. NMR spectra (in $CHCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 MHz ($^{1}H$) 62.9 MHz ($^{13}C$), 235.2 MHz ($^{19}F$) and 101.2 MHz ($^{31}P$). For $^{31}P$ NMR, 85% $H_3PO_4$ was used as external reference. For $^{19}F$ NMR, $CFCl_3$ was used as the reference. $^{13}C$, $^{19}F$, and $^{31}P$ NMR spectra were recorded under conditions of broad band decoupling. Due to the complex second-order nature of the $^{19}F$ and $^{31}P$ spectra, parameters reported for these systems are approximate. Chemical shifts upfield to the reference are assigned a negative sign. Infrared (IR) spectra were obtained as their thin films (NaCl disks) on a Beckman IR 20A spectrometer. Mass spectra were recorded on a Perkin Elmer RMU-6D spectrometer operating at 80 eV. Elemental analysis were performed by Integral Microanalytical laboratories.

Preparation of $N_3P_3F_5C{\equiv}CSiMe_3$ (1). n-Butyl lithium (45 mL, 70.0 mmoles) was reacted with trimethylsilylacetylene (6.7 g, 66 mmoles) in diethyl ether (150 mL at -78°C using a previously described apparatus.[14] The $LiC{\equiv}CSiMe_3$ thus obtained was added slowly (30 min.) to a cold (-78°C) stirred solution of $N_3P_3F_6$ (17.0g, 68 mmoles) in diethyl ether (200 mL). After 12 hr, the solvent was removed and petroleum ether (300 mL) was added to the residue. Filtration followed by the removal of petroleum ether from the filtrate gave a reddish brown liquid which was distilled under reduced pressure to yield a colorless liquid (10.2 g, 45.6% of theory), b.p. 30°C at 0.05 mm Hg. Anal. Calcd. for $C_5H_9F_5N_3P_3Si$: C, 18.35; H, 2.75; mol. wt. 327. Found: C, 18.48; H, 2.79; mol. wt. 327 (mass spectrum).

$^{1}$H NMR: $^{\delta}\equiv PF(C\equiv CSiMe_3) = -0.5$ (s) $^{31}$P NMR: $^{\delta}\equiv PF(C\equiv CSiMe_3) = 3.6$ (complex multiplet), $J_{PF} = 916.0$; $^{\delta}\equiv PF_2 = 8.2$ (complex multiplet), $J_{PF} = 950.0$. $^{19}$F NMR: $^{\delta}\equiv PF(C\equiv CSiMe_3) = -45.5$, $J_{PF} = 900.0$; $^{\delta}\equiv PF_2 = -68.4$, $J_{PF} = 820.0$; $^{\delta}\equiv PF_2 = -69.7$, $J_{PF} = 880$. $^{13}$C NMR: $^{\delta}\equiv PF\ (C\equiv CSiMe_3) = 92.6$ (complex multiplet), $J_{PC} = 332.8$, $^{2}J_{PC} = 56.0$; $^{\delta}\equiv PF(C\equiv CSiMe_e) = 112.7$ (d of d), $^{2}J_{PC} = 51.5$; $^{\delta}\equiv PF(C\equiv CSi\underline{Me}_3) = -1.5$ (s). IR: 2960 (w, ≡ C-H), 2145 (m, -C≡C- Str.), 1240 (S, P=N Str.), 950 (s, Si-C), 850 (S, P-F), 810 (s, P-F), 760 (m, P-F). The same product can be obtained, in lower yields, from $Me_3SiC\equiv CLi$ prepared from[15] the reaction of methyl lithium with bis (trimethylsily)acetylene.

Preparation of $N_3P_3F_3(OC_2H_5)_2C\equiv CH$ (2). To a refluxing suspension of KF (0.2g) in absolute ethanol (25 mL), compound (1) (5.0 g, 15.3 mmoles) was added from a syringe. After 3 hr, the solvent was removed and the residue obtained was extracted with petroleum ether (150 mL). The mixture was filtered and petroleum ether was removed from the filtrate. The dark brown liquid obtained was distilled under reduced pressure to give a colorless liquid (2.2 g, 46.8% of theory), b.p. 40°C at 0.05 mm Hg. Anal. Cacd. for $C_6H_{11}F_3N_3O_2P_3$: C, 23.45; H, 3.58; mol. wt. 307. Found: C, 23.21; H, 3.46; mol. wt. 307 (mass spectrum). $^{1}$H NMR: $^{\delta}-C\equiv C\underline{H} = 3.09$ (d), $^{3}J_{PH} = 13.56$, $^{\delta}-C\equiv C\underline{H} = 3.08$ (d), $^{3}J_{PH} = 13.75$; $^{\delta}-OC\underline{H}_2CH_3$: 4.16 (m), $^{\delta}-OCH_2C\underline{H}_3 = 1.38$ (m). $^{31}$P NMR: very complex spectrum; approximate $^{\delta}\equiv PF(C\equiv CSiMe_3)$ values are 11.8 and 3.2. $^{19}$F NMR: $^{\delta}\equiv PF\ (C\equiv CSiMe_3) = -65.5$; $^{\delta}\equiv PF(C\equiv SiMe_3) = -69.2$; $^{\delta}\equiv PF_2 = -42.5$, $J_{PF} = 895.0$ IR: 3280 (m, ≡ C-H), 2990 (m, CH Str.), 2065 (s, -C≡C-Str.), 1260 (S, P=N Str.), 1165 (m), 1045 (s, P-O Str.), 975 (m, P-F), 915 (m, P-F), 845 (m, P-F), 785 (m, P-F).

Preparation of $N_3P_3F_4(C{\equiv}C\text{-}SiMe_3)_2$ (3). Lithio trimethylsilylacetylene, $LiC{\equiv}C\text{-}SiMe_3$, prepared by the reaction of n-butyl Li (64 mL, 100 mmoles) and trimethylsilylacetylene (9.8 g 100 mmoles) was allowed to react with $N_3P_3F_6$ 12.5 g, 50 mmoles) in diethyl ether (200 mL) as before. The reaction mixture was stirred for 2 days and worked up to give a viscous liquid (7.25 g, 35.8% of theory), b.p. 65°C at 0.05 mm Hg. Anal. Calcd. for $C_{10}H_{18}F_4N_3P_3Si_2$: C, 29.63; H, 4.44; mol. wt. 405. Fould: C, 30.12; H, 4.38; mol. wt. 405 (mass spectrum).

$^1H$ NMR: $\delta_{-Si\underline{Me}_3} = -0.45$ (s). $^{31}P$ NMR: $\delta_{\equiv P(C\equiv SiMe_3)_2} = -27.0$, $^2J_{pp} = 80.0$; $\delta_{\equiv PF_2} = 7.5$, $J_{PF} = 900.0$; $\delta_{\equiv PF(C\equiv CSiMe_3)} = 1.5$; $J_{PF} = 920.0$. $^{19}F$ NMR: $\delta_{\equiv P\underline{F}_2}$: $-42.6$, $J_{PF}$: 9200; $\delta_{\equiv PF_2} = -44.5$, $J_{PF} = 890$; $\delta_{\equiv PF(C\equiv CSiMe_3)} = -68.6$, $J_{PF} = 915.0$. $^{13}C$ NMR: $\delta_{\equiv P(C\equiv \underline{C}SiMe_3)_2} = 112.2$ (c.m.), $\delta_{\equiv P(\underline{C}\equiv CSiMe_3)}$; $= 96.3$ (t,d), $J_{PC} = 256.0$; $\delta_{\equiv P(C\equiv CSi\underline{Me}_3)_2} = -1.1$ (s); $\delta_{\equiv PF(C\equiv \underline{C}SiMe_3)}$; 112.2 (c-m); $\delta_{\equiv PF(\underline{C}\equiv CSiMe_3)} = 93.8$ (c.m.), $J_{PC} = 300$, $^2J_{PC} = 56.0$; $\delta_{\equiv PF(C\equiv CSi\underline{Me}_3)} = -1.4$(s). IR: 2965 (m, CH Str.), 2140 (m,-C≡C-), 1265 (s, P=N), 930 (m, Si-C), 850 (m, P-F), 815 (m, P-F) 795 (m, P-F).

Attempts at separation of the mixture by distillation or crystallization proved unsuccessful. The materials apparently bind to silica gel and hence can not be eluted from a chromatography column.

Preparation of $N_3P_3F_2(OC_2H_5)_2(C{\equiv}CH)_2$ (4). The reaction of $N_3P_3F_4(C{\equiv}CSiMe_3)_2$ (3) (3.2g, 8.0 m moles) with KF (3.2 g) in absolute ethanol (40 mL) was

carried out as before to yield a dark brown liquid. Reduced pressure distillation of this liquid gave yielded a viscous oil (0.9 g, 36.7% of theory), b.p. 105°C at 0.05 mm Hg. Anal. Calcd. for $C_8H_{12}F_2N_3O_2P_3$: C, 30.67; H, 3.83; mol. wt. 313. Found: C, 29.94; H, 3.78; mol. wt. 313 (mass spectrum).
$^1H$ NMR: $\delta$-C≡C$\underline{H}$ = 3.0 (c.m.); $\delta$-O$\underline{CH_2}CH_3$ = 4.1 (c.m.); $\delta$-O$CH_2CH_3$ = 1.4 (c.m.).
$^{31}P$ NMR: $\delta$≡P(C≡CH)$_2$ - 25.0 (c.m.); $\delta$≡$PF_2$ = 7.5 (c.m.); $\delta$≡PFR = 2.5.
IR: = 3280 (m, -C≡CH Str.), 2460 (m, CH Str.), 2165 (s, - C≡C.), 1255 (s, P=N) 1170 (m), 1055 (s, P-O Str.), 965 (m, P-F), 915 (s, P-F), 845 (m, P-F), 790 (m).

Preparation of $N_3P_3F_5$C≡CPh(5). n-ButylLi (32 mL, 50 mmoles) was allowed to react with phenylacetylene (5.4 g, 50 mmoles) in diethyl ether (150 mL). After 24 hr, the above reaction mixture was added to a solution of $N_3P_3F_6$ (13.4 g, 50 mmoles) in diethyl ether (150 mL). The resultant reaction mixture was stirred for 24 hr and worked up as before. Reduced pressure distillation of the product obtained gave $C_8H_5N_3P_3F_5$ (7.7 g 46.5% of theory), b.p. 45°C at 0.1 mm Hg. (Lit. b.p. 82°C at 2.5 mm Hg).
$^1H$ NMR: $\delta$-$C_6H_5$: 7.3 (m). $^{31}P$ NMR: $\delta$≡$PF_2$ = 8.2 (t), $J_{PF}$ = 941.2; $\delta$≡PF(C≡C$C_6H_5$ = 6.0 (d), $J_{PF}$ = 910.8. $^{19}F$ NMR: $\delta$≡P$\underline{F}_2$ = -69.5, $J_{PF}'$ = 870.3; $\delta$≡$PF_2$ = -68.5, $J_{PF}$ = 903.2; $\delta$≡PF(C≡C$C_6H_5$ = -44.0, $J_{PF}$ = 893.8. $^{13}C$ NMR: $\delta$≡PF($\underline{C}$≡CSiMe$_3$ = 102.7 (complex d), $J_{PC}$ = 69.2; $\delta$≡PF(C≡$\underline{C}C_6H_5$ 118.0 (d), $^2J_{PC}$ = 6.1; $\delta$$C_6H_5$: 128.0, 131.9, 133.0. IR: 2180 (s, -C≡C), 1250 (s, P=N Str.), 1060 (w), 1010 (m), 980 (m, P-F), 930 (s, P-F), 880 (s, P-F), 830 (s, P-F).

Preparation of $N_3P_3F_4$(C≡CPh)$_2$ (6). Lithio phenylacetylene, LiC≡CPh prepared by the reaction of phenylacetylene (2.25g, 22.0 m moles) and n-butyl lithium (15 mL, 23 m moles) was allowed to react with $N_3P_3F_6$ (2.7 g, 11.0 m moles) in $Et_2O$ (200 mL). After 24 hr, the reaction mixture was worked as before to yield a dark brown oil which was dissolved in petroleum ether - methylene chloride (3:1) and cooled. The slightly yellowish crystals obtained was recrystallized from petroleum either-methylene chloride (3:1) to obtain 2,2-$N_3P_3F_4(C{\equiv}CPh)_2$, 1.2 g (27.3% of theory). $^1H$ NMR: $\delta_{\underline{C_6H_5}}$: 5.6 (m). $^{31}P$ NMR: $\delta_{\equiv \underline{P}F_2}$: 6.9 (t), $J_{PF} = 910.8$; $\delta_{\equiv \underline{P}(C{\equiv}CC_6H_5)_2} = -23.2$, $^2J_{PP} = 91.1$, $^3J_{PF} = 12.1$.

$^{19}F$ NMR: $\delta_{\equiv P\underline{F}_2}$: - 68.6 (d), $J_{PF} = 889.7$. $^{13}C$ NMR: $\delta_{\equiv P(\underline{C}{\equiv}CC_6H_5)_2} = 101.8$ (d), $J_{PC} = 56.6$; $\delta_{\equiv P(C{\equiv}\underline{C}C_6H_5)_2} = 119.1$ (d), $^2J_{PC} = 56.7$; $\underline{\delta}$ $C_6H_5$ = 128.7, 131.3 and 133.6. IR: 2140 (s, -C≡C.), 1220 (s, P=N), 1060 (w), 1010 (w, PF), 920 (s, PF), 870 (s, PF), 800 (s, PF).

The solvent was removed from the mother liquor remaining after isolation of the geminal isomer and the residual oil was distilled under reduced pressure. The distillate was found to contain two components. The major component was the geminal bis derivative (6) obtained above. The mass spectrum of the mixture showed only parent peaks due to $N_3P_3F_4(C{\equiv}CPh)_2$, while the $^{19}F$ and $^{31}P$ nmr spectra showed a small amount of $\equiv PF(C{\equiv}CPh)$ centers in the mixture.

## Results and Discussion

The reaction of $LiC{\equiv}CSiMe_3$ with $N_3P_3F_6$ proceeds smoothly to give the expected product, $N_3P_3F_5C{\equiv}CSiMe_3$ (1) in moderate yield. Elemental analyses, mass spectrometric data and spectroscopic (n.m.r., i.r.) properties of 1 are in accord with the assigned structure. Of particular value are the $^{31}P$ and $^{19}F$ nmr spectra which show the presence of the $\equiv PF_2$ and $\equiv PFR$ (R= $C\equiv CSiMe_3$) centers. The addition of two molar equivalents of $LiC\equiv CSiMe_3$ to $N_3P_3F_6$ produces a viscous liquid which was shown to be a mixture of the disubstituted isomers, $N_3P_3F_4(C\equiv CSiMe_3)_2$ (3). Further attempts at a separation of the components of the mixture proved unsuccessful. Some indication of the isomeric composition of 3 was obtained from an examination of the $^{31}P$ and $^{19}F$ nmr spectra. The $^{31}P$ spectrum clearly shows the presence of a $\equiv P(C\equiv CSiMe_3)_2$ center but the remaining portion of the spectrum is far too complex be ascribed only to the $\equiv PF_2$ region of the geminal isomer . The observation of $\equiv PF(C\equiv CSiMe_3)$ and two $\equiv PF_2$ resonances in the $^{19}F$ nmr spectrum demonstrates the existence of both geminal and non-geminal isomers in the mixture. A comparison of the relative areas of the $\equiv PF_2$ resonances and of the $\equiv PF(C\equiv CSiMe_3)$ resonances indicates that significant amounts of both geminal and non-geminal isomers are present.

Since it has been reported that the reaction of $LiC\equiv CPh$ with $N_3P_3F_6$ follows a geminal pathway,[9] we chose to reinvestigate the lithiophenylacetylene reaction. In large part, this reaction proceeds as previously reported leading to $N_3P_3F_5C\equiv CPh$ (5) and the geminal bis derivative, 2,2-$N_3P_3F_4(C\equiv CPh)_2$.[9] We also observed a small amount of the previously unreported non-geminal $N_3P_3F_4(C\equiv CPh)_2$ isomers. In a comparison of the isomer distribution at the stage of bis substitution in the reactions of $N_3P_3F_6$ with $LiC\equiv CR$ (R=$SiMe_3$, Ph), one observes a significant contribution from the non-geminal pathway in the trimethylsilyl derivative while a predominantly geminal pathway is observed in the formation of phenyl derivative. The sensitivity of this reaction to the nature of the β-substituent on the acetylenic center is remarkable even in the context of the established complexity of organometallic reactions of the cyclophosphazenes.[2] Geminal substitution is the preferred pathway in the reactions of organometallic reagents with $N_3P_3F_6$.[2,7] Formation of non-geminal isomers is usually ascribed to steric hinderance in the organometallic reagent.[2] It is not immediately obvious that this should be the case in alkynlphosphazenes. Although examination of the nmr data for 1 and 5 shows a striking variation in $^1J_{PC}$, the variation in $^{31}P$ shifts is less than is noted in various alkynlphosphazenes[16] and the $^{19}F$ shifts are virtually identical. Thus, significant differences in electronic structure between 1 and 5 are not expected.

We have explored the fluoride ion induced cleavage of the carbon-silicon bond in the trimethylsilylacetylene derivatives 1 and 3. The reaction of 1 with anhydrous KF in absolute ethanol leads to an inseparable mixture of trisubstituted isomers of the type $N_3P_3F_3(OC_2H_5)_2C{\equiv}CH$ (2). The $^1H$ nmr spectrum shows the presence of the terminal acetylene and ethoxy functions and the absence of the trimethylsilyl group. The $^{31}P$ nmr spectrum is complex but doesn't show any significant concentration of $\equiv PF_2$ or $\equiv PRR'$ centers. The $^{19}F$ spectrum confirms the predominance of $\equiv PFR$ ($R{=}C{\equiv}CH$, $OC_2H_5$) environments and shows a trace amount of a $\equiv PF_2$ center. Thus, the material is essentially a mixture of the three possible non-geminal isomers, 2,4,6-$N_3P_3F_3(OC_2H_5)_2C{\equiv}CH)$ with a trace of a geminal isomer. The tendency towards non-geminal substitution by the ethoxide ion is consistent with previous observations of the reactions of anionic oxygen nucleophiles with $N_3P_3Cl_6$.[17] The ethoxy function can be seen as arising from a variety of routes. The cleavage of the carbon-silicon bond results in the formation of trimethylsilyl fluoride and a carbanion which abstracts a proton from the solvent, thereby generating an ethoxide ion. The second ethoxy functions comes directly from the solvent or from the ethanol-KF mixture. The fact that the reaction stops at the tri-substituted stage can be ascribed to the higher energy barrier associated with geminal substitution by alkoxides.[17]

The reaction of the mixture of bis trimethylsilylacetylene derivatives, 3, with KF in absolute ethanol leads to the formation of a mixture of terminal acetylene derivatives having the composition $N_3P_3F_2(OC_2H_5)_2(C{\equiv}CH)_2$ (4). The $^{31}P$ and $^{19}F$ nmr spectra of 4 are very complex and outside of suggesting the presence of several environments, do not provide much useful information. These are nine possible isomers of 4 and most or all are presumed to be present.

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