Organophosphazenes. Part 17.[1] The Synthesis of Trimethylsilylacetylene and Terminal Acetylene Derivatives of Hexafluorocyclotriphosphazene †

Christopher W. Allen,* James L. Desorcie, and Kolikkara Ramachandran
Department of Chemistry, University of Vermont, Burlington, Vermont 05405, U.S.A.

The reactions of $LiC{\equiv}CSiMe_3$ with $N_3P_3F_6$ lead to the new alkynylphosphazenes $N_3P_3F_{6-n}(C{\equiv}CSiMe_3)_n$ (n = 1 or 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 $LiC{\equiv}CC_6H_5$ with $N_3P_3F_6$ showed that, at the stage of bis substitution, in addition to the previously reported major product, *gem*-$N_3P_3F_4(C{\equiv}CC_6H_5)_2$, small amounts of the non-geminal $N_3P_3F_4(C{\equiv}CC_6H_5)_2$ isomers are formed. The reactions of $N_3P_3F_{6-n}(C{\equiv}CSiMe_3)_n$ (n = 1 or 2) with KF in anhydrous ethanol lead to the terminal acetylene derivatives, $N_3P_3F_{4-n}(OC_2H_5)_2(C{\equiv}CH)_n$ (n = 1 or 2).

The reactions of organolithium and Grignard reagents with halogenophosphazenes 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 alkynyl [2,9,10] derivatives being less common. We are particularly interested in alkenyl- and alkynyl-phosphazenes because of the potential, as shown in our work on propenylphosphazenes, for further synthetic transformations into organophosphazene polymers [2,11,12] and new organophosphazenes.[2,7,12] A previous study by Chivers [9] involving phosphazene derivatives of phenylacetylene, $N_3P_3F_{6-n}(C{\equiv}CC_6H_5)_n$ (n = 1 or 2), demonstrated the viability of synthesis of alkynylphosphazenes. Alkynylphosphazenes have also been observed in the reactions of copper or lithiophosphazene anions with prop-2-ynyl bromide leading to materials of the type $N_3P_3Cl_4R(CH_2C{\equiv}CH)$ (R = alkyl or allyl).[10] Rearrangement from the prop-2-ynyl to the prop-1-ynyl derivative, $N_3P_3Cl_4R(C{\equiv}CCH_3)$, was also observed.[10] A prop-1-ynyl derivative, $N_3P_3F_5(C{\equiv}CCH_3)$, was previously reported as a by-product 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 mol dm^{-3} solution in hexane) were obtained from Aldrich Corp. Trimethylsilylacetylene was obtained from Petrarch systems. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Light petroleum (b.p. 35—55 °C) was distilled over sodium.

N.m.r. spectra (in $CHCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 (^1H), 62.9 (^{13}C), 235.2 (^{19}F), or 101.2 MHz (^{31}P). For ^{31}P n.m.r., 85% H_3PO_4 was used as external reference, for ^{19}F, $CFCl_3$ was used. The ^{13}C, ^{19}F, and ^{31}P n.m.r. 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 of the reference are assigned a negative sign. Infrared (i.r.) spectra were obtained from thin films (NaCl discs) on a Beckman IR 20A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Elemental analyses were performed by Integral Microanalytical Laboratories.

Preparations.—$N_3P_3F_5(C{\equiv}CSiMe_3)$ (1). n-Butyl-lithium (45 cm^3, 70.0 mmol) was treated with trimethylsilylacetylene (6.7 g, 66 mmol) in diethyl ether (150 cm^3) 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 $N_3P_3F_6$ (17.0 g, 68 mmol) in diethyl ether (200 cm^3). After 12 h the solvent was removed and light petroleum (300 cm^3) was added to the residue. Filtration followed by the removal of light petroleum from the filtrate gave a reddish brown liquid which was distilled under reduced pressure to yield a colourless liquid (10.2 g, 45.6% of theory), b.p. 30 °C at 0.05 mmHg [Found: C, 18.50; H, 2.80%; *M* 327 (mass spectrum). Calc. for $C_5H_9F_5N_3P_3Si$: C, 18.35; H, 2.75%; *M* 327]. N.m.r.: ^1H, δ − 0.5 [s, $\equiv PF(C{\equiv}CSiMe_3)$]; ^{31}P, δ 3.6 [complex m, J_{PF} = 916.0, $\equiv PF(C{\equiv}CSiMe_3)$] and 8.2 (complex m, J_{PF} = 950.0, $\equiv PF_2$); ^{19}F, δ −45.5 [complex d, J_{PF} = 900.0, $\equiv PF(C{\equiv}CSiMe_3)$], −68.4 (complex d, J_{PF} = 920.0, $\equiv PF_2$), and −69.7 (complex d, J_{PF} = 880, $\equiv PF_2$); ^{13}C, δ 92.6 [complex m, J_{PC} = 332.8, $^2J_{FC}$ = 56.0, $\equiv PF(\mathit{C}{\equiv}CSiMe_3)$], 112.7 [d of d, $^2J_{PC}$ = 51.5 Hz, $\equiv PF(C{\equiv}\mathit{C}SiMe_3)$], and −1.5 [s, $\equiv PF(C{\equiv}CSi\mathit{Me}_3)$]. I.r.: 2 960w (C−H str.), 2 145m (−C≡C− str.), 1 240s (P=N str.), 950s (Si−C), 850s (P−F), 810s (P−F), and 760 cm^{-1} (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(trimethylsilyl)acetylene.

$N_3P_3F_3(OC_2H_5)_2(C{\equiv}CH)$ (2). To a refluxing suspension of KF (0.2 g) in absolute ethanol (25 cm^3), compound (1) (5.0 g, 15.3 mmol) was added from a syringe. After 3 h, the solvent was removed and the residue obtained was extracted with light petroleum (150 cm^3). The mixture was filtered and light petroleum was removed from the filtrate. The dark brown liquid obtained was distilled under reduced pressure to give a colourless liquid (2.2 g, 46.8% of theory), b.p. 40 °C at 0.05 mmHg [Found: C, 23.20; H, 3.45%; *M* 307 (mass spectrum). Calc. for $C_6H_{11}F_3N_3O_2P_3$: C, 23.45; H, 3.60%; *M* 307]. N.m.r.: ^1H, δ 3.09 [d, $^3J_{PH}$ = 13.6, $-C{\equiv}CH$], 3.08 [d, $^3J_{PH}$ = 13.8, $-C{\equiv}CH$], 4.16 (m, $-OC\mathit{H}_2CH_3$), and 1.38 (m, $-OCH_2C\mathit{H}_3$); ^{31}P, very complex spectrum, approximate values δ 11.8 and 3.2 [$\equiv PF(C{\equiv}CH)$]; ^{19}F, δ −65.5 [$\equiv PF(C{\equiv}CH)$], −69.2 [$\equiv PF(C{\equiv}CH)$], and −42.5 (complex d, J_{PF} = 895.0 Hz, $\equiv PF_2$). I.r.: 3 280m (≡C−H), 2 990m (CH str.), 2 065s (−C≡C− str.), 1 260s (P=N str.), 1 165m, 1 045s (P−O str.), 975m (P−F), 915m (P−F), 845m (P−F), and 785m cm^{-1} (P−F).

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† *Non-S.I. units employed*: mmHg ≈ 134 Pa, eV ≈ 1.60 × 10^{-19} J.

$N_3P_3F_4(C\equiv CSiMe_3)_2$ (3). Lithio(trimethylsilyl)acetylene, $LiC\equiv CSiMe_3$, prepared by the reaction of n-butyl-lithium (64 cm^3, 100 mmol) and trimethylsilylacetylene (9.8 g, 100 mmol), was allowed to react with $N_3P_3F_6$ (12.5 g, 50 mmol) in diethyl ether (200 cm^3) as before. The reaction mixture was stirred for 2 d and worked up to give a viscous liquid (7.25 g, 35.8% of theory), b.p. 65 °C at 0.05 mmHg [Found: C, 30.10; H, 4.40%; *M* 4.05 (mass spectrum). Calc. for $C_{10}H_{18}F_4N_3P_3Si_2$: C, 29.65; H, 4.45%; *M* 405]. N.m.r.: ^1H, δ −0.45 (s, $-SiMe_3$); ^{31}P, δ −27.0 [complex t, $^2J_{PP} = 80.0$, $\equiv P(C\equiv CSiMe_3)_2$], 7.5 (complex m, $J_{PF} = 900.0$, $\equiv PF_2$), and 1.5 [complex m, $J_{PF} = 920.0$, $\equiv PF(C\equiv CSiMe_3)$]; ^{19}F, δ −42.6 (complex d, $J_{PF} = 9\,200$, $\equiv PF_2$), −44.5 (complex d, $J_{PF} = 890$, $\equiv PF_2$), and −68.6 [complex d, $J_{PF} = 915.0$, $\equiv PF(C\equiv CSiMe_3)$]; ^{13}C, δ 112.2 [complex m, $\equiv P(C\equiv CSiMe_3)_2$], 96.3 [t of d, $J_{PC} = 256.0$, $\equiv P(C\equiv CSiMe_3)_2$], 93.8 [complex m, $J_{PC} = 300$ Hz, $\equiv PF(C\equiv CSiMe_3)$], −1.1 [s, $P(C\equiv CSiMe_3)_2$], and −1.4 [s, $\equiv PF(C\equiv CSiMe_3)$]. I.r.: 2 965m, (m, CH str.), 2 140m $(-C\equiv C-)$, 1 265s (P=N), 930m (Si–C), 850m (P–F), 815m (P–F), and 795m cm^{-1} (P–F). Attempts at separation of the mixture by distillation or crystallization proved unsuccessful. The materials apparently bind to silica gel and hence cannot be eluted from a chromatography column.

$N_3P_3F_2(OC_2H_5)_2(C\equiv CH)_2$ (4). The reaction of $N_3P_3F_4(C\equiv CSiMe_3)_2$ (3) (3.2 g, 8.0 mmol) with KF (3.2 g) in absolute ethanol (40 cm^3) was carried out as before to yield a dark brown liquid. Distillation of this liquid under reduced pressure gave a viscous oil (0.9 g, 36.7% of theory), b.p. 105 °C at 0.05 mmHg [Found: C, 29.95; H, 3.80%; *M* 313 (mass spectrum). Calc. for $C_8H_{12}F_2N_3O_2P_3$: C, 30.65; H, 3.85%; *M* 313]. N.m.r.: ^1H, δ 3.0 (complex m, $-C\equiv CH$), 4.1 (complex m, $-OCH_2CH_3$), and 1.4 (complex m, OCH_2CH_3); ^{31}P, δ −25.0 [complex m, $\equiv P(C\equiv CH)_2$], 7.5 (complex m, $\equiv PF_2$), and 2.5 ($\equiv PFR$). I.r.: 3 280m $(-C\equiv CH$ str.), 2 460m (CH str.), 2 165s $(-C\equiv C)$, 1 255s (P=N), 1 170m, 1 055s (P–O str.), 965m (P–F), 915s (P–F), 845m (P–F), and 790m cm^{-1} (P–F).

$N_3P_3F_5(C\equiv CC_6H_5)$ (5). n-Butyl-lithium (32 cm^3, 50 mmol) was allowed to react with phenylacetylene (5.4 g, 50 mmol) in diethyl ether (150 cm^3). After 24 h the reaction mixture was added to a solution of $N_3P_3F_6$ (13.4 g, 50 mmol) in diethyl ether (150 cm^3). The resultant mixture was stirred for 24 h and worked up as before. Distillation of the product under reduced pressure gave compound (5) (7.7 g, 46.5% of theory), b.p. 45 °C at 0.1 mmHg (lit.,[9] b.p. 82 °C at 2.5 mmHg). N.m.r.: ^1H, δ 7.3 (m, C_6H_5); ^{31}P, δ 6.0 [d, $J_{PF} = 910.8$, $\equiv PF(C\equiv CC_6H_5)$] and 8.2 [t, $J_{PF} = 941.2$, $\equiv PF_2$]; ^{19}F, δ −69.5 (complex d, $J_{PF} = 870.3$, $\equiv PF_2$), −68.5 (complex d, $J_{PF} = 903.2$, $\equiv PF_2$), and −44.0 [complex d, $J_{PF} = 893.8$, $\equiv PF(C\equiv CC_6H_5)$]; ^{13}C, δ 102.7 [complex d, $J_{PC} = 69.2$, $\equiv PF(C\equiv CC_6H_5)$], 118.0 [d, $^2J_{PC} = 6.1$ Hz, $\equiv PF(C\equiv CC_6H_5)$], 128.0, 131.9, and 133.0 (C_6H_5). I.r.: 2 180s $(-C\equiv C)$, 1 250s (P=N str.), 1 060w, 1 010m, 980m (P–F), 930s (P–F), 880s (P–F), and 830s cm^{-1} (P–F).

$N_3P_3F_4(C\equiv CC_6H_5)_2$ (6). Lithio(phenyl)acetylene, $LiC\equiv CC_6H_5$, prepared by the reaction of phenylacetylene (2.25 g, 22.0 mmol) and n-butyl-lithium (15 cm^3, 23 mmol), was allowed to react with $N_3P_3F_6$ (2.7 g, 11.0 mmol) in Et_2O (200 cm^3). After 24 h the reaction mixture was worked up as before to yield a dark brown oil which was dissolved in light petroleum–methylene chloride (3 : 1) and cooled. The slightly yellowish crystals obtained were recrystallized from the same solvent, 1.2 g (27.3% of theory). N.m.r.: ^1H, δ 5.6 (m, $-C_6H_5$); ^{31}P, δ −23.2 [$^2J_{PP} = 91.1$, $^3J_{PF} = 12.1$, $\equiv P(C\equiv CC_6H_5)_2$] and 6.9 (t, $J_{PF} = 910.8$, $\equiv PF_2$); ^{19}F, δ −68.6 (d, $J_{PF} = 889.7$, $\equiv PF_2$); ^{13}C, δ 101.8 [d, $J_{PC} = 56.6$, $\equiv P(C\equiv CC_6H_5)_2$], 119.1 [d, $^2J_{PC} = 56.7$ Hz, $\equiv P(C\equiv CC_6H_5)_2$], 128.7, 131.3, and 133.6 (C_6H_5). I.r.: 2 140s $(-C\equiv C)$, 1 220s (P=N), 1 060w, 1 010w (P–F), 920s (P–F), 870s (P–F), and 800s cm^{-1} (P–F).

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 $N_3P_3F_4(C\equiv CC_6H_5)_2$, while the ^{19}F and ^{31}P n.m.r. spectra showed a small amount of $\equiv PF(C\equiv CC_6H_5)$ centres 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, $N_3P_3F_5(C\equiv CSiMe_3)$ (1), in moderate yield. Elemental analyses, mass spectrometric, and spectroscopic (n.m.r., i.r.) properties of compound (1) are in accord with the assigned structure. Of particular value are the ^{31}P and ^{19}F n.m.r. spectra which show the presence of the $\equiv PF_2$ and $\equiv PFR$ ($R = C\equiv CSiMe_3$) centres. The addition of 2 mol 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). Attempts at separation of the components of the mixture proved unsuccessful. Some indication of the isomeric composition was obtained from an examination of the ^{31}P and ^{19}F n.m.r. spectra. The ^{31}P spectrum clearly shows the presence of a $\equiv P(C\equiv CSiMe_3)_2$ centre but the remaining portion of the spectrum is far too complex to 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 n.m.r. spectrum and comparison of their relative areas demonstrates the existence of significant amounts of both geminal and non-geminal isomers in the mixture.

Since it has been reported that the reaction of $LiC\equiv CC_6H_5$ with $N_3P_3F_6$ follows a geminal pathway,[9] we chose to re-investigate the lithio(phenyl)acetylene reaction. In large part, this reaction proceeds as previously reported leading to $N_3P_3F_5(C\equiv CC_6H_5)$ (5) and the geminal bis derivative, 2,2-$N_3P_3F_4(C\equiv CC_6H_5)_2$.[9] We also observed a small amount of the previously unreported non-geminal $N_3P_3F_4(C\equiv CC_6H_5)_2$ isomers. In a comparison of the isomer distribution at the stage of bis substitution in the reactions of $N_3P_3F_6$ with $LiC\equiv CR$ ($R = SiMe_3$ or C_6H_5) one observes a significant contribution from the non-geminal pathway for the trimethylsilyl derivative, while a predominantly geminal pathway is observed in the formation of the phenyl derivative. The sensitivity of this reaction to the nature of the β substituent on the acetylenic centre 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 hindrance in the organometallic reagent.[2] It is not immediately obvious that this should be the case in alkynylphosphazenes. Although examination of the n.m.r. data for compounds (1) and (5) shows a striking variation in $^1J_{PC}$, the variation in ^{31}P shifts is less than noted for various alkylphosphazenes [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 $N_3P_3F_3(OC_2H_5)_2(C\equiv CH)$ (2). The ^1H n.m.r. spectrum shows the presence of the terminal acetylene and ethoxy-functions and the absence of the trimethylsilyl group. The ^{31}P n.m.r. spectrum is complex but doesn't show any significant concentration of $\equiv PF_2$ or $\equiv PRR'$ centres. The ^{19}F spectrum confirms the predominance of $\equiv PFR$ ($R = C\equiv$

CH or OC_2H_5) environments and shows a trace amount of a $\equiv PF_2$ centre. Thus, the material is essentially a mixture of the three possible non-geminal isomers, 2,4,6-$N_3P_3F_3(OC_2H_5)_2(C\equiv CH)$, 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-function comes directly from the solvent or from the ethanol–KF mixture. The fact that the reaction stops at the trisubstituted stage can be ascribed to the higher energy barrier associated with geminal substitution by alkoxides.[17]

The reaction of the mixture of bis(trimethylsilyl)acetylene 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 n.m.r. spectra are very complex and apart from suggesting the presence of several environments do not provide much useful information. There are nine possible isomers and most or all are presumed to be present.

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