residue. The ammonium solution was extracted with ether, the ethereal extract was dried with Na_2SO_4, the ether was distilled off, and the residue was distilled *in vacuo* to afford 4.4 g of **7d**. 4-Isobutyryl-2-methyl-2-methoxy-8-piperidinooct-6-yne-3-one (**7b**), 4-isobutyryl-2-methyl-2-methoxy-8-morpholinooct-6-yne-3-one (**7c**), 2-methyl-2-methoxy-8-morpholino-4-pivaloyloct-6-yne-3-one (**7e**), 4-benzoyl-2-methyl-2-methoxy-8-diethylaminooct-6-yne-3-one (**7f**), and 4-benzoyl-2-methyl-2-methoxy-8-morpholinooct-6-yne-3-one (**7g**) were synthesized by similar procedures.

4-Isobutyryl-2-methyl-2-methoxy-8-diethylaminooct-6-yne-3-one (7a). A mixture of alkyne **1** (4.48 g, 0.02 mol), paraform (0.5 g, 0.02 mol), CuCl (0.02 g, 0.02 mol), and diethylamine (1.46 g, 0.02 mol) in dioxane (50 mL) was stirred for 3 h at 50 °C. The product was isolated as described above for compound **7d** to afford 4.4 g of **7a**.

The yields, constants, elemental analysis data, and ^1H NMR spectra of β-diketones **7a—g** are given in Table 1.

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A synthesis of chlorofluoro(*N*-trimethylsilyl)imidophosphates

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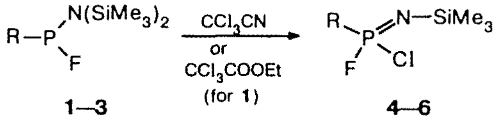
Reaction of bis(trimethylsilyl)amidofluorophosphites with the derivatives of trichloroacetic acid affords chlorofluoro(*N*-trimethylsilyl)imidophosphates.

Key words: chlorofluoro(*N*-trimethylsilyl)imidophosphates; bis(trimethylsilyl)amidofluorophosphites, ethyl trichloroacetate, trichloroacetonitrile, reactions.

Halo(*N*-trimethylsilyl)imidophosphates (*N*-trimethylsilyl-*P*-halophosphazenes) are of interest as the intermediates in the synthesis of various phosphazenes and polyphosphazenes.[1,2]

We have shown previously that the "halophilic"[3] reaction of bis(trimethylsilyl)amidophosphites with the derivatives of trichloroacetic acid is useful for the synthesis of compounds of such type. In the present work, it is found that in the case of bis(trimethylsilyl)amidofluorophosphites, this reaction affords the poorly studied[4] chlorofluoro(*N*-trimethylsilyl)imidophosphates. Thus, the reaction of bis(trimethylsilyl)amidofluorophosphites **1—3** with CCl_3CN gives phosphazenes **4—6**, respectively, whereas in the reactions with CCl_3COOEt, the desired product **4** is formed only from phosphite **1**.

Compounds **4—6** are colorless, nonviscous liquids fuming on air. Even when thoroughly protected from the moisture of air, they turn brown after several hours. The composition and structure of compounds **4—6** were established by the elemental analysis data and ^1H, ^{19}F, and ^{31}P NMR and IR spectroscopy (Table 1) and mass spectrometry.



1, 4: R = Et_2N
2, 5: R = Pr^iO
3, 6: R = Bu^iO

One can assume that the considered reaction proceeds *via* the stage of the positive halogen atom abstraction; this pathway was proposed previously by us for the silylated derivatives of phosphorous acid.[3]

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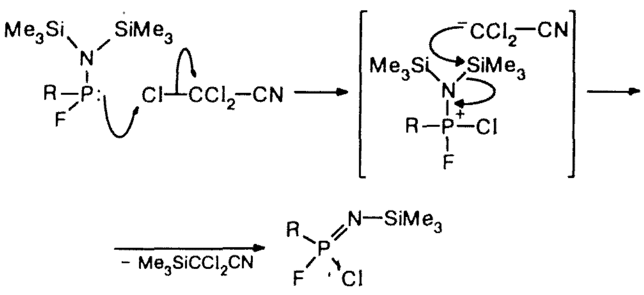

Table 1. ^{1}H, ^{19}F, and ^{31}P NMR and IR spectral parameters for chlorofluoro(*N*-trimethylsilyl)imidophosphates **4—6**

Compound	δ ^{1}H (*J*/Hz)	δ ^{19}F	δ ^{31}P	$^1J_{P,F}$ /Hz	ν(P=N) /cm^{-1}
4	0.09 (d, 9 H, $^4J_{H,P}$ = 0.9); 1.13 (t, 6 H, $^3J_{H,H}$ = 7); 3.14 m (4 H)	44.57 (d)	−10.00 (d)	1023	1400
5	0.3 (d, 9 H, $^4J_{H,P}$ = 1); 1.6 (dm, 6 H, $^3J_{H,H}$ = 6); 5.0 (m, 1 H)	44.57 (d)	−22.06 (d)	1042	1411
6	0.3 (d, 9 H, $^4J_{H,P}$ = 1); 1.16 (d, 6 H, $^3J_{H,H}$ = 6); 2.22 (m, 1 H); 4.11 (m, 2 H)	41.63 (d)	−20.74 (d)	1041	1413

Experimental

The ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded with a Bruker CXP-200 spectrometer using $SiMe_4$, CF_3COOH, and 85 % H_3PO_4 as the standards, respectively. The IR spectra were recorded with a Specord IR-75 instrument in a liquid film between KBr plates. The mass spectra (EI, 70 eV) were registered with a Finnigan MS 4021 mass spectrometer.

Diethylamidochlorofluoro(*N*-trimethylsilyl)imidophosphate (4). ***A.*** A solution of CCl_3CN (2.66 g, 18 mmol) was added dropwise to a stirred solution of diamidophosphite **1** (4.97 g, 18 mmol) in anhydrous Et_2O (15 mL) upon cooling (−10 °C). The mixture was stirred at −10 °C for 0.5 h and then at 20 °C for 1 h. The reaction mixture was evaporated to a minimum volume, the residue was distilled, and compound **4** was obtained in 79 % yield, b.p. 71—73 °C (10 Torr). Found (%): C, 35.01; H, 7.80. $C_7H_{19}ClFN_2PSi$. Calculated (%): C, 34.35; H, 7.82. MS, *m/z* (I_{rel} (%)): 247 [M+2]$^+$ (100), 229 (50).

B. Analogously, imidophosphate **4** was obtained in 85 % yield from the equimolar amounts of diethylamidophosphite **1** and CCl_3COOEt.

Isopropylchlorofluoro(*N*-trimethylsilyl)imidophosphate (5) was synthesized analogously from amidophosphite **2** (20 mmol) and CCl_3CN in 69 % yield, b.p. 47—50 °C (10 Torr). Found (%): H, 7.19. $C_6H_{16}ClFNOPSi$. Calculated (%): H, 6.96. MS, *m/z* (I_{rel} (%)): 232 [M]$^+$ (100), 218 (20), 216 (60), 174 (90).

Isobutylchlorofluoro(*N*-trimethylsilyl)imidophosphate (6) was synthesized analogously from amidophosphite **3** (20 mmol) and CCl_3CN in 20 % yield, b.p. 85—90 °C (27 Torr). Found (%): H, 7.32. $C_7H_{18}ClFNOPSi$. Calculated (%): H, 7.38. MS, *m/z* (I_{rel} (%)): 246 [M]$^+$ (100), 230 (30), 204 (1), 174 (40).

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