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Reactions of Some Nitrosoperfluoroalkanes with Trimethylsilyl Phosphites

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ABSTRACT

Nitrosotrifluoromethane or nitrosopentafluoroethane reacted with trimethylsilyl diethyl or tris(trimethylsilyl) phosphite to give phosphato-fluorocarbimino- or phosphato-trifluoroacetimino-phosphonates and fluorotrimethylsilane. Some intermediate compounds could be detected by NMR spectroscopy, namely, diethyl (N-trimethylsiloxy-N-trifluoromethyl)- or diethyl (N-trimethylsiloxy-N-pentafluoroethyl)amidophosphate and difluorocarbimino diethyl phosphate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Silylated phosphites [1] $(RO)_2POSiMe_3$ and 2-methyl-2-nitrosopropane [2] have been reported to give (*N*-trimethylsiloxy-*N*-*tert*-butyl)amidophosphates [3,4], $(RO)_2P(O)N(OSiMe_3)t\text{Bu}$. A similar adfjdition was found with activated ketones; e.g., hexafluoroacetone, where phosphonates [5,6] $(RO)_2P(O)C(CF_3)_2OSiMe_3$ were obtained. When heated, the latter compounds split off fluorotrimethylsilane and rearranged to yield the phosphates [5], $(RO)_2P(O)OC(CF_3){=}CF_2$, which could be reacted again with silylated phosphites at the CF_2 site to form (E/Z)-phosphato-phosphonates [7]. In the case of nitrosochlorofluoroalkanes, R^FNO ($R^F = CF_2Cl$, $CFClCF_2Cl$) and dialkyl phosphonates, $(RO)_2P(O)H$, the phosphorylated oximes $(RO)_2P(O)ON{=}CF_2$ and $(RO)_2P(O)ON{=}C(F)CF_3$ (R = Et) were obtained at 0° [8,9], and no further attack of trialkyl or dialkyl phosphites was observed. We have studied the reactions of nitrosoperfluoroalkanes R^FNO ($R^F = CF_3$ [10], C_2F_5 [10]) with the silylated phosphites $(RO)_2POSiMe_3$ (R = Et, $SiMe_3$), these being more nucleophilic [1] than the respective alkyl phosphites $(RO)_3P$ or $(RO)_2P(O)H$.

RESULTS AND DISCUSSION

The nitrosoperfluoroalkanes R^FCF_2NO (**1**: R^F = F; **2**: $R^F = CF_3$) and the silylated phosphites $(RO)_2POSiMe_3$ (**3a**: R = Et; **3b**: R = $SiMe_3$) in a 1:2 molar ratio below −70°C furnished the phosphato-phosphonates $(RO)_2P(O)ON{=}CR^FP(O)(OR)_2$ (**7a**: R^F = F, R = Et; **7b**: R^F = F, R = $SiMe_3$; **8a**: $R^F = CF_3$, R = Et; **8b**: $R^F = CF_3$, R = $SiMe_3$), colorless, moisture-sensitive liquids (Scheme 1). The reaction proceeded probably via intermediate **A** (Scheme 1) followed by a 1,4 trimethylsilyl group shift giving (*N*-trimethylsiloxy-*N*-trifluoromethyl)amidophosphates, which could be detected by ^{19}F and ^{31}P NMR spectroscopy in the case of **4a** and **5a** (besides **7a** and **8a**) only, provided a 1:1 molar ratio of the starting compounds was chosen. Above 30°C, both compounds were thermally unstable and decomposed under loss of fluorotrimethylsilane. Phosphate **4a** gave rise to the formation of the difluorocarbiminophosphate [8] **6a** following a PERKOW reaction pathway. Due to the high nucleophilicity of phosphite **3b**, the reaction was too fast to observe

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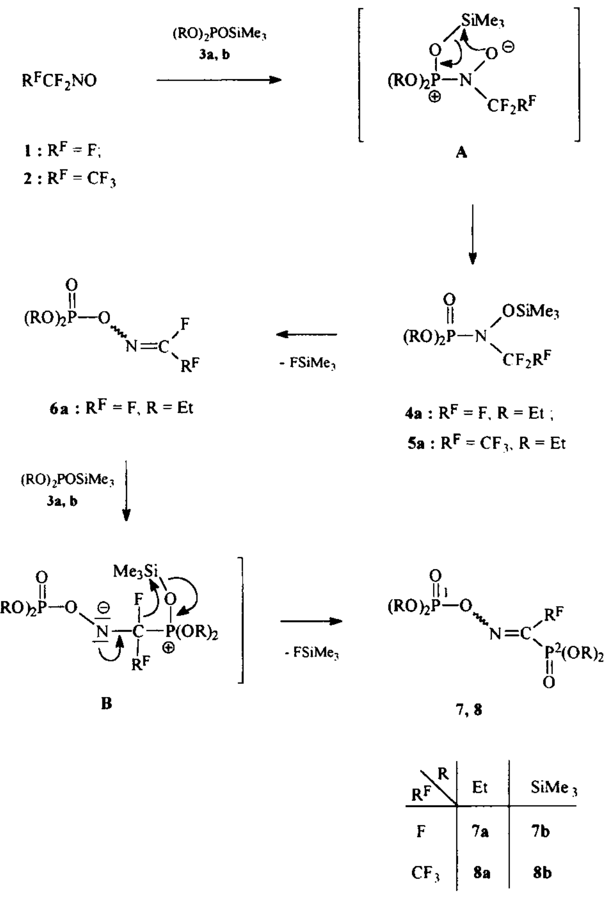

SCHEME 1

any intermediate compounds. Finally, a second phosphite attacked the α-carbon (intermediate **B**) to afford the phosphato-phosphonates **7**, **8**, and fluorotrimethylsilane.

The ^{31}P NMR shift values (Table 1) of the phosphates **4a**, **5a**, and **6a** and of the phosphato-phosphonates **7** and **8** were in the expected range [11]. Signals at higher field for compounds **7** and **8** were attributed to the phosphonato phosphorus P^2 where the characteristic coupling constants $^2J_{PF}$ (**7a**: 113.8; **7b**: 130.2 Hz) and $^3J_{PF}$ (**8a**: 2.8; **8b**: 5.3 Hz) were found. The $^1J_{PC}$ and $^3J_{PC}$ values observed in the ^{13}C NMR spectra (Table 1) gave additional structural evidence [7,12].

EXPERIMENTAL

The appropriate precautions in handling moisture-sensitive compounds were observed throughout this work. Elemental analyses were undertaken by Mikroanalytisches Laboratorium Beller, Göttingen, Germany. Mass spectra (EI, 70 eV) were carried out on a Varian MAT CH-7A instrument. The NMR spectra were obtained on a Bruker AC 80 instrument operating at 80.13 MHz (^1H, internal standard TMS), at 75.39 MHz (^{19}F, internal standard CCl_3F), at 32.44 MHz (^{31}P, external standard 85% H_3PO_4), and at 20.15 MHz (^{13}C, external standard TMS).

General Procedure. The following outlines the procedure for the preparation of compounds **7** and **8** (see Table 2). The blue nitrosoalkanes **1** and **2** were condensed into an evacuated 100 mL thick-wall glass flask filled with the silylated phosphites **3a** and **3b** at

TABLE 1 ^1H, ^{19}F, and ^{31}P NMR Data of Compounds **7** (R^F = F) and **8** (R^F = CF_3) (*J* in Hz)

	δ_H[a]			δ_F[a]		δ_P[a]			δ_C[a]	
Compound	*SiCH₃*	*CH₃* ($^3J_{HH}$)	*CH₂* ($^3J_{PH}$)	*CF* ($^2J_{PF}$, $^4J_{PF}$)	*CF₃* ($^3J_{PF}$)	*P¹*	($^5J_{PP}$)	*P²*	*SiCH₃*	*CR^F* ($^1J_{PC}$, $^3J_{PC}$)
7a[b]		1.2	3.6	−90.0		−2.7		−8.7		137.4[c]
		(7.1)	(9.3)	(113.8, 7.0)			(2.7)			(228.6, 8.5)
7b	0.12			−90.4		−19.9		−29.0	0.13	136.0[d]
				(130.2, 8.1)			(2.7)			(225.0, 8.4)
8a[e]		1.1	2.9		−74.3	−2.8		−6.0		136.8[f]
		(7.0)	(8.6)		(2.8)		(3.8)			(223.1, 8.4)
8b[g]	0.02				−73.0	−14.4		−16.4	0.02	137.3[h]
	0.18				(5.3)		(3.7)		0.03	(223.3, 8.3)

[a] High-field shifts from TMS, CCl_3F, and 85% H_3PO_4 were given negative signs.
[b] δ_C = 31.3 (CH_3, $^3J_{PC}$ = 7.3), 56.3 ($^2J_{PC}$ = 9.3).
[c] $^1J_{FC}$ = 277.2.
[d] $^1J_{FC}$ = 278.3.
[e] δ_C = 32.3 (CH_3, $^3J_{PC}$ = 7.1), 54.3 ($^3J_{PC}$ = 9.5), 125.4 (CF_3, $^1J_{FC}$ = 286.3).
[f] $^2J_{FC}$ = 32.0, $^2J_{PC}$ = 9.5, $4J_{PC}$ = 2.9.
[g] δ_C = 126.3 (CF_3, $^1J_{FC}$ = 285.7).
[h] $^2J_{FC}$ = 31.9, $^2J_{PC}$ = 9.3, $^4J_{PC}$ = 2.7.

TABLE 2 Experimental Details for the Preparation of Compounds **7** and **8**

Compound	*Reactants [g (mmol)]*	*Yield [g(%)]*	*Bp [°C(mm)]*
7a	**1**: 0.99(10)		
	3a: 4.20(20)	2.89(86)	56(0.001)
7b	**1**: 0.99(10)		
	3b: 5.86(20)	2.30(45)	68(0.001)
8a	**2**: 1.31(10)		
	3a: 4.20(20)	2.92(76)	90(0.001)
8b	**2**: 1.31(10)		
	3b: 5.86(20)	4.73(84)	102(0.001)

−196°C and slowly warmed to −70°C. An immediate color change took place. All volatiles were pumped off in vacuo and the remaining yellowish liquids distilled. Using a 1:1 ratio of nitrosoalkanes and **3a** under the same conditions, besides **7a** and **8a**, the intermediate compounds **4a**, **5a**, and **6a** could be detected by ^{19}F and ^{31}P NMR spectroscopy at 0°C (**4a**: 40%, **6a**: 20%; **5a**: 60%).

Diethyl (N-Trimethylsiloxy-N-trifluoromethyl) amidophosphate (**4a**). NMR: ^{19}F: $\delta = -73.8$ (CF_3, 3F, d, $^3J_{PF} = 2.8$ Hz); ^{31}P: $\delta = 7.6$.

Diethyl (N-Trimethylsiloxy-N-pentafluoroethyl) amidophosphate (**5a**). NMR: ^{19}F: $\delta = -74.4$ (CF_3, d, $^3J_{PF} = 2.8$ Hz), -89.2 (CF_2, d, $^3J_{PF} = 2.1$ Hz); ^{31}P: $\delta = 9.2$.

Difluorocarbimino Diethyl Phosphate [9] (**6a**). NMR: ^{19}F: $\delta = -94.3$ (CF, dd, $^2J_{FF} = 90.3$, $^4J_{PF} = 6.8$ Hz); -96.5 (CF, dd); ^{31}P: $\delta = -12.5$.

Diethyl (N-Diethylphosphato-fluorocarbimino) phosphonate (**7a**). MS (65°C), *m/z*(%): 335 (M^+, 10), 320 ($M^+ - CH_3$, 30), 307 ($M^+ - C_2H_4$, 10), 279 ($M^+ - 2C_2H_4$, 8), 251 ($M^+ - 3C_2H_4$, 15), 223 ($M^+ - 4C_2H_4$, 15), 154 [$(C_2H_5O)_2P(O)OH^+$, 15], 138 [$(C_2H_5O)_2P(O)H^+$, 100), 109 [$(C_2H_5O)P(O)OH^+$, 20], 101 (PC_3FNH^+, 25), and other fragments. Anal calcd for $C_9H_{20}FNO_7P_2$ (335.21): C, 33.65; H, 6.28; F, 5.91; P, 19.29. Found: C, 32.63; H, 5.96; F, 5.40; P, 18.92.

bis-(Trimethylsilyl) [N-bis(Trimethylsilyl)phosphato-fluorocarbimino]phosphonate (**7b**). MS (110°C), *m/z* (%): 496 ($M^+ - CH_3$, 25), 365 ($M^+ - (CH_3)_3SiOSi(CH_3)CH_2$, 30), 297 ($[[(CH_3)_3SiO]_2P(O)ONC(H)F^+$, 25), 242 ($[[(CH_3)_3SiO]_2P(O)OH^+$, 15), 226 ($[[(CH_3)_3SiO]_2P(O)\ H^+$, 15), 147 [$(CH_3)_3SiOSi(CH_3)_2^+$, 100], and other fragments. Anal calcd for $C_{13}H_{36}FNO_7P_2Si_4$ (511.72): C, 30.51; H, 7.09; F, 3.71; P, 12.11. Found: C, 30.46; H; 6.98; F, 3.50; P, 12.16.

Diethyl (N-Diethylphosphato-trifluoroacetimino)phosphonate (**8a**). MS (65°C), *m/z* (%): 385 (M^+, 10), 357 ($M^+ - C_2H_4$, 10), 329 ($M^+ - 2C_2H_4$, 15), 301 ($M^+ - 3C_2H_4$, 10), 273 (($M^+ - 4C_2H_4$, 10), 155 [$(C_2h_5O)_2P(OH)_2^+$, 30], 138 [$(C_2H_5O)_2P(O)H^+$, 10], 69 (CF_3^+, 100), and other fragments. Anal calcd for $C_{10}H_{20}F_3NO_7P_2$ (335.21): C, 31.18; H, 5.23; F, 14.80; P, 16.08. Found: C, 31.30; H, 5.27; F, 15.10; P, 15.12.

bis(Trimethylsilyl) (N-bis(Trimethylsilyl)phosphato-trifluoroacetimino)phosphonate (**8b**). MS (110°C), *m/z* (%): 546 ($M^+ - CH_3$, 20), 415 [$M^+ - (CH_3)_3SiOSi(CH_3)CH_2$, 30], 347 ($[[(CH_3)_3SiO]_2P(O)ONC(H)F^+$, 20), 242 ($[[(CH_3)_3SiO]_2P(O)OH^+$, 25), 147 [$(CH_3)_3SiOSi(CH_3)_2^+$, 100], and other fragments. Anal calcd for $C_{14}H_{36}F_3NO_7P_2Si_4$ (511.72): C, 29.94; H, 6.46; F, 10.15; P, 11.03. Found: C, 30.06; H; 6.46; F, 10.50; P, 11.12.

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