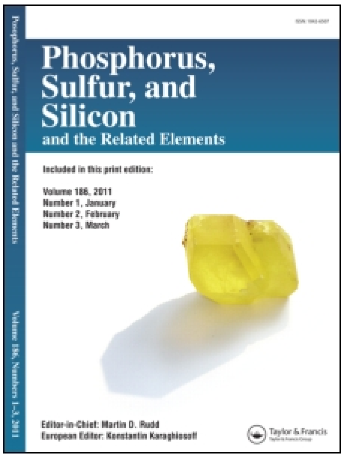

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3-BROMO-1,1,1-TRIFLUORO-PROPANE-2-OXIME AND TRIETHYLPHOSPHITE

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Triethylphosphite (**1**) and 3-bromo-1,1,1-trifluoro-propane-2-oxime (**2**) reacted in a PERKOW type reaction to yield [N-hydroxy-N-(1-trifluoromethyl-ethenyl)]amido diethylphosphate (**3**) which added water in a MARKOVNIKOV manner across the double bond to form [N-hydroxy-N-(1-trifluoromethyl-1-hydroxy-ethyl)]amido diethylphosphate (**4**). Abstraction of water using bis(cyclohexyl)carbodiimide gave the corresponding N-phosphorylated 3-methyl-3-trifluoromethyl-oxaziridine **5**, whose constitutional isomer, the iminophosphate **6** was prepared from chlorodiethyl phosphate (**7**) and 1,1,1-trifluoro-propane-2-oxime (**8**). Compound **6** was not available from a possible rearrangement of compound **3** under basic condition.

Keywords: 3-Bromo-1,1,1-trifluoro-propane-2-oxime; [N-hydroxy-N-(1-trifluoromethyl-ethenyl)]amido diethylphosphate; [N-hydroxy-N-(1-trifluoromethyl-1-hydroxyethyl)]amido diethylphosphate; 2-diethylphosphato-3-methyl-3-trifluoromethyl-oxaziridine; 1,1,1-trifluoro-propane-2-imino-diethyl phosphate

INTRODUCTION

3-Bromo-1,1,1-trifluoro-propane-2-oxime (**1**) is a versatile precursor for the synthesis of 1,2-oxazines via a nitroso alkene.[1] Trialkylphophites could react with α-bromo ketones to give either ARBUZOV (phosphonate formation) or PERKOW pathway products (enol phosphate formation) and alkyl bromide.[2] In the case of 3-bromo-1,1,1-trifluoropropanone[3,4] and triethylphosphite the respective enol phosphate was obtained.[4] Continuing our investigation of diacetyldioxime with phosphites[5] and hexaalkylphosphorus(III) amides[6] we describe here the interaction of triethylphosphite (**2**) with oxime **1**.

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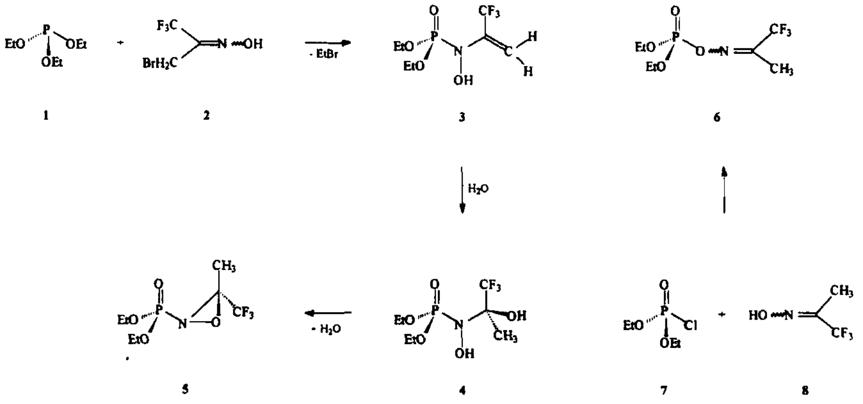
RESULTS AND DISCUSSION

The straightforward reaction of 3-bromo-1,1,1-trifluoro-propane-2-oxime (**1**) and triethylphosphite (**2**) produced [N-hydroxy-N-(1-trifluoromethyl-ethenyl)]amido diethylphosphate (**3**), which added water across the C=C bond to form [N-hydroxy-N-(1-trifluoromethyl-1-hydroxy-ethyl)]amido-diethylphosphate (**4**). Successfully water could be abstracted using bis(cyclohexyl)carbodiimide furnishing 2-diethylphosphato-3-methyl-3-trifluoromethyl-oxaziridine (**5**). Since amidophosphates **3** and **5** are constitutional isomers, a third one, namely 1,1,1-trifluoro-propane-2-imino-diethylphosphate (**6**), was accessible from chlorodiethylphosphate (**7**) and 1,1,1-trifluoropropane-2-oxime[7] (**8**) (see Scheme 1). Besides compound **3** all new moisture-sensitive substances were liquids.

The ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR data (see Table I and II) support the constitution of the new compounds. The δ_P values are in the expected range.[8] Additional confirmation is given by the ^{13}C NMR parameters.[9,10] The chiral center in compound **4** has no significant effect on the ethoxy groups at phosphorus.

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. NMR spectra were ob-



SCHEME 1

TABLE I ^1H, ^{19}F and ^{31}P NMR data of compounds **3–6** (J values are given in Hz)

Compound	$\delta_H{}^a$				$\delta_F{}^a$	$\delta_P{}^a$
	CH_3CH_2 ($^3J_{HH}$)	*CH_2* ($^3J_{PH}$)	*NOH*	*CH_3*	*CF_3* ($^4J_{PF}$)	
3^b	1.2	4.2	6.5		−69.3	22.9
	(7.4)	(9.3)			(2.3)	
4^c	1.2	4.0	6.6	2.1	−72.6	20.5
	(6.2)	(7.4)			(2.8)	
5	1.2	3.9		1.8^d	−76.3	17.5
	(6.2)	(6.8)			(2.3)	
6	0.9	3.9		1.8^e	−70.4	4.8
	(6.8)	(7.3)				

^{a}Highfield shifts from TMS, CCl_3F and 85% H_3PO_4 were given negative signs.
$^b\delta_H$ = 2.9 (=CH_2, 1H, *cis* to CF_3, $^2J_{HH}$ = 4.2), 3.4 (=CH_2, 1H, *trans* to CF_3, $^4J_{FH}$ = 3.0).
$^c\delta_H$ = 6.3 (C-OH).
$^{d4}J_{FH}$ = 1.0.
$^{e4}J_{PH}$ = 1.3).

tained 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). Compounds **2** and **8** were prepared according to literature procedures.[1,7]

[N-Hydroxy-N-(1-Trifluoromethyl-Ethenyl)]Amido Diethylphosphate (**3**)

Oxime **2** (2.06 g, 10 mmol) in 20 ml of diethylether and 1.66 g (10 mmol) of **1** were allowed to react for 8 h at ambient temperature. After fractional distillation 2.54 g (97%) of **3** (b. p. 45°C/0.01 Torr) were obtained. MS (140°C), *m/z* (%):

TABLE II ^{13}C NMR data of compounds **3–6** (δ_c highfield of TMS was given negative sign, J values were measured in Hz)

Compound	*CH_3CH_2* ($^3J_{PC}$)	*CH_3CH_2* ($^2J_{PC}$)	*CH_3* ($^3J_{CF}$, $^3J_{PC}$)	*CN* ($^2J_{CF}$, $^2J_{PC}$)	*CF_3* ($^1J_{CF}$, $^3J_{PC}$)
3^a	31.4	58.4		146.1	120.5
	(6.8)	(9.6)		(32.0, 9.4)	(284.3, 6.8)
4	31.4	58.3	15.2	29.4	120.8
	(7.2)	(9.5)	(22.7, 6.4)	(32.3, 8.9)	(286.3, 7.5)
5	31.4	53.5	15.0	72.3	121.0
	(6.9)	(12.0)	(19.0, 6.5)	(32.2, 6.0)	(285.7, 6.3)
6	31.2	57.4	15.3	136.4	120.9
	(6.8)	(9.5)	(21.3, −)	(31.6, −)	(287.3, −)

$^a\delta_c$ = 116.7 (=CH_2, $^3J_{CF_3}$ = 23.0, $^3J_{PC}$ = 6.5).

263 (M^+, 3), 248 (M^+—CH_3, 6), 194 (M^+—CF_3, 53), 137 ($(C_2H_5O)_2PO^+$, 100), 126 (M^+—$(C_2H_5O)_2PO$, 28), 121 ($(C_2H_5O)_2P^+$, 65), 112 (CF_3CNOH^+, 20) 95 ($CF_3CCH_2{}^+$, 11) and other fragments.

$C_7H_{13}F_3NO_4P$ (263.15)
Calcd. C 31.95 H 4.98 F 21.66 P 11.77%
Found C 32.34 H 5.13 F 20.90 P 11.40%

[N-Hydroxy-N-(1-Trifluoromethyl-1-Hydroxy-ethyl)]Amido Diethylphosphate (**4**)

Amidophosphate **3** (2.63 g, 10 mmol) in 20 ml of diethylether and 0.18 g (10 mmol) of water were allowed to react for 1 d at ambient temperature. After removing the solvent 2.25 g (80%) of **4** (m. p. 33°C) were obtained. MS (140°C), *m/z* (%): 281 (M^+, 7), 212 (M^+—CF_3, 6), 109 ($C_2H_5OP(O)OH^+$, 100), 98 (CF_3COH^+, 15), 69 ($CF_3{}^+$, 2) and other fragments.

$C_7H_{15}F_3NO_5P$ (281.17)
Calcd. C 29.90 H 5.38 F 20.27 P 11.02%
Found C 30.79 H 5.80 F 21.20 P 11.40%

2-Diethylphosphato-3-Methyl-3-Trifluoromethyl-Oxaziridine (**5**)

N,N-Dicyclohexylcarbodiimide (1.65 g, 8 mmol) was added to 2.25 g (8 mmol) of **4** in 15 ml diethylether at 0°C. After 12 h at ambient temperature the white precipitate was filtered off. The remaining solution was fractionally distilled, which gave 1.95 g (93%) of **5** (b. p. 68°C/0.01 Torr). MS (140°C), *m/z* (%): 263 (M^+, 45), 234 (M^+—C_2H_5, 35), 205 (M^+—2 C_2H_5, 48), 109 ($C_2H_5OP(O)OH^+$, 100), 112 (CF_3CNOH^+, 20) and other fragments.

$C_7H_{13}F_3NO_4P$ (263.15)
Calcd. C 31.95 H 4.98 F 21.66 P 11.77%
Found C 31.57 H 4.84 F 21.80 P 11.63%

1,1,1-Trifluoro-Propane-2-Imino Diethylphosphate (**6**)

Chlorodiethylphosphate (**7**) (1.72 g, 10 mmol), 0.71 g (10 mmol) of triethylamine and 1.27 g (10 mmol) of **8** were allowed to react for 1 d at ambient temperature. After separating the solution from triethylammonium chloride and fractional distillation 2.48 g (94%) of **6** (b. p. 45°C/0.01 Torr) were obtained.

MS (140°C), *m/z* (%): 263 (M^+, 10), 248 (M^+—CH_3, 12), 194 (M^+—CF_3, 39), 137 ($(C_2H_5O)_2PO^+$, 100), 126 (M^+—$(C_2H_5O)_2PO$, 40), 121 ($(C_2H_5O)_2P^+$, 45) and other fragments.

$C_7H_{13}F_3NO_4P$ (263.15)
Calcd. C 31.95 H 4.98 F 21.66 P 11.77%
Found C 32.10 H 5.16 F 21.50 P 11.35%

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