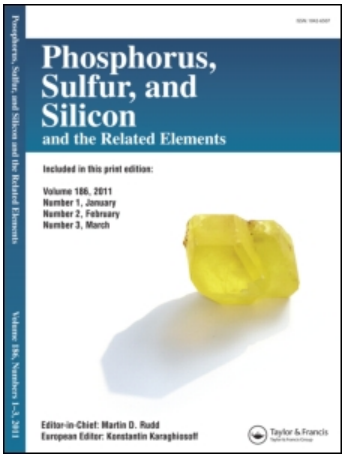

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[3,3,3-TRIFLUORO-2-HYDROXY-2-(TRIFLUOROMETHYL)PROPYL]-DIMETHYLPHOSPHINE OXIDE AND RELATED COMPOUNDS

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SHORT COMMUNICATION
[3,3,3-Trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]-dimethylphosphine Oxide and Related Compounds

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Hydrolysis of the oxaphosphetane **1** yielded the phosphine oxide **2**, $Me_2P(O)CH_2C(CF_3)_2OH$, which was transformed into the chlorooxaphosphetane **4** using a $SOCl_2$/pyridine mixture. Ring opening was observed also with hydrogen chloride. The resulting acyclic phosphorane **3** could be converted into the precursor **1** and by removing hexafluoroisopropanol into compound **4** which was fluorinated to give the fluorophosphorane **5**.

Trimethylphosphine reacts with hexafluoroacetone in diethyl ether (molar ratio 1 : 2) to give 2,2,2-trimethyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ^5-dioxaphospholane which rearranges at 80°C into 2-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-2,2-dimethyl-4,4-bis(trifluoromethyl)-1,2λ^5-oxaphosphetane, **1**.[1]

RESULTS

Hydrolysis of the oxaphosphetane **1** yielded the phosphine oxide **2** (m.p. 74°C) and hexafluoroisopropanol. The four-membered ring was also cleaved by hydrogen chloride to form the acyclic chlorophosphorane **3** (m.p. 124°C) which upon adding triethylamine furnished compound **1** again whereas mild heating and slowly pumping off hexafluoroisopropanol closed the ring with formation of the phosphetane **4** (m.p. 47°C). The four-membered ring system was opened also when a mixture of thionyl chloride and pyridine was allowed to react with compound **2**. The same reactants were found to give a dioxaphospholane ring with the phosphinate, $Me_2P(:O)OC(CF_3)_2C(CF_3)_2OH$[2]. The fluorophosphetane **5** was obtained upon fluorination of **4** using potassium heptafluoroisopropylate[3,4]. All three phosphoranes were colourless, moisture-sensitive compounds.

The 30 eV mass spectra show molecular ions in the case of **2** and **5**. Fragments of highest mass of compounds **3** and **4** are $M^+—CH_3$ (**3**) and $M^+—Cl$ (**4**). Further typical ions are $M^+—F$ (**2, 5**), $M^+—CF_3$ (**5**), $M^+—CF_3$ (**2, 4, 5**), and $M^+—HCl$ (**3**). The ^{31}P NMR shift values of **3**, **4**, and **5** (see Table I) are characteristic of penta-coordinate phosphorus revealing the covalent nature of the compounds. Two different pairs of CF_3 groups are observed in the ^{19}F spectra of **3** (δ_F = −77.3 ($OCH(CF_3)_2$), −79.5 ($CH_2C(CF_3)_2OH$)). The resonances of the

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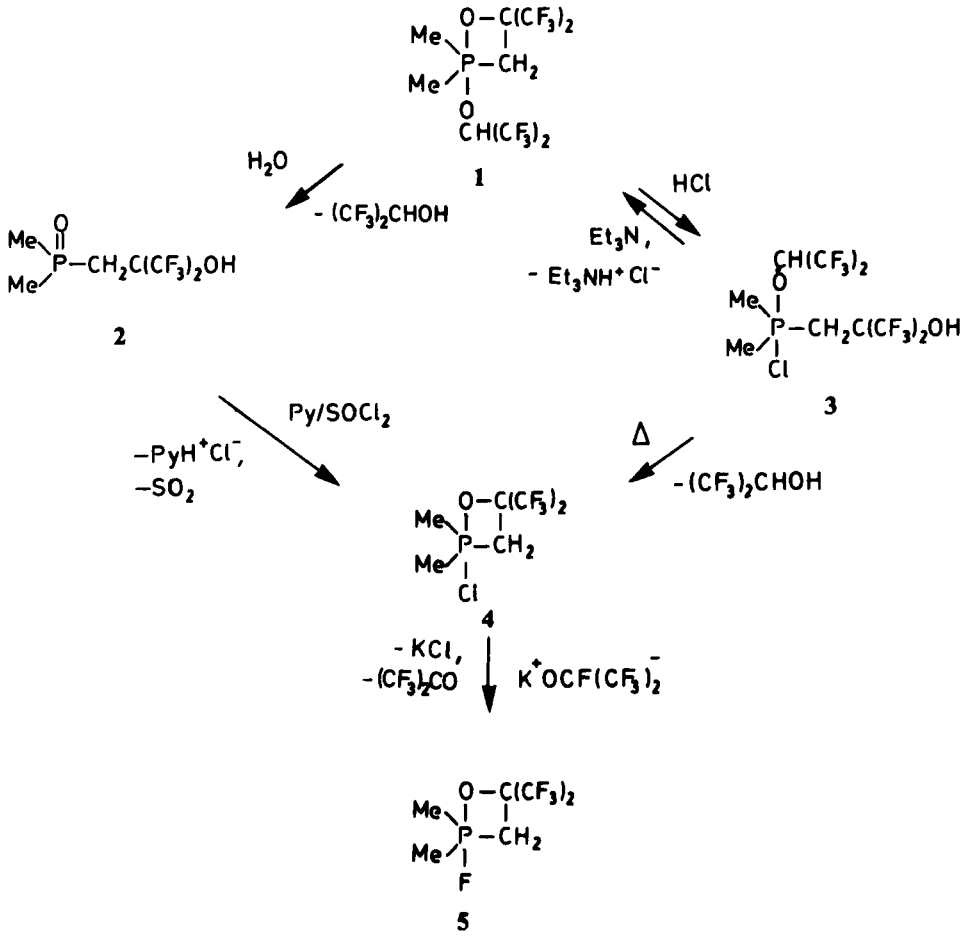

SCHEME 1

TABLE I

^{1}H, ^{19}F and ^{31}P NMR data of the compounds **2**, **3**, **4** and **5** (δ in ppm, J in Hz)

Compound	δ_H CH_3 ($^2J_{PH}$)	δ_H CH_2 ($^2J_{PH}$)	OH	δ_F $CH_2C(CF_3)_2$	δ_P
2	1.60 (13.5)	2.42 (12.0)	6.78	−79.3	+52.0
3[a]	1.90 (16.5)	4.05 (20.0)	5.95	−79.4	−25.0
4	2.35 (16.0)	4.20 (23.0)		−79.1	−20.8
5	1.75[b] (16.0)	3.75[c] (21.5)		−79.7[d]	−13.6

[a] $\delta_H[OCH(CF_3)_2] = 4.70$, $^3J_{HF} = 6.0$; $\delta_F[OCH(CF_3)_2] = -77.3$.
[b] $^3J_{FH} = 11.0$. [c] $^3J_{FH} = 5.3$. [d] $\delta_F(PF) = -40.6$, $^1J_{PF} = 650.3$.

$-CH_2C(CF_3)_2$-grouping of all compounds are observed in a small region around −79 ppm irrespective of the presence of a four-membered ring.

The P—H coupling constants, $^2J_{PH}$ of the phosphoranes are found to be 16 Hz (H_3C—P) or around 20 Hz ($-CH_2-$P).

EXPERIMENTAL

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work. IR spectra were recorded in KBr on a Perkin Elmer 577 instrument (vs = very strong, s = strong, m = medium, w = weak). Mass spectra were obtained at 30 eV on a Varian-MAT CH 7 spectrometer. NMR spectra were recorded on a Bruker WP 60 CW instrument at 60.0 MHz (^{1}H; TMS), 56.4 MHz (^{19}F; CCl_3F), and 24.3 MHz (^{31}P; ext. 85% H_3PO_4). Chemical shifts are reported as downfield positive.

Compound **1** and $KOCF(CF_3)_2$ were prepared, according to literature methods.[1,4]

[3,3,3-Trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]dimethylphosphine oxide (**2**). Water (0.20 ml, 10 mmole) was added to 1.60 g (3.9 mmole) **1** in 10 ml benzene and 1 ml of acetonitrile. The mixture was stirred for 12 hours at room temperature, the volatiles were pumped off, and the remaining solid was recrystallized from 10 ml of chloroform. The yield of **2** was 0.76 g (76%, m.p. 74°C).

IR: 3400 m (ν_{OH}); 2980 s, 2810 s (ν_{CH}); 1460 m, 1420 m, 1410 m, 1390 m (δ_{CH}); 1290 vs, 1220 vs, 1190 vs, 1110 vs (ν_{CF}); 1020 s, 940 vs, 870 s, 800 s, 750 m, 680 m, 630 m [cm^{-1}]. MS (190°C): *m/e*: 258 (M^+, 60%), 239 (M^+—F, 3), 189 (M^+—CF_3, 100), 91 ($(CH_3)_2P(O)CH_2^+$, 4), 77 ($(CH_3)_2PO^+$, 56), and other fragments. $C_6H_9F_6O_2P$ (258.13): Calcd.: C, 27.92; H, 3.52; F, 44.16. Found: C, 28.04; H, 3.61; F, 44.10.

[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]-[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]-chlorodimethylphosphorane (**3**). A solution of 4.00 g (10 mmole) of **1** in 20 ml of acetonitrile was allowed to react with 0.36 g (10 mmole) of gaseous hydrogen chloride for 1 day at 0–5°C. Volatile compounds were pumped off, the remaining solid was sublimed at 80°C/0.01 Torr. The yield of **3** was 95% (m.p. 124°C).

MS (70°C): *m/e*: 446, 444 (M^+, −), 431, 429 (M^+—CH_3, 4%), 409 (M^+—Cl, 15), 408 (M^+—HCl, 25), 389 (M^+—HCl—F, 5), 339 (M^+—HCl—CF_3, 100), 241 (M^+—HCl—$OCH(CF_3)_2$, 22). 189 (M^+—HCl—C_4F_9, 80) and other fragments. $C_6H_{10}ClF_6O_2P$ (429.76): Calcd.: C, 24.31; H, 2.27; F, 51.28. Found: C, 24.79; H, 2.57; F, 50.00.

Dehydrohalogenation of **3**. A solution of 3.50 g (8 mmole) of **3** in 30 ml of acetonitrile and 0.90 g (9 mmole) triethylamine were stirred at 5°C for 5 minutes. The solution was separated from triethylammonium chloride by filtration and the solvent was removed. The residue was 3.20 g (100%) **1**.[1]

2-Chloro-2,2-dimethyl-4,4-bis(trifluoromethyl)-1,2λ⁵-oxaphosphetane (**4**). A solution of 2.58 g (10 mmole) of **2** in 20 ml of acetonitrile was added slowly at 0°C to a mixture of 1.20 g (10 mmole) of thionyl chloride and 1.00 g (13 mmole) of pyridine in 10 ml of acetonitrile. 25 ml of solvent were removed and the remaining solution was washed with five 10 ml portions of pentane. After pumping off the pentane 2.10 g (76%) of **4** (m.p. 47°C) were obtained.

From a solution of 3.00 g (8 mmole) of **3** in 30 ml of acetonitrile the solvent was removed slowly at 30°C during 24 hours. The residue was extracted with five ml portions of pentane. After removing the pentane 1.10 g (60%) of **4** were obtained.

IR: 2990 m, 2820 m (ν_{CH}); 1470 w, 1420 w, 1410 w, 1390 w (δ_{CH}); 1295 s, 1250 s, 1240 vs, 1210 vs, 1140 vs (ν_{CF}); 1020 s, 940 s, 975 s, 800 m, 750 m [cm^{-1}]. MS (200°C): *m/e*: 278, 276 (M^+, −), 241 (M^+—Cl, 100%), 209, 207 (M^+—CF_3, 54), 114, 112 ($(CH_3)_2P(O)Cl^+$, 14), 77 ($(CH_3)_2PO^+$, 51) and other fragments. $C_6H_8ClF_6OP$ (276.81): Calcd.: C, 26.06; H, 2.92; F, 41.22. Found: C, 26.20; H, 2.89; F, 42.00.

2-Fluoro-2,2-dimethyl-4,4-bis(trifluoromethyl)-1,2λ⁵-oxaphosphetane (**5**). Potassium heptafluoroisopropylate[4] 1.00 g (4 mmole) in 10 ml of acetonitrile was added to 1.10 g (4 mmole) of **4** in 10 ml of the same solvent and stirred at 40°C for one day. The solution was filtered and the volatile components were pumped off. The yield was 1.00 g (96%) of **5** (m.p. 38°C; Subl. 40°C/0.01 Torr).

IR: 2980 m, 2850 m (ν_{CH}); 1420 m (δ_{CH}); 1310 s , 1220 vs, 1205 vs, 1190 s (ν_{CF}); 1160 m, 1130 s, 1100 s, 1090 s, 960 vs, 855 m, 715 m, 660 s [cm^{-1}]. MS (200°C): *m/e*: 260 (M^+, 0.1%), 245 (M^+—CH_3, 3), 241 (M^+—F, 5) 191 (M^+—CF_3, 100), 96 (M^+—$CH_2C(CF_3)_2$, 37), 94 ($(CH_3)_2P(F)OCH_2^+$, 32), 81 ($C_2F_3^+$, 42), 69 (CF_3^+, 14) and other fragments. $C_6H_8F_7OP$ (260.21): Calcd.: C, 27.70; H, 3.11; F, 51.13. Found: C, 27.54; H, 3.25; F, 51.50.

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