Synthesis of 3,3,4,4,4-pentafluoro-2-oxobutane-1-sulfonyl fluoride

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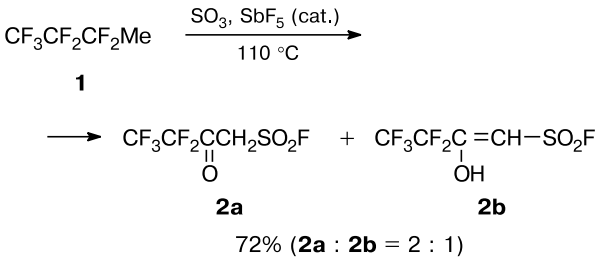
Polyfluorinated ketones $R^FCOCH_2SO_2F$ are not easily accessible.[1,2] We found that 1,1,1,2,2,3,3-heptafluorobutane[3] (**1**) reacts with an excess of sulfuric anhydride containing 1% SbF_5 to give 3,3,4,4,4-pentafluoro-2-oxobutane-1-sulfonyl fluoride (**2**) in good yield. The reaction product is a 2 : 1 mixture of keto (**2a**) and enol forms (**2b**) (^{1}H and ^{19}F NMR data).



Apparently, this transformation is a particular case of a novel general reaction, which can involve polyfluoroalkanes containing an electron-donating alkyl fragment bound to a fluorinated C atom with the F atoms possessing anionic fugacity.

^{1}H and ^{19}F NMR spectra were recorded for neat compounds on a Bruker AC-200F spectrometer (200 and 188.3 MHz, respectively). Chemical shifts (δ) are referenced to Me_4Si and $CFCl_3$ as the external standards. The mass spectrum was recorded on a YGMS 70-70 E spectrometer (70 eV). The IR spectrum was recorded on a UR-20 spectrophotometer.

3,3,4,4,4-Pentafluoro-2-oxobutane-1-sulfonyl fluoride (2). A steel autoclave (50 cm^3) was charged with compound **1** (20 g, 0.109 mol) and SO_3 (28.5 g, 0.356 mol) containing 1 wt.% SbF_5. The autoclave was heated at 110 °C for 5 h while stirring the reaction mixture. On cooling to ~20 °C, the mixture was distilled on a Vigreux column (~10 cm). The fractionation gave crude product **2** (30.5 g), b.p. 140—145 °C (contains ~10% FSO_3H). The product was stirred with dry NaCl (4.0 g) for 12 h; the organic part was removed *in vacuo* (1 Torr) and redistilled. The yield of compound **2** was 19.3 g (72%), b.p. 140—142 °C. Found (%): C, 19.20; H, 0.99; F, 46.52. $C_4H_2F_6O_3S$. Calculated (%): C, 19.67; H, 0.82; F, 46.72. The ^{1}H and ^{19}F NMR spectra of the product contained two sets of signals due to keto (**2a**) and enol forms (**2b**). Ketone **2a**. ^{19}F NMR, δ: 62.8 (br.s, 1 F, SO_2F); −81.9 (br.s, 3 F, CF_3); −122.3 (br.s, 2 F, CF_2). ^{1}H NMR, δ: 5.30 (d, 2 H, CH_2, J_{H-F} = 2.7 Hz). Enol **2b**. ^{19}F NMR, δ: 69.5 (br.s, 1 F, SO_2F); −83.2 (br.s, 3 F, CF_3); −122.6 (br.s, 2 F, CF_2). ^{1}H NMR, δ: 9.70 (s, 1 H, OH); 6.60 (d, 1 H, CH, J_{H-F} = 3.3 Hz). MS, *m/z* (I_{rel} (%)): 244 $[M]^+$ (0.6); 125 $[M - C_2F_5]^+$ (100); 119 $[C_2F_5]^+$ (14.7); 97 $[CH_2SO_2F]^+$ (3.6); 83 $[SO_2F]^+$ (1.1); 69 $[CF_3]^+$ (30.4); 67 $[FSO]^+$ (17.0); 64 $[SO_2]^+$ (12.8); 61 $[C_2FH_2O]^+$ (67.6); 42 $[C_2H_2O]^+$ (63.5). IR, ν_{max}/cm^{-1}: 1790 (C=O), 1450 (S=O), 3000 (C—H), 3560 (O—H).

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