Reaction of fluorosulfonyloxypentafluoroacetone in the presence of alkali metal fluorides

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2-Fluorosulfonyloxytetrafluoropropionyl fluoride (**3**) is the product of isomerization of fluorosulfonyloxypentafluoroacetone (**1**). In the presence of CsF at low temperatures compound **3** forms 2-fluorosulfonyloxyperfluoropropoxy anion, and at ~25 °C CsF catalyzes the decomposition of compounds **1** and **3** with the formation of trifluoropyruvoyl fluoride isolated as cyclodimer.

Key words: fluorosulfonyloxypentafluoroacetone, 2-fluorosulfonyloxytetrafluoropropionyl fluoride, trifluoropyruvoyl fluoride, hexafluoropropylene oxide, fluorosulfonic acid.

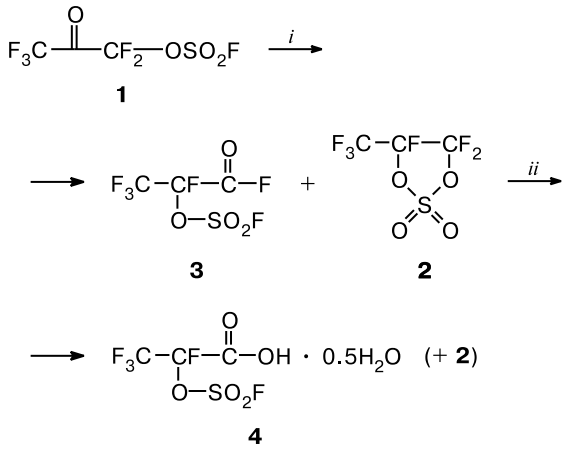
It has been shown previously[1] that hexafluoropropylene oxide (HFPO) reacts with sulfuric anhydride to form a mixture of fluorosulfonyloxypentafluoroacetone (**1**) and perfluoropropylene sulfate (**2**) with predomination of compound **1**. It was found that ketone **1** decomposed under the action of CsF in MeCN to give trifluoropyruvoyl fluoride,* representing a synthone with a high synthetic potential.[2,3] The compound was characterized as an adduct of trifluoropyruvic acid anilide with aniline and isolated in low yield.

According to Ref. 4, ketone **1** decomposes in the presence of both CsF and less nucleophilic NaF to form oligomerization products of undetermined structure. At the same time, under the action of NaI in an aprotic medium compound **1** isomerizes to 2-fluorosulfonyloxytetrafluoropropionyl fluoride (**3**) in 68% yield.

One of the fundamental tasks of the chemistry of fluoroaliphatic compounds is the development of new methods for their functionalization. Since the FSO_3CF fragment is a latent form of the carbonyl group, we studied a possibility of generation and use in synthesis of 2-fluorosulfonyloxyhexafluoropropoxy anion, whose formation could be expected upon the reaction of acyl fluoride **3** with an alkaline metal fluoride.

We found that using such a lowly active source of fluoride ion as KHF_2 in $PhNO_2$ results in the quantitative isomerization of ketone **1**, which was obtained by a modified procedure[4] (see Experimental), to a mixture of acyl fluoride **3** and sulfate **2** in the ratio **3** : **2** = 7 : 1. This ratio remains unchanged in time and, most likely, corresponds to an equilibrium mixture of isomers **3** and **2**. The hydrolysis of the obtained mixture affords (Scheme 1) 2-fluorosulfonyloxytetrafluoropropionic acid (**4**) (under these conditions, only acyl fluoride **3** is hydrolyzed).

Scheme 1



i. $[KHF_2]/PhNO_2$; *ii*. $[H_2O]$/pentane.

As it turned out, in the presence of CsF in diglyme a mixture of compounds **3** and **2** interacts with HFPO at −30—−35 °C (Scheme 2**) to form a mixture of fluorosulfonyloxyacyl fluoride (**6**), cyclic dimer of trifluoropyruvoyl fluoride (**7**), and cycloadduct of trifluoropyruvoyl

* Probably, a cyclodimer of trifluoropyruvoyl fluoride was obtained, which, however, was not isolated and characterized.

** Both acyl fluoride **3** and sulfate **2**, which undergoes opening by CsF in diglyme to form **3**, are involved in the formation of anion **5**.

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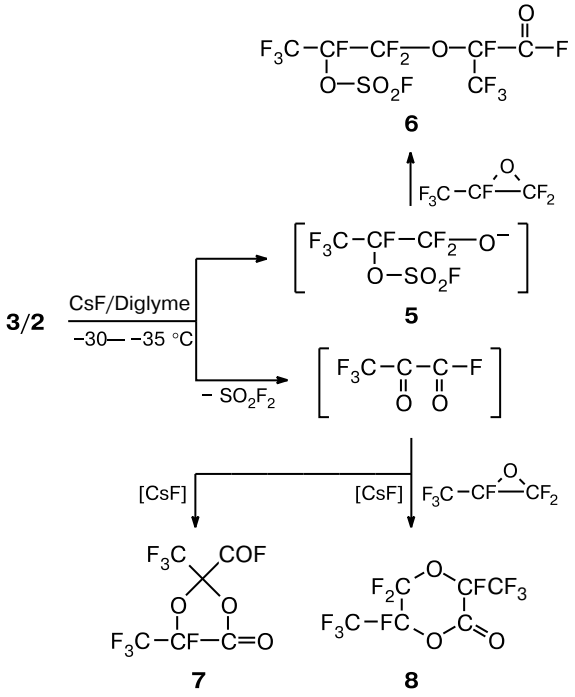
fluoride and HFPO (**8**) (**6** : **7** : **8** = 7 : 2 : 1) (oxalactones **7** and **8** and the methods of their synthesis from trifluoropyruvoyl fluoride were described[5]). The yield of compound **6** was 33%. Although lactones **7** and **8** are formed in rather small amounts, their formation indicates that the decomposition of compounds **2** and **3** to trifluoropyruvoyl fluoride cannot completely be prevented even at such low temperatures.

Scheme 2



When heating a mixture of compounds **2** and **3** or, which is more convenient, their precursor ketone **1**, HFPO, CsF, and diglyme to ~25 °C, the single reaction product is oxalactone **8** formed in a yield higher than 80%. Similarly, oxalactone **7** is formed in high yield from **1** under the action of CsF.

Thus, although ketone **1** and its isomers **2** and **3** easily decompose under the action of F^-, we succeeded to perform the sequence of transformations of **1**, generating anion **5** and to synthesize a compound containing the 2-fluorosulfonyloxyfluoropropoxy group.

Experimental

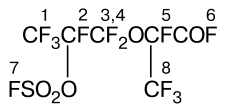
^{19}F NMR spectra were recorded on a Bruker 200SY instrument (188.3 MHz) in CCl_4 solutions using CF_3COOH as an external standard.

Fluorosulfonyloxypentafluoroacetone (1). A mixture of HSO_3F (100 mL), Cr_2O_3 (10 g), and HFPO (60 g, 0.36 mol) was shaken in a 200-mL steel autoclave for 8 h at ~25 °C, then the autoclave was cooled to ~0 °C, freshly distilled SO_3 (29 g, 0.36 mol) was added to the reaction mixture, the autoclave was shaken for 8—10 min more, and the liquid part of the reaction mixture was decanted from the precipitate. The fraction with b.p. 50—100 °C was isolated by distillation, the distillate was washed with 12—15 mL of concentrated H_2SO_4, and the organic layer was separated and distilled above concentrated H_2SO_4. Ketone **1** was obtained in a yield of 84.5 g (95%), b.p. 56—58 °C (b.p. and the ^{19}F NMR spectrum are identical to the literature data[1,4]). The HSO_3F and Cr_2O_3 remained after the treatment of the reaction mixture can multiply be used for the synthesis of ketone **1**.

2-Fluorosulfonyloxytetrafluoropropionyl fluoride (3) and perfluoropropylene sulfate (2). Ketone **1** (13.8 g, 56 mmol) was added dropwise to a suspension of KHF_2 (1 g) in anhydrous $PhNO_2$ (25 mL). After the end of the exothermic reaction, the mixture was stirred for 15 min at 45 °C and heated to 50—60 °C (100 Torr), and volatile products were distilled off and collected in a cooled receiver (−78 °C). The distillation of the distillate gave 13.3 g (95%) of a mixture of acyl fluoride **3** and perfluoropropylene sulfate **2** (**3** : **2** = 88 : 12) (according to the ^{19}F NMR data) (*cf.* Refs 1 and 4).

2-Fluorosulfonyloxytetrafluoropropionic acid (4). Water (17 mL, 95 mmol) was gradually added with stirring to a solution of the obtained mixture of **3** and **2** (15 g, 60 mmol) in pentane (20 mL). The reaction mixture was washed with dilute aqueous solutions of $CaCl_2$, the aqueous layer was extracted with ether, the extract was evaporated, and the residue was distilled above concentrated H_2SO_4. 2-Fluorosulfonyloxytetrafluoropropionic acid semihydrate **4**, b.p. 55—59 °C (10 Torr), was obtained in a yield of 12.8 g (4% based on compound **3** taken in the reaction). Found (%): C, 13.93; H, 0.77; F, 37.45. $C_3H_2F_5O_{2.5}S$. Calculated (%): C, 14.23; H, 0.79; F, 37.55. ^{19}F NMR: −127.0 (FSO_3); 7.0 (CF_3); 54.5 (CF).

Reaction of a mixture of compounds 3 and 2 with hexafluoropropylene oxide in the presence of CsF. A mixture of compounds **3** : **2** (88 : 12) (18.5 g, 75 mmol) was added at −30 to −32 °C to a suspension of CsF (1.13 g) in anhydrous tetraglyme (6 mL) and diglyme (3 mL). The mixture was stirred for 30 min, and then HFPO (13.3 g, 80 mmol) was gradually introduced within 2 h. The mixture was stirred for 30 min, cooled to −40 °C, and poured into ice-cold water. The organic layer was separated (according to the ^{19}F NMR data, the layer contains a mixture of compounds **6** : **7** : **8** = 7 : 2 : 1), rapidly shaken with a small amount of P_2O_5, and decanted into a distillation device. 2-(2-Fluorosulfonyloxyhexafluoropropoxy)tetrafluoropropionyl fluoride (**6**) was isolated by rectification in a yield of 8 g (33%), b.p. 48—50 °C (63 Torr). Found (%): C, 18.08; F, 56.11. $C_6F_{12}O_5S$. Calculated (%): C, 17.48; F, 55.34. ^{19}F NMR, δ: −126.5 (1 F(7)); −102.0 (1 F(6)); AB quartet with centers at 0.5 and 8.5 (1 F(3) + 1 F(4)), J_{ab} = 254 Hz; 3.2 (3 F(1)); 6.5 (3 F(8)); 54.7 (1 F(5)); 65.2 (1 F(2)).



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Perfluoro-5-fluorocarbonyl-3,5-dimethyl-1,3-dioxolan-2-one (7). Ketone **1** (25.7 g, 0.104 mol) was added at −35 °C to a suspension of CsF (0.3 g) in diglyme (1.5 mL). The reaction mixture was slowly warmed to −15—−10 °C, stirred for 30 min,

then stirred for 3 h at ~20 °C, and distilled *in vacuo*, collecting the fraction that boils out below 60 °C (40 Torr) to a cooled receiver (−78 °C). The distillation of the distillate gave oxalactone **7** in a yield of 12.6 g (84%), b.p. 71—73 °C (b.p. and the ^{19}F NMR spectrum are identical to those described in the literature[5]).

Perfluoro-3,6-dimethyl-1,4-dioxan-2-one (8). Anhydrous diglyme (3 mL) and CsF (0.8 g) were placed in a steel autoclave (100 mL) and cooled under Ar atmosphere to −30 °C, and ketone **1** (37.9 g, 154 mmol) was added. Then HFPO (25.6 g, 154 mmol) was condensed into the evacuated autoclave cooled to −196 °C, and the autoclave was shaken for 8 h at ~25 °C and cooled to 0 °C. Gaseous SO_2F_2 was bleed, and the reaction mixture was transferred to a distillation device. The products volatile below 45—50 °C (35—40 Torr) were distilled off to a receiver (−78 °C). Dissolved SO_2F_2 was distilled off from the distillate on a column equipped with the complete condensation packing, and the distillation of the residue gave oxalactone **8** (39.2 g, 84%), b.p. 70—72 °C (b.p. and the ^{19}F NMR spectrum are identical to those described in the literature[5]).

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