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# The Reactions of 1,2-bis(fluorosulfonyloxy)tetrafluoroethane with Nucleophiles

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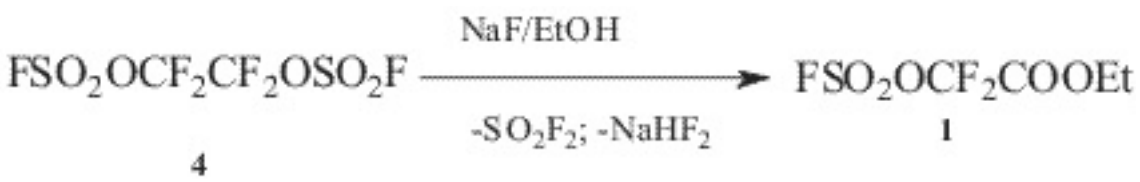
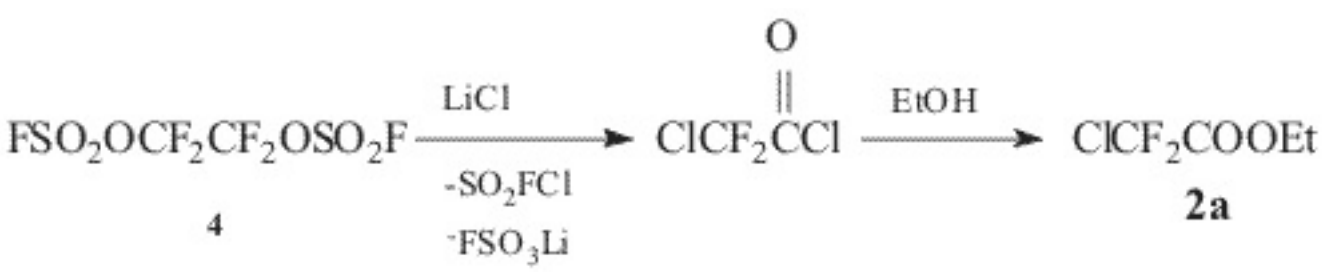
The perfluoroalkylfluorosulfates are cleaved under the action of nucleophilic agents with the formation of carbonyl compounds – perfluoroacyl fluorides or ketones[1-4]. In contrast to their saturated analogues the reactions of nucleophiles with fluorinated aliphatic and aralkyl fluorosulfates, where $FSO_3$-group is located in α-position towards sp2-hybridized C-atom in the composition of vinyl or carbonyl group, afford the products of substitution of $FSO_3$-group for nucleophilic residue[5-7].

Thus, it was shown[7] that the reactions of ethyl fluorosulfonyloxydifluoroacetate (**1**) with soft nucleophiles give substituted ethyl difluoroacetates $RCF_2$ COOEt (**2**) (R = Br, I, PhS, i-$C_3F_7O$).

The ester **1** was obtained by alcoholysis of fluorosulfonyloxydifluoroacetyl fluoride (**3**) but the source of acetylfluoride **3** hadn't been indicated*. In the given work we have shown that the ester **1** is formed smoothly by alcoholysis of 1,2-bis(fluorosulfonyloxy)tetrafluoroethane (**4**) in the presence of NaF. Bis-fluorosulfate **4** is available by anodic oxidation of tetrafluoroethelene in $HSO_3F/[KOSO_2F]$[8].




It should be noted that esters **2** can be prepared directly from bis-fluorosulfate **4**. Thus, the reaction of **4** with LiCl in diglime leads to the formation of chlorodifluoroacetyl chloride (**5**) that was characterized in the form of ester **2** (R = Cl) (**2a**).



Ethyl fluorosulfonyloxydifluoroacetate

Bis-fluorosulfate **4** (15 g, 50 mmol) was gradually added to suspension of NaF (2.7 g, 65 mmol) in 25 ml of abs. EtOH, after gas evolution ceased the reaction mixture was stirred for 30 min, filtered, washed with diluted HCl acid, the organic layer was separated, dried over $MgSO_4$ and distilled to give 9.1 g (82%) of ester **1**, b.p. 74-76º/100 Torr (lit. data[7]: b.p. 75-76°/100 Torr). NMR $^{19}F$ spectrum was identical to that described in[7].

Ethyl Chlorodifluoroacetate

Bis-fluorosulfate **4** (20g, 67 mmol) was gradually added to solution of 9.45g (225 mmol) of LiCl in 50 ml of dry diglime, the reaction mixture was stirred at 55-60°/5 h, the volatile products evolved were passed through abs. EtOH at ~0°, after the reaction was completed the alcoholic solution was washed with cold water, organic layer was separated, dried over $MgSO_4$ and distilled to give 6.9 g (65%) of ester **2a**, b.p. 96-98° (lit. Data: b.p. 97°)[9].

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