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LETTERS TO THE EDITOR

Interaction of Sulfofluoride Group in the Organofluorine Compounds with Silver Oxide and Carbonate

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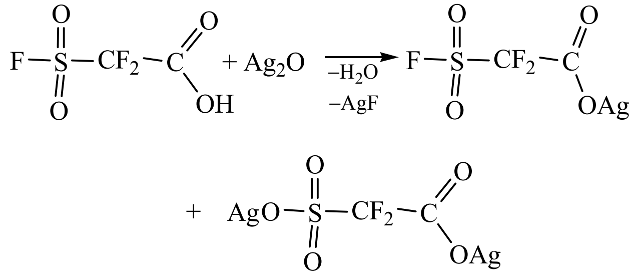
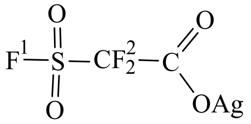
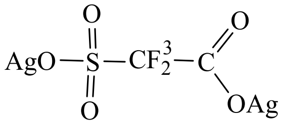
Organofluorine bifunctional compounds containing sulfofluoride and fluorocarbonyl groups can be obtained in some processes that are suitable for large-scale realization, for example, the electrochemical fluorination of some compounds [1], or the ring opening of the corresponding perfluorosultone rings [2].

For the successful use of these compounds in the modern membrane, catalytic, and other advanced technologies synthetic methods are required, which allow a consecutive utilization of the reactivity of sulfofluoride and fluorocarbonyl functions. In particular, when solving the problem of obtaining silver 2,2-difluoro-2-(fluorosulfonyl)acetate, the reaction of this acid with silver oxide (method *a*) was examined assuming that sulfofluoride group will not be affected. However, the reaction of equimolar amounts of the starting compounds affords a mixture of the salts of sulfonic and carboxylic acids.

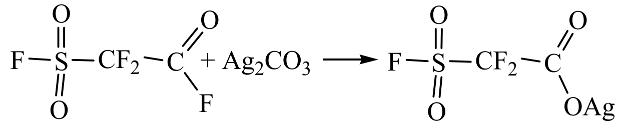

$$\mathrm{FSO_2CF_2COOH + Ag_2O \xrightarrow[-AgF]{-H_2O} FSO_2CF_2COOAg + AgOSO_2CF_2COOAg}$$

Indeed, in the ^{19}F NMR spectrum there are the signals of two different substances: mono- and disilver derivatives of the mixed acids [δ_F, ppm: –107.86 (F^3), –99.77 (F^2), 38.46 (F^1)].


$$\mathrm{F^1{-}SO_2{-}CF^2_2{-}COOAg}$$


$$\mathrm{AgO{-}SO_2{-}CF^3_2{-}COOAg}$$

Nonetheless, the synthesis of silver 2,2-difluoro-2-(fluorosulfonyl)acetate was successfully performed by using the silver carbonate and carboxylic acid fluoride instead of the silver oxide and carboxylic acid.


$$\mathrm{FSO_2CF_2COF + Ag_2CO_3 \longrightarrow FSO_2CF_2COOAg}$$

The NMR spectrum of the reaction product contains only the singlet signals characterizing the fluorine atoms of the sulfofluoride and difluoromethylene groups of this silver salts (δ_F 38.46 ppm). The integral intensity of the latter signal is two times greater.

Unlike the method *a*, in the realized process (method *b*) the disubstituted silver salts did not form. This is most likely associated with a different basicity of silver carbonate and oxide. Silver carbonate is a less basic reagent, therefore the substitution does not involve both functional groups, but only the fluorocarbonyl function.

The ^{19}F NMR spectra were measured on a Bruker AM-500 instrument operating at 470.60 MHz at 24°C. The salts samples were obtained as ~5% solutions in distilled water. The chemical shifts were measured relative to external fluorotrichloromethane.

Synthesis of silver difluoro(fluorosulfonyl) acetate. *a*. A mixture of 61.2 g (0.26 mol) of silver oxide prepared in accordance with the procedure [3], and 82.7 g (0.46 mol) of difluoro(fluorosulfonyl)acetic acid as a 60% aqueous solution was heated on a water bath at 60°C for 5 h until the precipitate formed. The latter was subsequently dried in a vacuum with heating the flask on a water bath and then kept in a desiccator over phosphorus pentoxide.

b. To 86.3 g (0.48 mol, an excess) of difluoro (fluorosulfonyl)acetyl fluoride was added in small portions 35.7 g (0.13 mol) of silver carbonate (pure grade, TU 6-09-3743-74). The resulting precipitate was washed with water and dried in a vacuum. Yield 22.9 g (62%).

Thus, in the organofluorine compounds the sulfofluoride function transforms into the salt by the action of silver oxide. At the treatment of 2,2-difluoro-2-(fluorosulfonyl)acetylfluoride (mixed acid fluoride of carboxylic and fluorosulfonic acids) with silver carbonate only the acid fluoride function is converted into the salt, while sulfofluoride group is not affected.

ACKNOWLEDGMENTS

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