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The new method of preparing 2,2-bis(trifluoromethyl)propionyl fluoride

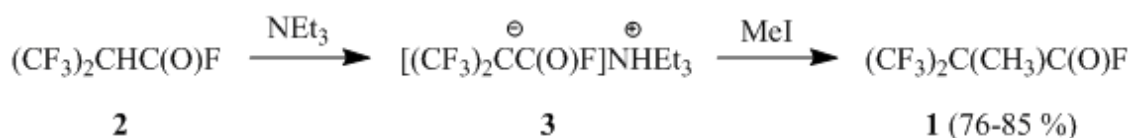
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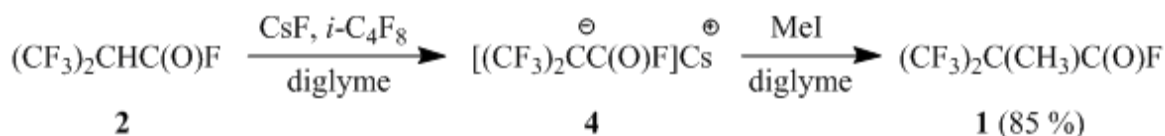
Abstract: The new method of preparing 2,2-bis(trifluoromethyl)propionyl fluoride (**1**) is suggested.

Keywords: 2-trifluoromethyl-3,3,3-trifluoropropionyl fluoride, 2,2-bis(trifluoromethyl)propionyl fluoride, acyl fluorides.

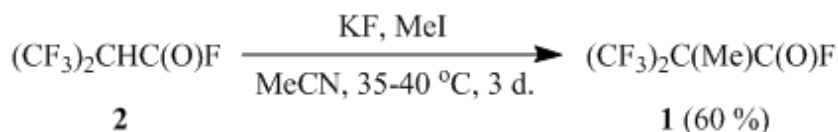
Earlier it was shown that α -hydrohexafluoroisobutyryl fluoride (**2**) reacts with methyl iodide in the presence of triethylamine in a sealed glass tube or autoclave to give 2,2-bis(trifluoromethyl)propionyl fluoride (**1**) [1-2]; the formation of ammonium salt **3** as the intermediate of the process has been registered by ^{19}F NMR spectrum [1]:



At the same time, acyl fluoride **2** afforded the corresponding cesium salt **4** (similar to **3**) under the action of cesium fluoride in diglyme only in the presence of perfluoroisobutene, that performed as an acceptor of hydrogen fluoride [3]. The further alkylation of salt **4** led to the formation of acyl fluoride **1**.



We have found that acyl fluoride **1** can be smoothly obtained by the reaction of acyl fluoride **2** with MeI in acetonitrile in the presence of two equivalents of potassium fluoride. The reaction is performed under atmospheric pressure and can be scaled up easily that allows to consider it as a convenient method of preparing 2,2-bis(trifluoromethyl)propionyl fluoride (**1**).



Experimental

The ^1H and ^{19}F NMR spectra were recorded on a Bruker AM300 spectrometer at 300.13 and 282.4 MHz, respectively, using CDCl_3 as external standard. Chemical shifts for ^1H spectra were referenced to the residual ^1H resonances of the CDCl_3 (δ 7.25) and are reported as parts per million relative to tetramethylsilane. Fluorine chemical shifts are reported in ppm relative to CFCl_3 . Downfield shifts are reported as positive values.

2,2-Bis(trifluoromethyl)propionyl fluoride (1). α -Hydrohexafluoroisobutyryl fluoride (**2**) (210 g, 1.06 mol), methyl iodide (150 g, 1.06 mol) and KF (123 g, 2.12 mol) were added sequentially to 420 ml of abs. MeCN at -50°C, the reaction mixture was stirred at -50°/30 min, three day at 35-40°C (the reaction was controlled by ^{19}F NMR). When the reaction was completed the reaction product was distilled off and then purified by rectification. 135 g of acyl fluoride (60%) was obtained, b.p. 46-47°C (lit. data: b.p. 47-47.5°C [1]); ^1H NMR δ : 2.67 (s, 3 H, CH_3); ^{19}F NMR δ : -70.54 (d, 6 F, $4J_{\text{FF}} = 11.3$ Hz, CF_3), 39.18 (m, 1 F, C(O)F).

References

1. Yu.A. Cheburkov, M.D. Bargamova, I.L. Knunyants. Russ.Chem.Bull., 1964, 13(2), 339-341
2. A.F. Gontar, V.L. Don, E.V. Igoumnova, S.M. Igoumnov. 2,2-Bis(trifluoromethyl)propionic acid. Synthesis and properties. **Fluorine notes**, 2010, 3(70).
3. L.L. Gervits, K.N. Makarov, Yu.A. Cheburkov, I.L. Knunyants. JFC, 1977, 9, 45-52.

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