

2,5-Furandicarboxylic Acid Fluoro-Containing Esters Synthesis

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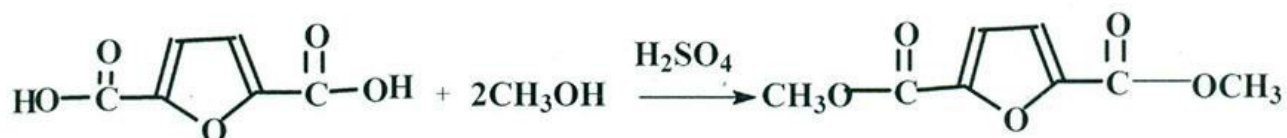
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Abstract: The Fluoro-containing esters based on 2,5-furandicarboxylic acid as well as on its derivatives and 2,2,3,3,4,4,5,5-Octafluoropentan-1-ol (fluorotelomer alcohol n-2) have been synthesized. Sulphuric acid, tetrabutoxytitanium and potassium bisulphate were used as etherification catalysts. The reaction was controlled by NMR- ^1H , ^{19}F and ^{13}C . It was proved, that tetrabutoxytitanium partial re-esterification occurred when using it at 125°C due to the fact, that 2,2,3,3,4,4,5,5-octafluoroamyloxy-group is replacing butoxy-group. The best results have been achieved when carrying out the reaction using of 2,5-furandicarboxylic acid dichloroanhydride..

Key words: 2,5-Furandicarboxylic acid, 2,2,3,3,4,4,5,5-Octafluoropentan-1-ol, Sulphuric acid, Tetrabutoxytitanium, Potassium bisulphate, 2,5-Furandicarboxylic acid dichloroanhydride, NMR-spectroscopy.

Fluoro-containing esters synthesis is usually carried out proceeding from anhydrides, chloroanhydrides, esters of fluorine containing acids and fluorine containing alcohols. The reaction is carried out under the conditions of acidic catalysis, the yield of esters reaches 73% [1,2]

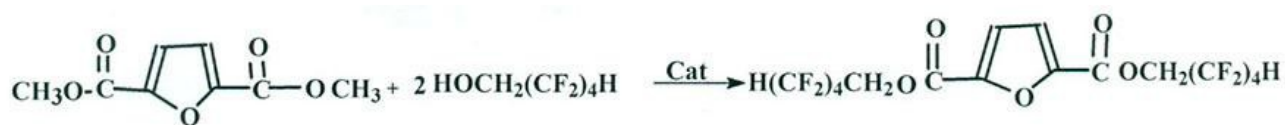
2,5-Furandicarboxylic acid (FDCA), which is a product of oxidation of 5-hydroxymethylfurfural (5-HMF) – one of the main synthons of modern organic synthesis was used as aliphatic carboxylic acid. While boiling the corresponding acid with methanol over sulphuric acid as catalyst [2] dimethyl ester (DMEFDCA) was preliminarily obtained for the synthesis of fluoro-containing esters. The yield of target product amounted to 55%. The structure of DMEFDCA has been confirmed by NMR- ^1H and ^{13}C spectra which correspond to literature data (Scheme 1):



Scheme 1

Several target compound – fluorine containing ethers of 2,5-furandicarboxylic acid - synthesis paths have been studied (Schemes 2-5):

Using the reaction of DMEFDCA re-esterification when it is interacting with 2,2,3,3,4,4,5,5-octafluoropentan-1-ol (Scheme 2):



Scheme 2

H_2SO_4 were used as catalysts of re-esterification (according to Scheme 2), CF_3COOH , as well as $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (TBT) [2-4]. In the last case DMF was used as solvent. The reaction was controlled according to data of NMR- ^1H and ^{19}F . No re-esterification reaction products were found over sulphuric and trifluoroacetic acids.

The formation of target product was observed while carrying out the reaction of DMEFDCA with 2,2,3,3,4,4,5,5-octafluoropentane-1-ol taken at a mole ratio 1:2 and TBT as catalyst (mole ratio DMEFDCA:TBT=3:1) in the solution of DMF. Using NMR ^{19}F spectra was the most convenient way of controlling re-esterification comparing integral signal intensities at -127.5 ppm (OCH_2CF_2 group in the initial alcohol) and -121.8 ppm for group ($\text{COOCH}_2\text{CF}_2$) in the reaction product. Besides that, the signals appeared at -127.2 and -132.3 ppm while signals preserving at -127.5 and -132.3 ppm, typical for 2,2,3,3,4,4,5,5-octafluoropentane-1-ol which had not reacted. NMR- ^1H spectra are characterized by signals presence in the area of 7.23 ppm (protons of furan ring) and 3.9 ppm (CH_3OOC from DMEFDCA). Comparing of their integral intensities were in accordance with NMR- ^{19}F spectral data.

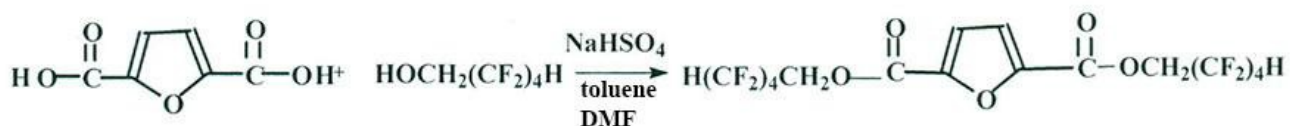
A suggestion was made, that in the current reaction TBT acts not only as catalyst, but also enters into re-esterification reaction with 2,2,3,3,4,4,5,5-octafluoropentane-1-ol at 125 °C.

The reaction between TBT and 2,2,3,3,4,4,5,5-octafluoropentane-1-ol was carried out at 125 °C and at a mole rate of reagents 1 : 2 for 3 hours to find out the that particular issue. In NMR- ^{19}F spectrum two duplets appear in the area of -127.1- 128.2 and -131.3- 132.7 ppm. The signals at -122.7 and -139.1 typical for signals of CF_2CF_2 groups positioned in the middle of 2,2,3,3,4,4,5,5-octafluoropentane-1-ol molecule chain remain their places.

From the data of NMR- ^{13}C spectrum [ppm:103-120 [5 triplets from groups $(\text{CF}_2)_4$; 74.9 (CH_2O); 34.0, 17.8 and 12.2 for $\text{CH}_2\text{CH}_2\text{CH}_3$ groups as in TBT] we can make a conclusion, that at 125 °C at least one butoxy-group in TBT (butanol b.p. is 117 °C) is replaced by alkoxy-group of 2,2,3,3,4,4,5,5-octafluoropentane-1-ol. Thus, the conclusion, that TBT is not only a catalyst but a reagent too in the studied reaction is proved experimentally. When carrying

out the reaction at 150 °C with increased amount of TBT (mole ratio of DMEFDCA:TBT= 1 :1) the yield of target product reached 80% in 10 hours (according to NMR-spectroscopy data). However, isolation of target product was accompanied by certain difficulties, therefore another obtaining method of target product had been considered.

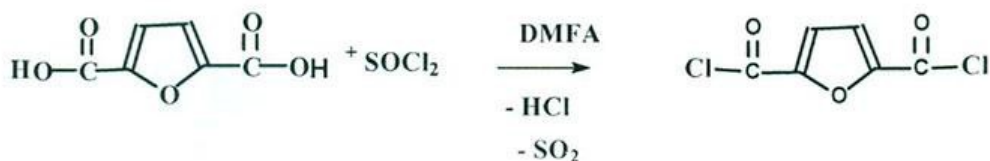
Another catalyst NaHSO₄ [3] was used for synthesis of fluoro-containing ethers based on 2,5-furancarboxylic acid (Scheme 3).



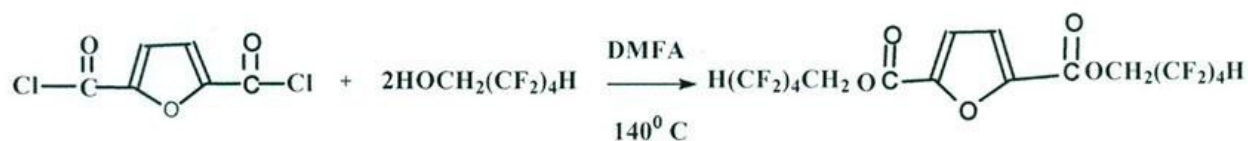
Scheme 3

The reaction proved as unrealizable even at prolong boiling over 60 hours due to light solubility of FDCA in toluene. That is why DMF was added into reaction mixture besides toluene. The reaction was carried out at 150 °C. While analyzing spectra NMR-¹H, ¹³C and ¹⁹F it was stated, that forming of fluoro-containing FDCA ester occurred, its yield was going up as reaction period increased and had reached 70% in 60 hours of boiling. Complex salt [NaHSO₄ x DMF] was forming as by-product. Isolation of target product in a pure form could not have been performed.

That is why 2,5- furandicarboxylic acid dichloroanhydride [5,6] was synthesized in advance (Scheme 4) and at its next interaction with 2,2,3,3,4,4,5,5-octafluoropentanol-1-ol di-2,2,3,3,4,4,5,5-octafluoropentyl 2,5-furandicarboxylate – powder-like product, well-soluble in methanol, acetone, R-113 and hexafluorobenzene was synthesized with yield of 80%. M.P. = 45-47 °C, (Scheme 5):



Scheme 4



Scheme 5

IR-spectra, ν , cm⁻¹: 3433 (CH of furan ring); 1748 (C=O ester); 1134-1114 (CF₂).

NMR- ^1H spectra (solution in C_6F_6), δ , ppm: 8.0 (s, 2H of furan ring); 7.29- (t. CHCF_2).

NMR- ^{19}F spectra (solution in C_6F_6), δ , ppm: -139.76 ÷ -140.0 (d. CF_2H); -131.5 (s, $\text{CF}_2\text{CF}_2\text{H}$); -126.6 (s, $\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$); -121.1 (s, OCH_2CF_2).

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