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Communication

Unusual reaction of sulphur tetrafluoride: conversion of the methyl group into difluoromethyl and trifluoromethyl groups

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Abstract

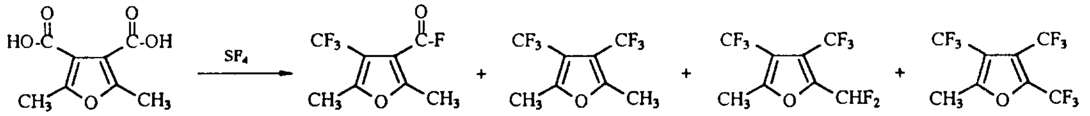
The reaction of 2,5-dimethyl-3,4-furandicarboxylic acid (**1**) with sulphur tetrafluoride gave crystalline 2,5-dimethyl-4-trifluoromethyl-3-furanoyl fluoride (**2**) and a liquid composed of 2-methyl-5-difluoromethyl-3,4-bis(trifluoromethyl)furan (**4**), 2-methyl-3,4,5-tris(trifluoromethyl)furan (**5**) and only small amounts of the expected 2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**3**).

Keywords: Sulphur tetrafluoride; Fluoromethylfurans; Furandicarboxylic acid; Methyl group fluorination; NMR spectroscopy; Mass spectrometry

Reactions of sulphur tetrafluoride proceeding with the substitution of a hydrogen by fluorine are considered to be anomalous. The classical example is the reaction with anthrone which affords 10,10-difluoroanthrone in 85% yield [1]. Replacement of bridgehead hydrogen atoms by fluorine is common for the reactions of sulphur tetrafluoride with adamantane [2] and various adamantane derivatives [3–6]. Another example is the substitution of tertiary hydrogens, along with fluorination of the carbonyl groups, which occurs in the reaction with cyclic lactide [7]. Also, it has been earlier discovered in this laboratory that replacement of fluorine for the formyl hydrogen occurs in the reactions of sulphur tetrafluoride with tertiary formamides to give *N*-trifluoromethylamines almost quantitatively [8].

In the present paper we report, for the first time, a sulphur tetrafluoride fluorination of the methyl group. Thus, reaction with 2,5-dimethyl-3,4-furandicarboxylic acid (**1**) gave, besides the expected acid fluoride **2** and small amounts of 2,5-dimethyl-3,4-bis(trifluoromethyl)furan (**3**), higher fluorinated compounds **4** and **5** formed by the substitution by fluorine of two or all three hydrogen atoms in one of the methyl groups (see Scheme 1). The reaction required temperatures over 100 °C, under which conditions large amounts of tar were formed thus lowering the yield of isolable products. At lower temperatures, only 2,5-dimethyl-3,4-furanoyl difluoride was formed; it was recovered, after alkaline hydrolysis, as the starting acid **1**.

In a typical experiment, 2,5-dimethylfurandicarboxylic acid (**1**) (1 g, 5 mmol) and sulphur tetrafluoride (7 g, 65 mmol) were reacted in a 30 ml capacity stainless steel pressure tube. After completion of the reaction, the tube was cooled to ca. 15 °C and the gases (SF_4, SOF_2) slowly released. The dark brown liquid residue was poured into



1 **2** **3** **4** **5**

Temp. (°C)	Time (h)	Yield (mol%)			
100	24	39	2	5	7
120	60	0	2	5	8
150	12	10	3	5	10

Scheme 1.

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water, neutralised with K_2CO_3 and steam-distilled. A crystalline solid deposited in the Liebig's type condenser and an organic layer separated in the distillate. The solid was identified by elemental analysis, GC–MS and NMR methods as the acid fluoride **2**. The liquid, as found by the GC–MS technique (Hewlett Packard 5890 instrument, 30 m capillary column coated with HP5 oil) consisted of compounds **3**, **4** and **5**. Compound **5** appeared as the shortest retention time peak and compound **3** corresponded to the longest retention time peak. Individual compounds **4** and **5** were isolated by preparative GLC (silicon oil SE-52 on Chromosorb G, 3.5 m × 10 mm column) and their structures were fully confirmed by ^1H and ^{19}F NMR spectroscopy [Varian 200 MHz instrument, internal TMS for ^1H and internal $CFCl_3$ for ^{19}F (positive upfield)].

2,5-Dimethyl-4-trifluoromethyl-3-furanoyl fluoride (**2**): m.p. 143–143.5 °C. Analysis: Found: C, 45.75; H, 3.0; F, 36.15%. $C_8H_6F_4O_2$ requires: C, 45.73; H, 2.9; F, 36.17%. ^1H NMR δ: 2.45 (q, $^4J_{H,F} = 2.3$ Hz, CH_3); 2.59 (d, $^4J_{H,F} = 1.2$ Hz) ppm. ^{19}F NMR δ: -34.1 (q, $^4J_{F,F} = 11.8$ Hz, COF); 50.1 (dq, $^4J_{F,F} = 11.8$ Hz, $^4J_{H,F} = 2.3$ Hz, CF_3) ppm. GC–MS m/z: 210 (50%, M^+); 191 [30, $(M-F)^+$]; 190 [40, $(M-HF)^+$]; 181 [10, $(M-F-CO)^+$]; 162 [40, $(M-HF-CO)^+$]; 69 (10, CF_3^+); 43 (100, CH_3CO^+).

2,5-Dimethyl-3,4-bis(trifluoromethyl)furan (**3**): ^1H NMR δ: 2.40 (s, CH_3) ppm. ^{19}F NMR δ: 57.4 (s, CF_3) ppm. GC–MS m/z: 232 (7%, M^+); 213 [50, $(M-F)^+$]; 163 [100, $(M-CF_3)^+$]; 69 (20, CF_3^+); 43 (80, CH_3CO^+).

2-Methyl-5-difluoromethyl-3,4-bis(trifluoromethyl)furan (**4**): ^1H NMR δ: 2.55 (s, CH_3); 6.75 (t, $^2J_{H,F} = 53.2$ Hz, CHF_2) ppm. ^{19}F NMR δ: 57.4 (s, CF_3); 116.4 (d, $^2J_{H,F} = 52.2$ Hz, CHF_2) ppm. GC–MS m/z: 268 (90%, M^+); 249 [100, $(M-F)^+$]; 217 [20, $(M-CHF_2)^+$]; 199 [45, $(M-CF_3)^+$]; 189 [50, $(M-CHF_2CO)^+$]; 169 (20, $C_6H_2F_5^+$); 151 (15, $C_6H_3F_4^+$); 79 [10, CHF_2CO^+); 69 (40, CF_3^+); 51 (35, CHF_2^+); 43 (40, CH_3CO^+).

2-Methyl-3,4,5-tris(trifluoromethyl)furan (**5**): ^1H NMR δ: 2.56 (narrow multiplet, CH_3) ppm. ^{19}F NMR δ: 57.44 (s, CF_3, 6F); 57.48 (s, CF_3, 3F). GC–MS m/z: 286 (80%, M^+); 267 [100, $(M-F)^+$]; 217 [75, $(M-CF_3)^+$]; 197 [15, $(M-CF_3-HF)^+$]; 189 [40, $(M-CF_3CO)^+$]; 169 (25, $C_6H_2F_5^+$); 69 (60, CF_3^+); 43 (10, CH_3CO^+).

In all experiments, considerable amounts of crystalline sulphur deposited on the walls of the reaction tube. This suggests a redox process for the fluorination of methyl groups, similar to that previously proposed for the conversion of formamides into *N*-trifluoromethylamines [8].

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