

Reactions of tetrafluorophthalic and difluoropyromellitic acids with sulphur tetrafluoride

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Abstract

Fluorination of tetrafluorophthalic acid (1) with an SF₄/HF mixture at 190–300 °C afforded, beside the expected perfluoro-*o*-xylene (2) and perfluoro-*o*-toluyl fluoride (4), considerable amounts of octafluoro-1,3-dihydroisobenzofuran (3). The reaction with difluoropyromellitic acid (5) at 190 °C gave a mixture of perfluoro-2,4,5-trimethylbenzoyl fluoride (9), perfluoro-2,5-dimethylterephthaloyl difluoride (10a), perfluoro-2,4-dimethylisophthaloyl difluoride (10b) and perfluoro-5-methyl-6-fluoroformyl-1,3-dihydroisobenzofuran (11), but at 300 °C perfluorodurene (6), perfluoro-5,6-dimethyl-1,3-dihydroisobenzofuran (7) and perfluoro-2,4,5-trimethylbenzoyl fluoride (9) were obtained in a 3:1:0.8 ratio.

Introduction

Treatment of benzenecarboxylic acids with sulphur tetrafluoride is a general and easy way of preparing trifluoromethyl benzenes [1]. The reactions with sterically crowded arenepolycarboxylic acids [1–4] and also tetrachlorophthalic acid [5], instead of the respective trifluoromethyl arenes, give predominantly or exclusively cyclic tetrafluoroethers, i.e. derivatives of isobenzofuran. According to an early report [6], fluorination of phthalic and pyromellitic acids with sulphur tetrafluoride gives 1,2-bis(trifluoromethyl)benzene and 1,2,4,5-tetrakis(trifluoromethyl)benzene as the only products. However, it has been recently found that the reactions of sulphur tetrafluoride with pyromellitic acid or its dianhydride and also with 4,5-bis(trifluoromethyl)phthalic acid give, beside the expected tetrakis(trifluoromethyl)benzene, a 8–14% yield of cyclic tetrafluoroethers [7]. Those results have stimulated further search for arenepolycarboxylic acids which on treatment with sulphur tetrafluoride are capable of forming cyclic fluoroethers.

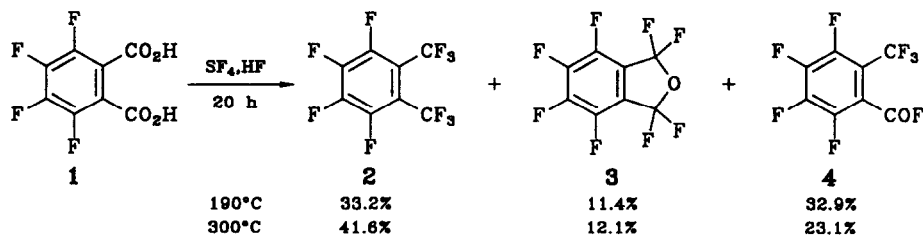
The present paper describes results obtained with tetrafluorophthalic acid (1) and difluoropyromellitic acid (5) whose reactions with sulphur tetrafluoride have not been previously reported.

Results and discussion

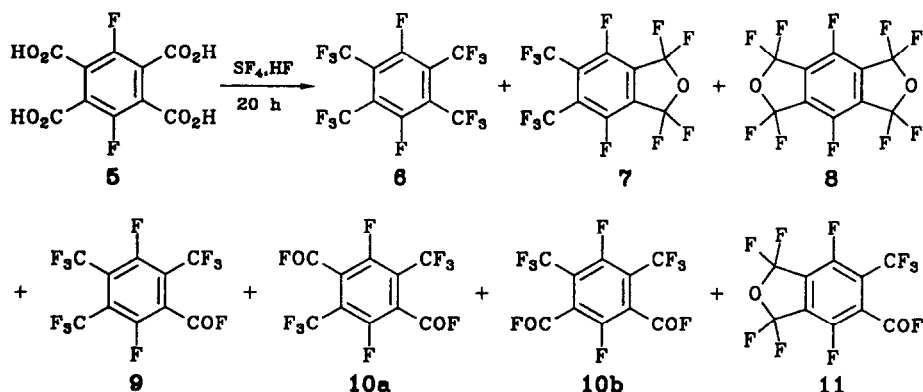
Both tetrafluorophthalic and difluoropyromellitic acids are much less reactive towards sulphur tetrafluoride than their non-fluorinated analogues, such that high temperatures and an excess of anhydrous hydrogen fluoride

were necessary for the fluorination reactions to proceed. The reactions were carried out at 190 °C and 300 °C using SF₄ and HF in a 1:1.5 ratio.

Fluorination of tetrafluorophthalic acid (**1**), regardless of the reaction temperature, gave a mixture of perfluoro-*o*-xylene (**2**), octafluoro-1,3-dihydroisobenzofuran (**3**) and perfluoro-*o*-toluyl fluoride (**4**). Increasing the reaction temperature from 190 °C to 300 °C resulted in a slightly increased yield of compound **2** at the expense of acid fluoride **4**. The yield of isobenzofuran **3** remained practically unchanged, thus showing the remarkable stability of the carbon–oxygen bonds in this compound. This is in contrast to 1,1,3,3-tetrafluoro-1,3-dihydroisobenzofuran, non-fluorinated in the benzene ring, which in the presence of anhydrous hydrogen fluoride readily cleaves at 90 °C [8].



The reaction of sulphur tetrafluoride with difluoropyromellitic acid (**5**) at 190 °C resulted in only partial fluorination and gave a complex mixture consisting mainly of acid fluorides **9**, **10a**, **10b** and **11**, together with small amounts of benzofurans **7** and **8**. At 300 °C, perfluorodurene (**6**) and perfluoro-5,6-dimethyl-1,3-dihydrofuran (**7**) were formed in 62% and 20% yields, respectively, but still considerable amounts of acid fluoride **11** remained unaffected.



Temp.	Ratio of products (GLC %)						Total yield
	6	7	8	9	10a+10b	11	
190°C	—	1.2	1.7	37.5	42	17.6	76.6%
300°C	62	20	1.9	16	—	—	89.4%

Mixtures of products obtained both from acid **1** and acid **5**, because of their complexity, were hardly capable of separation by preparative GLC methods. Nevertheless, partial GLC separation and careful analysis of the ^{19}F NMR spectra in conjunction with the reported spectra of similar compounds [4, 5, 7, 9] allowed identification of all components in these mixtures.

The present results, and the previously reported results of the fluorination of pyromellitic and 4,5-bis(trifluoromethyl)phthalic acids [7], suggest that in reactions of benzenepolycarboxylic acids with sulphur tetrafluoride, in addition to steric factors, the total electron-withdrawing effect of the benzene ring substituents contributes significantly to the formation of cyclic tetrafluoroethers.

Experimental

The ^{19}F NMR spectra were recorded in CDCl_3 at 470 MHz with a Brücker 500 MHz spectrometer; chemical shifts are in ppm relative to internal CFCl_3 (positive upfield). The IR spectra were measured with a Beckmann Acculab instrument. The GLC analyses were performed with a Shimadzu GC-14A chromatograph using a 3.5 m $\times$ 2 mm column packed with 5% silicon oil SE-52 on Chromosorb G. For the preparative GLC work, a GCHF-18.3 (Germany) apparatus equipped with a 4.0 m $\times$ 10 mm column was used.

Starting materials

The preparation of tetrafluorophthalic acid (**1**) by acidolysis of octafluoro-1,3-dihydroisobenzofuran has been described previously [9].

Difluoropyromellitic acid (**5**) was prepared as follows. Perfluoro-1,3,5,7-tetrahydrobenzo[1,2-*c*:4,5-*c'*]difuran [4] (7 g, 0.02 mol) and concentrated sulphuric acid (25 ml) were heated in a 30 ml stainless-steel autoclave at 180–200 °C for 5 h, the resulting solution being poured into iced water (200 ml) and then extracted with ether (5 $\times$ 50 ml). The extract was washed with water, concentrated to a half of its initial volume and vigorously agitated with 5% aqueous KOH (2 $\times$ 75 ml). The alkaline solution was strongly acidified with concentrated hydrochloric acid and extracted with ether (5 $\times$ 50 ml). A solid residue obtained after evaporation of ether was dried over P_4O_{10} affording acid **5** as a white powder (2.7 g; yield 45.4%). Analytical and spectral data were in agreement with those previously reported [10].

Reactions of acids 1 and 5 with sulphur tetrafluoride

General procedure

Stainless-steel autoclaves of 30 or 100 ml capacity (depending on the reaction scale) were used for reactions at 190 °C and a 60 ml nickel autoclave for reactions at 300 °C.

The acid and liquid anhydrous hydrogen fluoride were placed in the autoclave, which was cooled to –78 °C and evacuated, and sulphur tetrafluoride was condensed into it. The charged autoclave was heated in a rocking muffle

and then allowed to cool to ambient temperature. The gases generated (SOF_2 , SF_4 , HF) were slowly released and the contents of the autoclave poured into iced water, neutralised with potassium hydrogen carbonate and subjected to steam distillation (no external steam was required) in a standard glass apparatus.

Reactions of tetrafluorophthalic acid (1)

Method A — Acid **1** (12 g, 0.05 mol), anhydrous hydrogen fluoride (10 ml, 0.5 mol) and sulphur tetrafluoride (35 g, 0.32 mol) were reacted at 190 °C for 20 h. A colourless liquid (10.6 g) was obtained. GLC analysis revealed two peaks and the IR spectrum showed a strong carbonyl absorption at 1860 cm^{-1} . Preparative GLC separation gave two fractions. The shorter retention time fraction was found by ^{19}F NMR spectroscopy to contain compounds **2** and **3**. The longer retention time fraction was almost pure acid fluoride **4**. A combination of the GLC peaks area and the integrated ^{19}F NMR spectra allowed determination of the ratio of compounds **2**, **3** and **4** as 2.9:1:2.9 and the overall yield as 77.5%.

Method B — Acid **1** (3.9 g, 0.015 mol), anhydrous hydrogen fluoride (4 ml, 0.2 mol) and sulphur tetrafluoride (14 g, 0.13 mol) were reacted at 300 °C for 20 h to give a colourless liquid (3.2 g) consisting of compounds **2**, **3** and **4** in a 3.4:1:1.9 ratio. Overall yield, 76%. No carbonyl absorption was found in the IR spectrum.

Reactions of difluoropyromellitic acid (5)

Method A — Acid **5** (4 g, 0.014 mol), anhydrous hydrogen fluoride (6 ml, 0.3 mol) and sulphur tetrafluoride (20 g, 0.185 mol) were reacted at 190 °C for 20 h. A white crystalline product (3.7 g) showing a strong carbonyl absorption at 1865 cm^{-1} was obtained. Two preparative GLC fractions were collected. On the basis of integrated ^{19}F NMR spectra, the shorter retention time fraction was found to contain compounds **7** (1.8%), **8** (2.4%), **9** (55%), **10** (28.5%) and **11** (12.3%), while the longer retention time fraction consisted of compounds **9** (3.3%), **10** (68.2%) and **11** (28.5%). Overall yield, 76.6%.

Method B — Acid **5** (2 g, 0.007 mol), hydrogen fluoride (4 ml, 0.2 mol) and sulphur tetrafluoride (14 g, 0.13 mol) were reacted at 300 °C for 20 h. A white crystalline product (1.8 g) consisting of compounds **6** (62%), **7** (20%), **8** (1.9%) and **9** (16%) was obtained. Overall yield, 69.4%.

^{19}F NMR data for compounds 2–11

Perfluoro-*o*-xylene (**2**): 54.8 (m, CF_3); 132.8 (m, F-3 and F-6); 145.4 (m, F-4 and F-5) ppm (ref. [11], -21.6, 58.4 and 70.7 ppm relative to CF_3COOH).

Octafluoro-1,3-dihydroisobenzofuran (**3**): in agreement with previously reported spectrum [9].

Perfluoro-*o*-toluyl fluoride (**4**) (nc): -57.3 (dq, $^4J=10.7$ Hz, $^5J=5.3$ Hz, COF); 57.5 (d, $^4J=19.2$ Hz, CF_3); 134.4 and 135.5 (m, F-3 and F-6);

144.7 (td, $^3J=20.5$ Hz, $^4J=9.3$ Hz, F-4); 145.4 (td, $^3J=20.5$ Hz, $^4J=6$ Hz, F-5) ppm.

Perfluorodurene (**6**) (nc): 55.8 (m, CF₃); 109.3 (m, F-3 and F-6) ppm.

Perfluoro-5,6-dimethyl-1,3-dihydroisobenzofuran (**7**) (nc): 55.5 (m, CF₃); 69.3 (s, CF₂) ppm. Signals corresponding to the F-4 and F-7 nuclei were not found.

Perfluoro-1,3,5,7-tetrahydrobenzo[1,2-*c*:4,5-*c'*]difuran (**8**): in agreement with previously reported spectrum [4].

Perfluoro-2,4,5-trimethylbenzoyl fluoride (**9**) (nc): -57.0 (s, COF); 55.8 (m, CF₃, 6F); 59.4 (d, $^4J=18.4$ Hz, CF₃, 3F); 110.1 and 111.0 (m, F-3 and F-6) ppm.

Perfluoro-2,5-dimethylterephthaloyl difluoride (**10a**) (nc): -57.4 (s, COF); 58.8 (d, $^4J=16$ Hz, CF₃); 113.1 (m, F-3 and F-6) ppm.

Perfluoro-2,4-dimethylisophthaloyl difluoride (**10b**) (nc): -57.2 (s, COF); 58.7 (d, $^4J=19.2$ Hz, CF₃); 111.9 (sept., $^4J=19.2$ Hz, F-3); 114.6 (m, F-6) ppm.

Perfluoro-5-methyl-6-fluoroformyl-1,3-dihydroisobenzofuran (**11**) (nc): -58.3 (s, br., COF); 58.3 (d, $^4J=18.2$ Hz, CF₃); 68.8 (s, CF₂); 116.5 and 117.9 (m, F-4 and F-7) ppm.

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