Journal of Fluorine Chemistry, 60 (1993) 251–255

Reactions of tetrafluorophthalic and difluoropyromellitic acids with sulphur tetrafluoride

Wojciech Dmowski

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw (Poland)

(Received February 18, 1992; accepted May 9, 1992)

Abstract

Fluorination of tetrafluorophthalic acid (**1**) with an SF_4/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 arenepolycaboxylic 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.

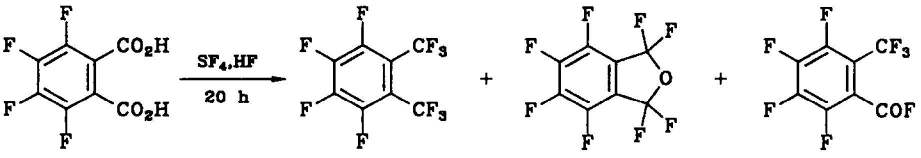
Results and discussion

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

0022-1139/93/$6.00

were necessary for the fluorination reactions to proceed. The reactions were carried out at 190 °C and 300 °C using SF_4 and HF in a 1:1.5 ratio.

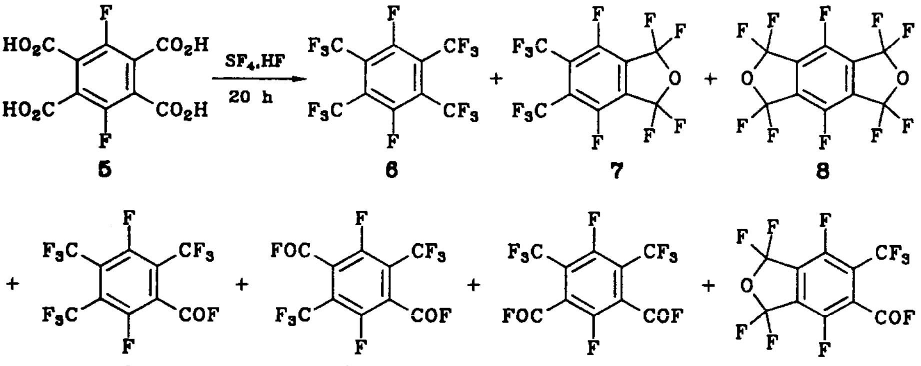
Fluorination of tetrafluorophthalic acid (**1**), regardless of the reaction temperature, gave a mixture of perfluoro-*o*-xylene (**2**), octafluoro-1,3-dihydroisobenzofuran (**3**) and perfluoro-*o*-toluyl fluoride (**4**). Increasing the reaction temperature from 190 °C to 300 °C resulted in a slightly 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].



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

	2	3	4
190°C	33.2%	11.4%	32.9%
300°C	41.6%	12.1%	23.1%

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.



5 **6** **7** **8**

9 **10a** **10b** **11**

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	–	–	69.4%

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×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×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 (5×50 ml). The extract was washed with water, concentrated to a half of its initial volume and vigorously agitated with 5% aqueous KOH (2×75 ml). The alkaline solution was strongly acidified with concentrated hydrochloric acid and extracted with ether (5×50 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, CF_3); 109.3 (m, F-3 and F-6) ppm.

Perfluoro-5,6-dimethyl-1,3-dihydroisobenzofuran (**7**) (nc): 55.5 (m, CF_3); 69.3 (s, CF_2) 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, CF_3, 6F); 59.4 (d, $^4J=18.4$ Hz, CF_3, 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, CF_3); 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, CF_3); 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, CF_3); 68.8 (s, CF_2); 116.5 and 117.9 (m, F-4 and F-7) ppm.

References

1 Chia-Lin J. Wang, *Org. React.*, *34* (1985) 319.
2 A. I. Burmakov, L. A. Alekseeva and L. M. Yagupol'skii, *Zh. Org. Khim.*, *6* (1970) 2498.
3 L. M. Yagupol'skii, A. I. Burmakov, L. A. Alekseeva and B. V. Kunshenko, *Zh. Org. Khim.*, *9* (1973) 689.
4 J. Porwisiak and W. Dmowski, *J. Fluorine Chem.*, *51* (1991) 131.
5 W. Dmowski and J. Wielgat, *J. Fluorine Chem.*, *37* (1987) 429.
6 W. R. Hasek, W. C. Smith and V. A. Englehardt, *J. Am. Chem. Soc.*, *82* (1960) 543.
7 W. Dmowski and J. Porwisiak, *J. Fluorine Chem.*, *60* (1993) 233.
8 W. Dmowski and R. A. Koliński, *Pol. J. Chem.*, *48* (1974) 1697.
9 W. Dmowski and J. Wielgat, *J. Fluorine Chem.*, *41* (1988) 241.
10 W. Dmowski and K. Piasecka-Maciejewska, *Org. Prep. Proceed. Int.*, *24* (1992) 194.
11 F. A. M. Ayabadejo, *Spectrochem. Acta*, *25A* (1969) 1009.