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A re-investigation of the reactions of pyromellitic acid and its dianhydride with sulphur tetrafluoride

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Abstract

The fluorination of pyromellitic acid (**1**) with sulphur tetrafluoride or pyromellitic dianhydride (**2**) by means of an SF_4–HF mixture gave, besides the expected 1,2,4,5-tetrakis(trifluoromethyl)benzene (**3**), considerable amounts of 5,6-bis(trifluoromethyl)-1,1,3,3-tetrafluoro-1,3-dihydroisobenzofuran (**4**) and detectable quantities of 1,1,3,3,5,5,7,7-octafluoro-1,3,5,7-tetrahydrobenzo[1,2-*c*:4,5-*c*′]difuran (**5**). Acidic hydrolysis of **4** gave 4,5-bis(trifluoromethyl)phthalic acid (**6**) which on treatment with SF_4 and HF yielded compounds **3** and **4**.

Introduction

Recently, studies on the chemistry of poly(trifluoromethyl)benzenes have been undertaken in this laboratory [1]. For this reason we required significant quantities of 1,2,4,5-tetrakis(trifluoromethyl)benzenes (**3**). This compound has been reported by Hasek *et al.* [2] to be formed as a sole product of the fluorination of pyromellitic acid with sulphur tetrafluoride. We have found that the reaction both with pyromellitic acid or its dianhydride gives, beside **3**, cyclic compounds **4** and **5**. This report deals with this finding in detail.

Results and discussion

Pyromellitic acid dihydride (**1**) and sulphur tetrafluoride in a 1:15 molar ratio were reacted and worked-up as described previously [2]. A few runs were conducted at temperatures within the range 150–200 °C to give white, finely crystalline products. The GLC analyses revealed that, contrary to the earlier report [2], these products were not a single compound but mixtures of three components in an average ratio of 87:11.5:1.5. The same result was obtained by reacting pyromellitic dianhydride (**2**), sulphur tetrafluoride and anhydrous hydrogen fluoride in a 1:13:7 ratio**. The ratio of compounds

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**Pyromellitic dianhydride does not react with sulphur tetrafluoride in the absence of hydrogen fluoride.

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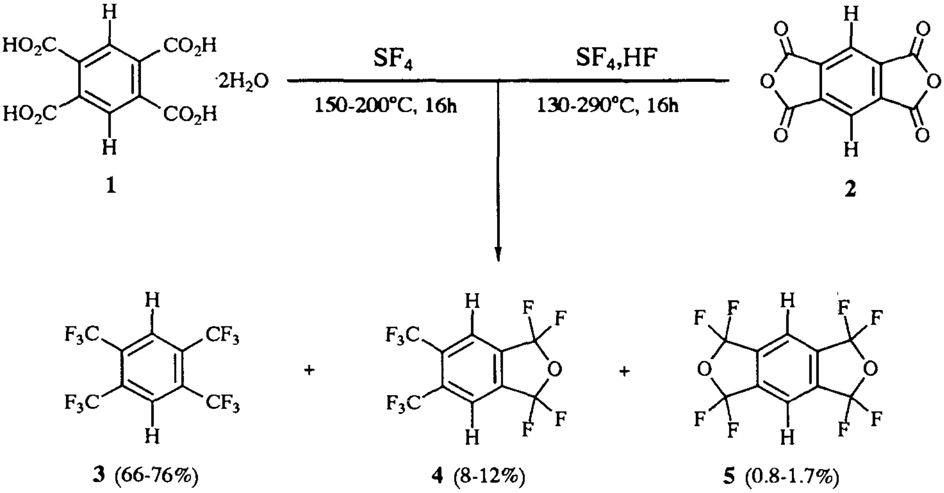
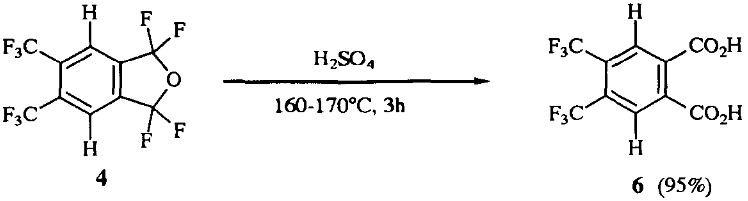
formed in this reaction varied slightly from 85:13.5:1.5 at 130 °C to 88:11:1 at 290 °C. These compounds were separated by chromatography on silica gel with n-hexane and the most abundant compounds have been identified by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy, respectively, as 1,2,4,5-tetrakis(trifluoromethyl)benzene (**3**) and 5,6-bis(trifluoromethyl)-1,1,3,3-tetrafluoro-1,3-dihydroisobenzofuran (**4**). The minor component has been identified by comparison of its GLC retention time with that of an authentic sample [3] as 1,1,3,3,5,5,7,7-octafluoro-1,3,5,7-tetrahydrobenzo[1,2-*c*:4,5-*c*′]difuran (**5**). The infrared spectra of crude products obtained from anhydride **2**, in contrast to those from acid **1**, revealed the total absence of acid fluorides (Scheme 1).



Scheme 1.

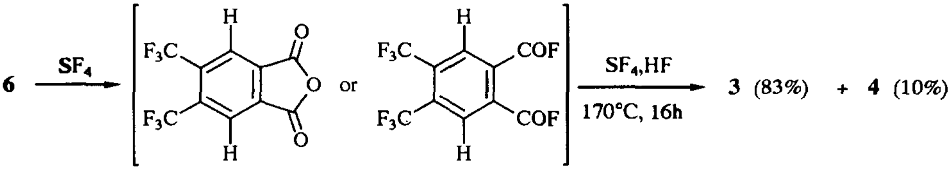
It has been found that treatment of a mixture of compounds **3**, **4** and **5** with concentrated sulphuric acid at 160–170 °C results in quantitative hydrolysis of both **4** and **5** to the respective carboxylic acids which can be easily removed by neutralizing with aqueous potassium hydroxide. This provides an alternative and more convenient method than chromatography for isolating pure 1,2,4,5-tetrakis(trifluoromethyl)benzene (**3**). Hydrolysis of chromatographically-isolated **4** gave, almost quantitatively, pure 4,5-bis(trifluoromethyl)phthalic acid (**6**) (Scheme 2).



Scheme 2.

Acids **6** reacts with sulphur tetrafluoride, preferably in the presence of anhydrous hydrogen fluoride, yielding compounds **3** and **4** in a 9:1 ratio.

This suggests that in reactions of **1** or **2** with SF_4, 4,5-bis(trifluoromethyl)phthalic anhydride or difluoride are intermediates to both **3** and **4** (Scheme 3).



Scheme 3.

The formation of compounds **3** and **4** from acids **1** and **6** contradicts earlier experiments according to which cyclic tetrafluoro ethers, derivatives of benzoisofuran, are formed only from sterically highly crowded benzenedicarboxylic and benzenepolycarboxylic acids such as mellitic and benzenepentacarboxylic [4, 5], benzene-1,2,3,4-tetracarboxylic [6], dichloro-, dibromo- and dinitro-pyromellitic [3, 5, 7] and tetrachlorophthalic acids [8].

Experimental

Melting points were determined in capillaries and are reported uncorrected. ^1H, ^{19}F and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Brucker 500 MHz spectrometer; chemical shifts are quoted in ppm from internal TMS for protons and carbon nuclei (positive downfield) and from internal $CFCl_3$ for fluorine nuclei (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 3.5m × 2 mm column packed with 5% silicon oil SE-52 on Chromosorb G.

Pyromellitic dianhydride (**2**) was a commercial laboratory reagent (Fluka AG). Pyromellitic acid dihydride (**1**) was prepared by refluxing anhydride **2** with water followed by crystallization.

Reaction of pyromellitic acid dihydrate (1) with sulphur tetrafluoride

Acid **1** (25 g, 0.086 mol) was placed in a 250 ml stainless-steel autoclave, the autoclave immersed in an acetone–Dry Ice bath, evacuated and then sulphur tetrafluoride (160 g, 1.5 mol) condensed into it. The charged autoclave was heated in a rocking muffle at the required temperature (runs at 150, 170 and 200 °C) for 16 h. After completion of the reaction, the autoclave was allowed to cool to ambient temperature, the gases (SOF_2, SF_4, HF) were released and the contents of the autoclave poured into ice water. The IR spectrum of a sample of the crystalline precipitate showed a strong carbonyl absorption at 1850 cm^{-1}. Ammonium hydroxide (25%, 50 ml) was added and the mixture was again placed in the autoclave, heated at 160 °C for 1 h, then subjected to steam distillation (no external steam was required) in a standard glass apparatus. A white, nicely crystalline product (18–20 g, 60–67%) containing compounds **3**, **4** and **5** in a ratio *c.* 87:11.5:1.5 (GLC estimate) was obtained.

*Reactions of pyromellitic dianhydride (**2**) with sulphur tetrafluoride*

Anhydride **2** (22 g, 0.1 mol), anhydrous hydrogen fluoride (15 ml, 0.75 mol) and sulphur tetrafluoride (140 g, 1.3 mol) were reacted and worked-up as described above. Four runs over the temperature range 130–290 °C* were carried out. In all cases fluorination was complete: IR spectra of the crude products showed no carbonyl absorption. Ammonium hydroxide (25%, 50 ml) was added and the mixture was steam-distilled to give crystalline mixtures of compounds **3**, **4** and **5** (27–30 g, 78–86%) in the ratios 85:13.5:1.5, 86:12.5:1.5, 88:10:2 and 88:11:1 from runs at 130, 170, 200 and 290 °C, respectively.

*Chromatographic separation of compounds **3** and **4***

A mixture of crystalline compounds **3**, **4** and **5** (25 g) was thoroughly ground with silica gel (30 g, 230–400 mesh), placed on the top of a 65-mm diameter and 700-mm long column filled with 1000 g silica gel and the column eluted with 6000 ml of n-hexane. Twenty fractions, 200 ml each, were collected and analyzed by GLC. Fractions 4–8 contained compound **3**, and fractions 14–20 compound **4**. Both compounds were isolated from the respective eluents by freezing in an acetone–Dry Ice bath for 48 h. The crystalline precipitates were filtered and kept for few days over paraffin chips to remove the residual solvent. 1,2,4,5-Tetrakis(trifluoromethyl)benzene (**3**) was obtained as white crystals (19 g, GLC purity 99.2%), m.p., 71.5–72 °C (ref. [2], m.p., 73–74 °C). Analysis: Found: F, 65.1%. $C_{10}H_2F_{12}$ requires: F, 65.1%. ^1H NMR δ: 8.34 (s) ppm. ^{19}F NMR δ: 60.5 (s) ppm. ^{13}C NMR δ: 121.4 (q, CF_3, $^1J(C\text{–}F) = 277$ Hz); 128.1 (s, CH); 132.6 (m, $\underline{C}\text{–}CF_3$) ppm.

5,6-Bis(trifluoromethyl)-1,1,3,3-tetrafluoro-1,3-dihydroisobenzofuran (**4**) (nc) was also obtained as white crystals (3.6 g, purity 99.5%), m.p., 76.5–77 °C. Analysis: Found: F, 57.8%. $C_{10}H_2F_{10}O$ requires: F, 57.9%. ^1H NMR δ: 9.19 (s) ppm. ^{19}F NMR δ: 60.2 (s, CF_3); 70.1 (s, CF_2) ppm. ^{13}C NMR δ: 121.5 (q, CF_3, $^1J(C\text{–}F) = 278$ Hz); 125.0 (t, CF_2, $^1J(C\text{–}F) = 261$ Hz); 123.1 (s, CH); 136.2 (t, $\underline{C}\text{–}CF_2$, $^2J(C\text{–}F) = 32.6$ Hz); 134.4 (m, $\underline{C}\text{–}CF_3$) ppm. Compounds **3** and **4** are volatile and sublime at ambient temperature.

*Chemical purification of compound **3***

A product containing compounds **3**, **4** and **5** (28 g) was mixed with concentrated sulphuric acid (30 ml) and heated in a stainless-steel autoclave at 160–170 °C for 3 h, then poured into ice water. A solid material was extracted with diethyl ether (3 × 100 ml), the extract washed with 5% aqueous potassium hydroxide (2 × 70 ml) and water, and dried over $MgSO_4$. The solvent was evaporated under atmospheric pressure on a water bath and the solid residue was steam-distilled and dried over P_4O_{10} to give **3** of >99.5% purity (17.2 g, 72% recovery).

The alkaline solution was acidified with concentrated hydrochloric acid, extracted with ether (3 × 100 ml) and the extract dried over $MgSO_4$. Evaporation

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*A nickel autoclave was used for runs carried out above 200 °C.

of the solvent gave a mixture of benzenepolycarboxylic acids (6.6 g) as a white solid.

*4,5-Bis(trifluoromethyl)phthalic acid (**6**)*

Compound **4** (4 g, 0.012 mol) and concentrated sulphuric acid (15 ml) were heated in a stainless-steel autoclave at 160 °C for 3 h, then poured into water and the resulting solution extracted with diethyl ether (5×50 ml). The extract was washed with water, concentrated to half its volume and vigorously agitated with 5% aqueous potassium hydroxide (2×50 ml). The alkaline solution was acidified with concentrated hydrochloric acid and then extracted with diethyl ether (5×50 ml). The solid residue obtained after evaporating off the ether on a rotary evaporator was dried over P_4O_{10} and afforded **6** as a white powder (3.5 g, 95%), m.p., 202–206 °C (ref. [9], m.p., 228 °C). Analysis: Found: C, 39.8; H, 1.3; F, 32.95%. $C_{10}H_4F_6O_4$ requires: C, 39.75; H, 1.3; F, 33.1%. ^{1}H NMR (in DMSO-d_6) δ: 8.29 (s); 13.8 (br) ppm. ^{19}F NMR (in DMSO-d_6) δ: 57.9 (s) ppm. ^{13}C NMR (in DMSO-d_6) δ: 122.1 (q, CF_3, ^1J(C–F)=276 Hz); 128.2 (m, $\underline{C}$–CF_3); 128.5 (s, CH); 137.0 (s, $\underline{C}$–COOH); 166.3 (s, COOH) ppm. IR (Nujol) (cm^{-1}): 1730 [ν(COOH)]; 1440 [ν(arom.)].

*Reaction of 4,5-bis(trifluoromethyl)phthalic acid (**6**) with sulphur tetrafluoride*

Acid **4** (3.2 g, 0.0105 mol), anhydrous hydrogen fluoride (2 ml, 0.1 mol) and sulphur tetrafluoride (10 g, 0.093 mol) were placed in a 30 ml stainless-steel autoclave, heated at 170 °C for 16 h and the reaction product then worked-up as described above for anhydride **2**. The white crystals obtained after steam distillation (3.4 g, 93%) were found by GLC methods to contain 89.5% of compound **3** and 10.5% of compound **4**.

References

1 W. Dmowski and J. Porwisiak, *13th Int. Symp. Fluorine Chem.*, Bochum (Germany), Sept. 2–6, 1991, Abstract B58; *J. Fluorine Chem.*, *54* (1991) 120; *J. Fluorine Chem.*, *59* (1992) 321.
2 W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, *82* (1960) 543.
3 J. Porwisiak and W. Dmowski, *J. Fluorine Chem.*, *51* (1991) 131.
4 A. I. Burmakov, L. A. Alekseeva and L. M. Yagupol'skii, *Zh. Org. Khim.*, *6* (1970) 2498.
5 L. M. Yagupol'skii, A. I. Burmakov, L. A. Alekseeva and B. V. Kunshenko, *Zh. Org. Khim.*, *9* (1973) 689.
6 A. I. Burmakov, L. A. Alekseeva and L. M. Yagupol'skii, *Zh. Org. Khim.*, *6* (1970) 144.
7 V. G. Lukmanov, L. A. Alekseeva and L. M. Yagupol'skii, *Zh. Org. Khim.*, *13* (1977) 2129.
8 W. Dmowski and J. Wielgat, *J. Fluorine Chem.*, *37* (1987) 429.
9 G. Pawlowski and H. Hanach, *Synth. Commun.*, *11* (1981) 351.