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Polyhaloaromatics. Part VI*. The first synthesis of perfluorodurene

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Abstract

The final stages in preparation of pure perfluorodurene (**3**) are described. The synthesis involves cleavage of perfluoro-1,3,5,7-tetrahydrobenzo[1,2-*c*:4,5-*c*′]difuran (**1**) with SbF_5 and anhydrous HF and treatment of the resulting mixture of perfluoro-2,5-dimethylterephthaloyl difluoride (**2a**) and perfluoro-2,4-dimethylisophthaloyl difluoride (**2b**) with SF_4 and HF at 300–330 °C. Compound **3** has been characterised by elemental analysis, ^{19}F and ^{13}C NMR spectroscopy and mass spectrometry.

Introduction

The general route to aromatic fluorocarbons, including perfluorinated methylbenzenes, is a cobalt trifluoride fluorination of the appropriate aromatic or cycloaliphatic hydrocarbons, followed by defluorination of perfluoroalicyclic compounds with a hot metal, preferably iron [1]. More recently, a method for the synthesis of perfluoroalkylbenzenes by reacting perfluorobenzene with difluorocarbon sources (tetrafluoroethylene, PTFE) at 500–700 °C has been developed [2]. However, to the best of our knowledge, perfluorodurene has been obtained by none of these methods.

Perfluorodurene has been found recently to be the main product of the reaction of difluoropyromellitic acid with an SF_4/HF mixture at 330 °C, but because of the complexity of the mixture of products it was not isolated [3]. The present paper reports the first preparative-scale synthesis of pure perfluorodurene.

Results and discussion

In our approach to perfluorodurene, the starting material was perfluoro-1,3,5,7-tetrahydrobenzo[1,2-*c*:4,5-*c*′]difuran (**1**). This compound was obtained previously in two steps from dichloropyromellitic acid by treatment with sulphur tetrafluoride followed by halogen exchange with potassium fluoride in sulpholane [4]. Heating compound **1** with antimony pentafluoride and an excess of anhydrous hydrogen fluoride at 150 °C for 10 h resulted in total cleavage of both tetrafluoroether rings to give a 1:1 mixture of perfluoro-2,5-dimethylterephthaloyl difluoride (**2a**) and perfluoro-2,4-dimethylisophthaloyl difluoride (**2b**). The fluorocarbonyl groups in **2a** and **2b** are very resistant towards further fluorination with sulphur tetrafluoride, but after prolonged treatment with an SF_4/HF reagent at 300–330 °C both compounds were fully converted into perfluorodurene (**3**) (Scheme 1).

Phthaloyl difluorides **2a** and **2b** are unusually resistant towards water; they were purified by steam distillation without hydrolysis. The **2a**/**2b** ratio was determined from the integrated ^{19}F NMR spectrum of the mixture.

Perfluorodurene (**3**) was also purified by steam distillation. This compound, as well as the acid fluorides **2**, is sufficiently volatile such that there was no need to use external steam. Perfluorodure (**3**) was obtained in a 60% overall yield and in high purity as a white, nicely crystalline, volatile compound; the IR spectrum showed only a trace absorption corresponding to the fluorocarbonyl group. Elemental analysis, ^{19}F and ^{13}C NMR spectroscopy, and mass spectrometry all gave satisfactory proof of the identity of compound **3**.

Experimental

Melting points were determined in capillaries and are uncorrected. The ^{19}F and ^{13}C NMR spectra were recorded, respectively, at 470 MHz with a Brücker 500 MHz spectrometer and at 50 MHz with a Varian 200 MHz spectrometer, both in $CDCl_3$ solutions. Mass spectra were obtained at 70 eV with an AMD-604 spectrometer and the IR spectra were measured with a Beckmann Acculab instrument.

Perfluoro-2,5-dimethylterephthaloyl difluoride (2a) and perfluoro-2,4-dimethylisophthaloyl difluoride (2b)

Liquid anhydrous hydrogen fluoride (15 ml) and antimony pentafluoride (0.8 ml, 2.4 g, 11 mmol) were

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*For Part V, see ref. 4.

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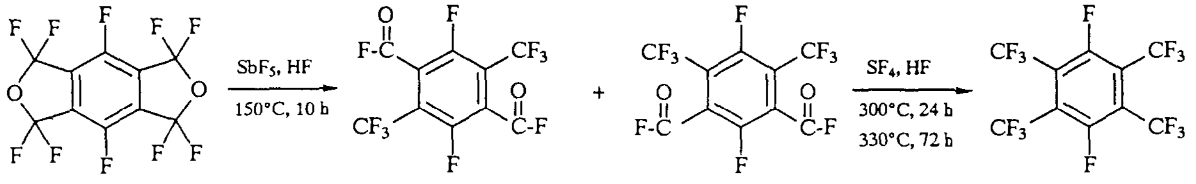

1 **2a** **2b** **3**

Scheme 1.

placed in a 30 ml stainless-steel pressure tube precooled to *c.* −5 °C and then compound **1** (6.84 g, 20 mmol) was added. The tube was sealed and heated at 150 °C for 10 h in a rocking oven. Excess hydrogen fluoride was released at room temperature, the tube was cooled to 0 °C, opened, and the dark contents poured into ice/water (50 ml). The mixture was neutralized with aqueous ammonia to pH = 6.5 and subjected to steam distillation (no external steam was required). The white, crystalline product was filtered off and dried over P_4O_{10} (5 g, 73%). The integrated ^{19}F NMR spectrum revealed that the product was a 1:1 mixture of perfluoro-2,5-dimethylterephthaloyl difluoride (**2a**) and perfluorodimethylisophthaloyl difluoride (**2b**) m.p. 68–80 °C. Analysis: Calc. for $C_{10}F_{10}O_2$: C, 35.1; F, 55.54%. Found: C, 35.15; F, 55.50%. ^{19}F NMR: in agreement with previously reported spectra [3]. ^{13}C NMR δ: compound **2a**: 119.8 (q, $^1J_{C,F}=275$ Hz, CF_3); 122 (C-1, C-2, C-4 and C-5); 149.2 (d, $^1J_{C,F}=353.5$ Hz, COF); 152.7 (d, $^1J_{C,F}=266.5$ Hz, C-3 and C-6) ppm. Compound **2b**: 119.8 (q, $^1J_{C,F}=275$ Hz, CF_3); 122 (C-1, C-2, C-4 and C-5); 149.2 (d, $^1J_{C,F}=353.5$ Hz, COF); 151.5 (d, $^1J_{C,F}=260$ Hz, C-3); 154.0 (d, $^1J_{C,F}=271.4$ Hz, C-6) ppm. IR (CCl_4) (cm^{-1}): 1860 (vs).

Perfluorodurene (3) (nc)

A mixture consisting of acid fluorides **2a** and **2b** (3.9 g, 11 mmol), anhydrous hydrogen fluoride (2 ml, 100 mmol) and sulphur tetrafluoride (7 g, 65 mmol) was reacted in a 60 ml nickel autoclave at 300 °C for 24 h. The ^{19}F NMR and IR spectra of a sample taken from the autoclave (after reducing the pressure) revealed only partial conversion of the COF groups to CF_3 groups. Hydrogen fluoride (3 ml) and sulphur tetrafluoride (10 g, 93 mmol) were added again and the reaction continued at 300 °C for 24 h and then at 330 °C for 72 h. The product was poured into ice/water, neutralized with ammonia and steam distilled (no external steam was required). The white crystals were filtered and dried over P_4O_{10} to give pure perfluorodurene (**3**) (trace absorption of the COF group only) (3.1 g, 82.4%), m.p. 64–64.5 °C. Analysis: Calc. for $C_{10}F_{14}$: C, 31.1; F, 68.9%. Found: C, 30.9; F, 68.7%. ^{19}F NMR: in agreement with the previously reported spectrum [3]. ^{13}C NMR δ: 120.0 (q, $^1J_{C,F}=278.6$ Hz, CF_3); 123.8 (broad, C-1, C-2, C-4 and C-5); 154.5 (d, $^1J_{C,F}=272$ Hz, C-1 and C-6). MS *m/z*: 386 (45%, M^+); 367 (65%, M^+-F); 336 (12%, $C_9F_{12}^+$); 317 (100%, $C_9F_{11}^+$); 298 (10%, $C_9F_{10}^+$); 286 (6%, $C_8F_{10}^+$); 267 (40%, $C_8F_9^+$); 248 (12%, $C_8F_8^+$); 229 (4%, $C_8F_7^+$); 217 (3%, $C_7F_7^+$); 198 (7%, $C_7F_6^+$); 179 (8%, $C_7F_5^+$); 141 (2%, $C_7F_3^+$); 69 (15%, CF_3^+).

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