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POLYHALOAROMATICS. PART II. SYNTHESIS OF OCTAFLUORO-1,3-DIHYDROISOBENZOFURAN AND ITS CONVERSION TO TETRAFLUOROTEREPHTHALIC ACID

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SUMMARY

A high yield preparation of the title compound via treatment of 4,5,6,7-tetrachloro-1,1,3,3-tetrafluoro-1,3-dihydroisobenzofuran with potassium fluoride in sulpholane is described. Hydrolysis of octafluoro-1,3-dihydroisobenzofuran with concentrated sulphuric acid provides a new and efficient route to tetrafluoroterephthalic acid.

INTRODUCTION

The chemistry of perfluoroaromatic and perfluoroheterocyclic compounds, albeit highly developed, is based on a rather limited number of starting materials. Thus, hexafluorobenzene, octafluorotoluene, octafluoronaphthalene, or pentafluoropyridine are the precursors of most polyfluoroaromatics [1-4]. Therefore, there is still a need to search for new simple perfluoroaromatic compounds which can be easily prepared from accessible and inexpensive materials. This paper describes a high-yield preparation of the new compound octafluoro-1,3-dihydroisobenzofuran, which deserves attention as a reactive intermediate for per- and polyfluoroaromatic chemistry.

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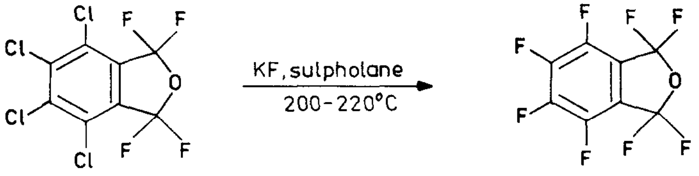
RESULTS AND DISCUSSION

In the preceding paper [5] we reported an efficient one-step synthesis of 4,5,6,7-tetrachloro-1,1,3,3-tetrafluoro-1,3-dihydroisobenzofuran (1) from tetrachlorophthalic anhydride. The aromatic ring fluorines in 1 easily undergo substitution by fluorine atoms. Thus, using a four-fold excess of potassium fluoride in sulpholane all four chlorines were substituted to give octafluoro-1,3-dihydroisobenzofuran 2 in a 83 - 92% yield. The halogen exchange reaction proceeded at 200 - 220°C with a noticeable exothermic effect and was practically complete in 15 minutes. The large excess of potassium fluoride was found to be necessary to achieve the total halogen exchange. A decrease of the KF to 1 ratio (two-fold excess) resulted in formation of a certain amount (ca. 20%) of a monochloroheptafluoro-derivative (GLC- -MS identification, only). Compound 2 is easily removable from the reaction mixture by distillation.



1

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The structure of octafluoro-1,3-dihydroisobenzofuran (2) was deduced from its elemental analysis, mass spectrum, and ^{19}F and ^{13}C NMR spectra. The chemical shifts of the aromatic ring fluorines are consistent with those reported for a number of ortho-substituted tetrafluorobenzenes [6,7]; the most high field signals are usually those of fluorines meta to a substituent. The assignment of signals of the C-4, C-7 and C-5, C-6 aromatic ring carbons* was based on chemical shift data reported for numerous perfluoroaromatics [8].

On treatment with hot concentrated sulphuric acid, octafluoro-1,3-dihydroisobenzofuran (2) readily undergoes carbon-oxygen bond

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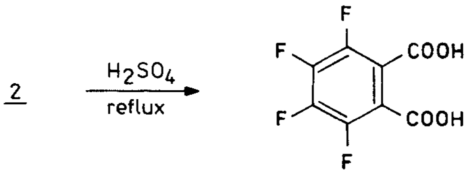
* Numbering of the ring carbon atoms is consistent with the IUPAC rules.

cleavage to form tetrafluorophthalic acid (3) in nearly quantitative yield.



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The overall yield (*ca.* 68%) of tetrafluorophthalic acid from tetrachlorophthalic anhydride via compounds 1 and 2 is nearly four times as high as in the early method [9] and is comparable to the more recent route involving tetrahalophthaloyl halides [10].

EXPERIMENTAL

Boiling and melting points are uncorrected. ^{19}F and ^{13}C NMR spectra were recorded with a Brucker MSL 300 spectrometer and the mass spectrum was obtained with a Finnigan 8200 instrument at 70 eV. The IR spectrum of compound 2 was measured with a Beckmann Acculab.

Potassium fluoride (FLUKA A.G.,pure grade) was dried at 200°C for 48 hours and used while hot. Sulpholane was freshly vacuum distilled.

Preparation of octafluoro-1,3-dihydroisobenzofuran (2) (nc).

The halogen exchange reaction was carried out in an electrically-heated 250 ml cylindrical glass reactor (SOVIREL) fitted with a strong anchor-shaped stirrer, thermometer, reflux condenser, and a gas inlet valve. The stirrer and the thermometer were placed as close as possible to the bottom of the reactor. The gas inlet valve was connected to an argon cylinder, and the reflux condenser outlet was protected with a tube filled with blue silica-gel. During the reaction the gas inlet was closed.

Compound 2 (30 g, 0.091 mole), potassium fluoride (80 g, 1.38 mole), and sulpholane (170 ml) were placed in the reactor and heated slowly with stirring. When the temperature reached *ca.* 210 - 220°C visible exothermic effect occurred, the viscosity of the reaction mixture increased, and within a few minutes material appeared in the reflux condenser. At this moment the heater was switched off until the rapid reaction ceased, then heating was continued to maintain the reaction temperature at 220 - 230°C for half an hour, during which period the stirring speed was controlled so as not allow the boiling to occur. Then, after the reaction mixture had cooled to ca. 180°C, the reflux condenser was replaced with a simple distillation system; the temperature was then increased stepwise up to 250°C (vigorously stirring was maintained) thus allowing the product to distill off (vapour temperature 128 - 132°C). At the end of the distillation a slow stream of argon was introduced into the reactor to sweep out the residual product. The distillate (20 - 22 g, 83 - 92%) was octafluoro-1,3-dihydroisobenzofuran (2) of 98 - 99% purity (GLC estimate; 3% Silicon Oil SE-52 on Chromosorb G).

Rectification through a Fischer-type column (BÜCHI) gave compound 2 of 99.9% purity as a colourless liquid with delicate acidic odour; b.p. 128.3°C (Found: C, 36.3; F, 57.5%. C_8F_8O requires: C, 36.4; F, 57.55%); ^{19}F NMR ($CDCl_3$, CCl_3F): 67.4 ppm (s, 4F, CF_2 groups), 138.3 ppm(2F at positions 4 and 7), 143.0 ppm(2F at positions 5 and 6); ^{13}C NMR ($CDCl_3$, TMS): 116.1 ppm(tm, $^2J_{C-F}$=2.2 Hz, C-8 and C-9), 123.7 ppm(t, $^1J_{C-F}$=261.3 Hz, C-1 and C-3), 142.3 ppm(dm, $^1J_{C-F}$=261 Hz, C-5 and C-6), 144.5 ppm(dm, $^1J_{C-F}$=265 Hz, C-4 and C-7); MS: m/z 264(35%)M^+, 245(20)M^+-F, 217(100)M^+-CFO, 198(13)M^+-CF_2O, 179(12)M^+-CF_3O, 148(21)$C_6F_4{}^+$; IR(film): ν(arom) = 1525 cm^{-1} (vs).

Hydrolysis of compound 2 to tetrafluorophthalic acid (3).

Octafluoro-1,3-dihydroisobenzofuran (2) (10.6 g, 0.04 mole) and concentrated sulphuric acid (15 ml) were stirred together at reflux temperature until a homogeneous solution formed (3 hours). The solution was poured into iced water (150 ml) and extracted with diethyl ether (5 x 60 ml). The extract was condensed to a half of its initial volume and shaken well with 5% aqueous sodium hydroxide (100 ml). The aqueous layer was separated, acidified with hydrochloric acid, and extracted with diethyl ether (5 x 40 ml). Evaporation of the ether gave tetrafluorophthalic acid (9 g, 94%), which was dried over phosphorus pentoxide for 48 hours to give material with m.p. 154-156°C (reported m.p. 154-156°C [11]; 155-156°C [12]).

ACKNOWLEDGMENT

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