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New pentafluoro-λ^6-sulfanyl (SF_5) perfluoroalkyl benzene derivatives

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Abstract

Preparation of the following new SF_5-perfluoroalkyl benzene derivatives, *m*-$SF_5CF_2CF_2C_6H_4X$ (X = NO_2, NH_2, OH, I, $NHCOCH_3$, SO_2Cl, SO_3H, SO_3K) has been achieved. The new compounds were characterized by their respective IR, NMR and HRMS or elemental analysis. © 2002 Published by Elsevier Science B.V.

Keywords: Pentafluorothiofluoroalkyl benzene derivatives; IR and NMR spectroscopy; HRMS and MS

1. Introduction

Recently, we reported the synthesis of a new class of ω-SF_5-perfluoroalkyl benzene compounds, $SF_5(CF_2)_nC_6H_5$ ($n = 2, 4, 6, 8$) [1]. As part of our ongoing research into SF_5-hydrocarbons, we have developed the chemistry of corresponding $SF_5(CF_2)_n$-aromatic compounds; in particular, we have used $SF_5CF_2CF_2C_6H_5$ as the representative of this new class of compounds. In view of the great importance of fluorinated aromatic compounds and the properties associated with the SF_5 group, these new derivatives will serve as a springboard for the development of new and improved pharmaceuticals, agricultural chemicals and polymeric materials. SF_5-aromatic compounds ($SF_5C_6H_4X$) were first prepared by Sheppard in 1962 [2] and more recently by Bowden et al. [3]; one of the major drawbacks associated with the synthetic pathways used by these authors is the use of extremely strong oxidizing agents such as AgF_2 and F_2.

2. Results and discussion

We have found that the $SF_5CF_2CF_2C_6H_5$, **1**, synthon is an excellent reagent for preparing a number of derivatives. As was expected, the $SF_5CF_2CF_2$-grouping is *meta* directing in electrophilic substitution reactions. This is borne out in the nitration and chlorosulfonation described below. The nitration of **1** was accomplished by using 90% nitric acid and low temperatures (0–5 °C). The product, *m*-$SF_5CF_2CF_2C_6H_4NO_2$, **2**, was reduced using $SnCl_2$ giving *m*-$SF_5CF_2CF_2C_6H_4NH_2$, **3**. During the reaction, a complex amine chlorostannate precipitate was formed.

In order to obtain *m*-$SF_5CF_2CF_2C_6H_4X$ (I, OH) derivatives, the diazonium salt intermediates were prepared:

$$m\text{-}SF_5CF_2CF_2C_6H_4NH_2 + NaNO_2 + 2HCl \rightarrow [m\text{-}SF_5CF_2CF_2C_6H_4N_2{}^+Cl^-] + NaCl + 2H_2O$$

Its preparation was achieved at low temperatures (0–5 °C); during the course of the reaction, precipitation of the corresponding amine hydrochloride followed by dissolution and the formation of a light yellow solution were observed. This solution was then used to prepare the iodo derivative **4**:

$$m\text{-}SF_5CF_2CF_2C_6H_4N_2{}^+Cl^- + KI \rightarrow m\text{-}SF_5CF_2CF_2C_6H_4I + N_2 + KCl$$

In a like manner, using sulfuric acid the phenol derivative **5**, an orange oil, was prepared by heating:

$$m\text{-}SF_5CF_2CF_2C_6H_4N_2{}^+HSO_4{}^- + H_2O \rightarrow m\text{-}SF_5CF_2CF_2C_6H_4OH + N_2 + H_2SO_4$$

A major by-product thought to be 2-nitro-5-(1,1,2,2-tetrafluoro-2-SF_5-ethyl)-phenol was also isolated.

The anilide, *m*-$SF_5CF_2CF_2C_6H_4NHC(O)CH_3$, **6**, was formed from **3** using acetic anhydride catalyzed with sulfuric acid. The sulfonyl chloride derivative, *m*-$SF_5CF_2CF_2C_6H_4SO_2Cl$, **7**, was prepared by treating **1** with a large excess of chlorosulfonic acid:

$$m\text{-}SF_5CF_2CF_2C_6H_5 + xClSO_3H \rightarrow m\text{-}SF_5CF_2CF_2C_6H_4SO_2Cl + H_2SO_4 + HCl$$

The base hydrolysis of **7** gave the corresponding potassium sulfonate salt **8** which when passed through an

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ion-exchange column gave the corresponding sulfonic acid **9**.

The infrared (IR) spectral data for the new compounds **2–9** are listed in Section 3. Since all compounds contained the $SF_5CF_2CF_2$ group, bands characteristic for this group were identified in each of the spectra. The IR spectra of all new compounds showed very intense bands in the 800–900 cm^{-1} region and are attributed to the S–F stretching modes; bands in the 605–613 cm^{-1} region are due to one of the S–F deformation modes. Cross et al. have reported the SF_5 stretching frequency as a strong band in the 850–920 cm^{-1} region with a deformation mode near 600 cm^{-1} [4]. The strong absorption peaks in the 1100–1300 cm^{-1} region were attributed to C–F stretching vibrations. The CF_2 groups have strong absorption bands in the 1100–1400 cm^{-1} region [5].

The ^{19}F NMR results for compounds **2–9** are included in Table 1. The eight new compounds contain the $SF_5CF_2CF_2$ group and their ^{19}F NMR spectra showed expected similarities [6–8]. The axial fluorine (A) of the SF_5 group (AB_4 pattern) appears as a pentet or a nine-line pattern in which either each line is further split into a triplet or appears as a multiplet and is found in the range of 65.0–66.7 ppm. The splitting of the A fluorine into a triplet was caused by long range couplings with the fluorine atoms of the neighboring $CF_2{}^a$ groups. The equatorial fluorines (B_4) appeared as a doublet of a pentet or a doublet of a multiplet between 44.8 and 45.6 ppm. Long range coupling to the CF_2 groups was also observed for the equatorial fluorines. The experimental coupling constants for the fluorinated group $CF_2{}^bCF_2{}^a{-}SF_4{}^BF^A$ (see Table 1) are: J_{AB} ranges between 145 and 147 Hz and for J_{Aa} between 3.8 and 4.8 Hz. Additional coupling constants, J_{Ba} and J_{Bb} range between 12.7 and 15.2 Hz. The values for the chemical shifts and coupling constants agree with reported values for other $SF_5CF_2CF_2$ derivatives [1,7,8]. The chemical shifts for the CF_2 fluorines adjacent to the SF_5 group ranged between -93.5 and -98.7 ppm and were identified as multiplets or doublets of a pentet; the chemical shift values compared well with published data [7,8]. The chemical shifts for the internal CF_2 groups that were resolved showed pentets ranging from -113.7 to -111.3 ppm. The ^1H NMR data for aromatic compounds are summarized in Table 1. The protons have chemical shifts ranging between 6.96 and 8.51 ppm and appear as a singlet (H2), triplet (H5), and two doublets (H4, H6); the chemical shifts and splitting patterns are in agreement with values expected for 1,3-disubstituted benzene derivatives. The experimental coupling constants between the ring protons ranged between 7.6 and 8.2 Hz. The protons of the NH_2 group resonate as a broad singlet at 3.6 ppm.

The major mass spectral peaks for each new compound **2–7** are listed in Section 3. In addition to the parent ion, peaks such as $(M{-}SF_5)^+$, $(M{-}SF_5CF_2)^+$, $SF_5{}^+$, $C_6H_4CF_2{}^+$, $C_6H_5CF^+$ or $C_6H_4CF^+$, $C_6H_4{}^+$, $C_2F_4C_2H^+$, $CF_2C_2H^+$, $SF_3{}^+$ and $CF_2{}^+$ were observed with varying intensities for each compound. In the mass spectrum of compound **2**, peaks at $m/e = 30$ (NO^+) and $m/e = 46$ ($NO_2{}^+$) were found; additional peaks at $m/e = 176$, 126 and 76 were also observed due to the $(M{-}SF_5{-}NO_2)^+$, $(M{-}SF_5CF_2{-}NO_2)^+$ and $(M{-}SF_5CF_2CF_2{-}NO_2)^+$ fragments. The spectra of aromatic halogen compounds have characteristic peaks due to the loss of a halogen radical; for compound **4**, peaks at $m/e = 303$ and 126 due to $(M{-}I)^+$ and $(M{-}SF_5CF_2{-}I)^+$ were found. The mass spectrum for (**7**) contained, in addition to a weak parent molecular ion, peaks at $m/e = 367$, 303, 176, 174 and 126 which were attributed to the $(M{-}Cl)^+$, $(M{-}SO_2Cl)^+$, $(M{-}SF_5{-}SO_2Cl)^+$, $(M{-}SF_5CF_2{-}O{-}Cl)^+$ and $(M{-}SF_5CF_2{-}SO_2Cl)^+$ fragments; the chlorine isotopic 3:1 doublet was observed for all fragments containing chlorine. In lieu of elemental analyses, the HRMS of the parent ions for **4–6** were obtained.

3. Experimental details

The reactants, benzene, 99.9% HPLC grade, chlorosulfonic acid, 99%, HSO_3Cl, 99%, and nitric acid (90% ACS reagent) were used as obtained from Aldrich Chemical Co. Anhydrous diethyl ether, methylene chloride (high purity solvent), sodium nitrite, $SnCl_2{\cdot}2H_2O$ and hydrochloric acid (36.5–38.0%) were obtained from J.T. Baker Co. and used without further purification. Potassium iodide was used as obtained from Sigma Chemical Co. Sodium hydroxide pellets were used as obtained from EM Science. In addition to the purchased chemicals listed above, the compound $SF_5CF_2CF_2C_6H_5$ was prepared according to the literature [1].

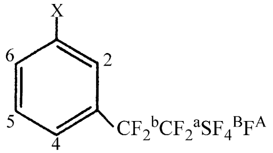
IR spectra were obtained using a Perkin-Elmer 2000 FTIR system operating at 2.0 cm^{-1} resolution. For liquid and solid samples, KBr plates were used. NMR spectra were obtained using a Varian EM-390 spectrometer operating at 84.6 MHz for ^{19}F and/or a Bruker AMX-400 spectrometer operating at 376.5 MHz for ^{19}F, 400.1 MHz for ^1H and/or a Bruker 500. The standards, $CFCl_3$ (Freon-11) and $(CH_3)_4Si$ were used. The solvents used were $CDCl_3$ or D_2O.

Mass spectra were obtained using a Hewlett-Packard HP5890 series II gas chromatograph (GC) equipped with a HP5970 mass selective detector operated at 70 eV and a 30 m DB-5 column. For a standard run, the column was maintained at 50 °C for 2 min, followed by an increase in temperature of 11 °C min^{-1} until the temperature of the column reached 280 °C. The precise molecular weights determination (HMRS) for compounds **4–6** were obtained on a Kratos MS 50TC; chemical ionization with methane. The elemental analysis determinations were performed by Mikroanalytisches Laboratorium Beller in Göttingen, Germany.

3.1. Preparation of *m*-$SF_5CF_2CF_2C_6H_4NO_2$, 2

To 25 ml of 90% HNO_3 in a 100 ml round-bottomed flask cooled to 0–5 °C was added dropwise, with stirring, 3.00 g

Table 1
Proton and fluorine NMR data[a]



	δ_2	δ_4	δ_5	δ_6	φ_A	φ_B	φ_a	φ_b
X = NO_2 (b), (d)	8.51, s, overlap with H4	8.50, d, $J_{45} = 7.93$, H2 + H4 = 2.0H	7.80, t, $J \approx 7.8$, 1.0H	7.98, d, $J_{56} = 7.72$, 1.0H	65.5, p–t, $J_{AB} = 147$, $J_{Aa} = 4.5$, 1.0F	45.6, d–p, 4.0F	−94.1, d–p, $J_{Aa} \approx 4$, $J_{aB} \approx 14$, 2.0F	−111.3, p, $J_{bB} \approx 14$, 2.0F
X = NH_2[b] (a), (d)	6.87, s, overlap with H4	6.85, d, $J_{45} \approx 8.2$, H2 + H4 = 2.0H	6.96, t, $J_{45} = J_{56} = 7.81$, 1.0H	6.97, d, $J_{56} = 7.81$, 1.0H	66.7, p–t (br.), $J_{AB} = 146$, $J_{Aa} \approx 4$, 1.0F	45.3, d–m, 4.0F	−93.5, d–p (br.), 2.0F	−111.4, p (br.), 2.0F
X = I (a), (d)	7.93, s, overlap with H4	7.92, d, $J_{45} \sim 7.8$, H2 + H4 = 2.0H	7.25, t, $J = 7.81$, 1.0H	7.58, d, $J = 7.8$, 1.0H	66.1, p–m, $J_{AB} = 147$, 1.0F	45.4, d–p, 4.0F	−93.8, d–p, $J_{Aa} = 3.8$, $J_{aB} \approx 14$, 2.0F	−111.6, p, $J_{bB} \approx 14$, 2.0F
X = OH (a), (e)	7.07, s, 1.0H	7.04, d (br.), $J_{45} = 8.20$, 1.0H	7.38, t, $J = 8.01$, 1.0H, J = average of $J_{45} + J_{56}$	7.19, d, $J_{56} = 7.81$, 1.0H	66.0, t, nine lines, $J_{AB} = 147$, $J_{Aa} = 4.8$, 1.0F	45.7, skewed d–m, 4.0F	−95.0, d–p, $J_{Aa} = 4.8$, $J_{aB} = 12.0$, 2.0F	−112.3, p, $J_{bB} = 12.7$, 2.0F
X = NHAc[c] (a), (e)	7.73, s, 1.0H	7.81, d, $J_{45} = 7.81$, 1.0H	7.45, t, $J = 7.80$, 1.0H	7.34, d, $J_{56} = 7.81$, 1.0H	66.7, nine lines (br.), 1.0F, $J_{AB} = 146$	45.3, skewed d–m, 4.0F	−93.5, m, poorly resolved, 2.0F	−111.4, poorly resolved, 2.0F
X = SO_2Cl (a), (e)	8.30, s, overlap with H4	8.31, d, $J_{45} = 7.82$, H2 + H4 = 2.0H	7.87, t, $J = 7.7$, 1.0H, J = average of $J_{45} + J_{56}$	8.02, d, $J_{56} = 7.63$, 1.0H	65.3, p, $J_{AB} = 147$, 1.0F	45.5, d–p, 4.0F	−94.2, p, $J_{aB} = 13.5$, 2.0F	−111.6, p, $J_{bB} = 13.5$, 2.0F
X = SO_3H (a), (e)	7.97, s, 1.0H	7.54, d, $J_{45} = 7.81$ 1.0H	7.45, t, $J_{45} = J_{56} = 7.81$	7.92, d, $J_{56} = 7.81$, 1.0H	65.8, nine lines, $J_{AB} = 146$, 1.0F	44.8, skewed d–m, 4.0F	−95.8, not resolved, 2.0F	−113.0, not resolved, 2.0F
X = SO_3K (a), (e)	8.10, s, overlap with H4	8.07, d, $J_{45} = 7.81$, H2 + H4 2.0H	7.74, t, J = average of $J_{45} + J_{56} = 7.9$, 1.0H	7.89, d, $J \approx 7.7$, 1.0H	66.6, nine lines, b, $J_{AB} = 145$, 1.0F	45.3, skewed d–m, 4.0F	−98.7, d–p, $J_{aB} = 15.2$, $J_{Aa} = 4.6$, 2.0F	−113.7, p, $J_{bB} = 12.7$, 2.0F

[a] ^1H NMR spectrum at: (a) 500 MHz; (b) 400 MHz; (c) 90 MHz. ^{19}F NMR spectrum at: (d) 376.5 MHz; (e) 84.7 MHz.

[b] $\delta_{NH_2} = 3.6$, broad s, 2.1H.

[c] $\delta_{NH} = 7.7$, broad s, 0.8H.

(9.87 mmol) of $SF_5CF_2CF_2C_6H_5$, **1**. After 2 h of stirring, the mixture was poured into 50 ml of ice water and extracted three times (75 ml) with methylene chloride. The extract was dried ($MgSO_4$), the solvent distilled away at atmospheric pressure and low-pressure distillation gave 2.82 g (8.08 mmol) of a light yellow liquid *m*-$SF_5CF_2CF_2C_6H_4NO_2$, boiling point 134–136 °C at 18 Torr. The yield of the reaction was 82%.

The IR spectrum for **2** shows the following peaks (cm^{-1}): 3099 (mw), 2886 (w), 1984 (vw), 1932 (vw), 1840 (vw), 1814 (vw), 1762 (vw), 1623 (m), 1593 (w), 1539 (s), 1485 (mw), 1443 (mw), 1353 (s), 1298 (ms), 1267 (s), 1245 (m), 1201 (s), 1164 (ms), 1124 (s), 1111 (ms), 1087 (mw), 1070 (m), 1051 (w), 1004 (vw), 962 (w), 932 (mw), 880 (vs), 818 (s), 800 (s), 749 (ms), 717 (s), 687 (s), 668 (m), 650 (mw), 608 (s), 575 (s), 534 (vw), 498 (vw), 454 (vw), 418 (mw).

The major mass spectral peaks include (*m*/*z*, molecular ion, relative percentage): 349 (M^+, 4%); 222 ($M–SF_5^+$, 15%); 176 ($M–SF_5–NO_2^+$, 13%); 172 ($M–SF_5CF_2^+$, 100%); 145 ($CF_3C_6H_4^+$, 29%), 127 (SF_5^+, 10%); 126 ($CF_2C_6H_4^+$, 45%); 125 ($CF_2CF_2C_2H^+$, 19%); 114 ($CF_2C_5H_4^+$, 5%); 107 ($CFC_6H_4^+$, 8%); 89 (SF_3^+, 9%); 76 ($C_6H_4^+$, 4%); 75 ($CF_2C_2H^+$, 9%); 50 (CF_2^+, 6%); 30 (NO^+).

Analysis: calculated for $SF_5CF_2CF_2C_6H_4NO_2$: C, 27.51; H, 1.15%. Found: C, 27.81; H, 1.13%.

3.2. Preparation of *m*-$SF_5CF_2CF_2C_6H_4NH_2$, **3**

Into a 100 ml round-bottomed flask equipped with a Teflon-coated stirring bar, 25 ml of concentrated HCl and 7.11 g (31.5 mmol) of $SnCl_2{\cdot}2H_2O$ were added. The reagents were stirred and then 2.75 g (7.9 mmol) of *m*-$SF_5CF_2CF_2C_6H_4NO_2$ was added dropwise. The reaction mixture was stirred for 48 h at 75–80 °C (an additional 5.00 g (22.2 mmol) of $SnCl_2{\cdot}2H_2O$ was added after 24 h) and then stirred for an additional 24 h at room temperature. The reaction mixture was then added to about 50 ml of ice-cold water and neutralized with a concentration NaOH solution. The organic phase was extracted three times with diethyl ether (75 ml), washed with water and dried over magnesium sulfate. The ether was distilled away at atmospheric pressure. A low-pressure distillation gave 2.04 g (6.38 mmol) of a light yellow liquid *m*-$SF_5CF_2CF_2C_6H_4NH_2$, boiling point 116–118 °C/16 Torr. The yield of reaction was 81%.

The IR spectrum contains the following bands (cm^{-1}): 3484 (mw), 3399 (m), 3227 (w), 3071 (vw), 3031 (vw), 1627 (s), 1601 (m), 1499 (ms), 1465 (ms), 1388 (vw), 1322 (ms), 1309 (ms), 1233 (ms), 1202 (s), 1178 (m), 1154 (ms), 1137 (ms), 1112 (vs), 1072 (m), 1044 (w), 1028 (vw), 998 (mw), 968 (vw), 943 (mw), 875 (vs), 816 (ms), 799 (s), 767 (s), 727 (mw), 711 (m), 678 (ms), 662 (mw), 611 (ms), 580 (ms), 550 (m), 503 (w), 449 (mw), 416 (m).

The major mass spectral peaks include (*m*/*z*, molecular ion, relative percentage): 319 (M^+, 65%); 192 ($M–SF_5^+$, 14%); 173 ($M–SF_5–F^+$, 9%); 172 ($M–SF_5–HF^+$, 8%); 142 ($M–SF_5CF_2^+$, 100%); 140 ($M–SF_5CF_2–2H^+$, 5%); 127 (SF_5^+, 6%); 125 ($CF_2CF_2C_2H^+$, 6%); 114 ($CF_2C_5H_4^+$, 9%); 95 ($CFC_5H_4^+$, 5%); 89 (SF_3^+, 8%); 75 ($CF_2C_2H^+$, 5%); 71 ($C_4H_4F^+ < 6\%$); 65 ($C_5H_5^+$, 10%); 63 ($C_5H_3^+$, 5%); 39 ($C_3H_3^+$, 6%).

Analysis: calculated for $SF_5CF_2CF_2C_6H_4NH_2$: C, 30.09; H, 1.88; S, 10.03; F, 53.6%. Found: C, 30.33; H, 2.10; S, 9.69; F, 53.7%.

3.3. Preparation of *m*-$SF_5CF_2CF_2C_6H_4I$, **4**

m-$(SF_5CF_2CF_2)C_6H_4NH_2$ (1.65 g, 5.2 mmol) was diazotized at 0 °C in 30 ml of 6 N HCl by slowly adding a sodium nitrite solution (0.6 g in 7.5 ml of water). After complete addition, stirring was maintained for 30 min; a lightly yellow solution was obtained. A solution of KI (1.43 g in 5 ml of water), pre-cooled to 0 °C, was then slowly added. Stirring was maintained at 0 °C for 3 h, and after warming to ambient temperature, continued for another 18 h. Ether extraction (1×25 ml), and washing of the extract with water left, after removal of the solvent, 1 g of crude product; liquid (faint iodine discoloration) that was shown by GC–MS to be very pure.

Infrared spectrum (neat, KBr, cm^{-1}): 3071 (w), 1573 (w–m), 1475 (w–m), 1279 (m), 1261 (m), 1199 (s), 1161 (m), 1119 (s), 1062 (w–m), 1038 (w), 996 (w–m), 951 (w), 928 (w–m), 907 (m, sh), 875 (vs), 813 (s), 786 (m–s), 764 (m), 724 (s), 678 (m), 672 (w–m), 607 (vs).

Mass spectrum (DB5, 30 m, 50 °C: 2 min, then 11 °C $min^{-1} \rightarrow 280$ °C; mass, percent, fragment): 430, 52%, M^+; 303, 14, $(M–SF_5, I)^+$; 253, 100, $(M–CF_2SF_5)^+$; 127, 10, SF_5^+, I^+; 126, 15, $C_6H_4CF_2^+$; 107, 9, $C_6H_4CF^+$; 89, 5, SF_3^+; 75, 8, $C_6H_3^+$.

High resolution mass spectrum: $M^+ = 429.89320$. Calculated for $^{12}C_8{}^1H_4{}^{19}F_9{}^{127}I^{32}S$: $M = 429.89348$.

3.4. Preparation of *m*-$SF_5CF_2CF_2C_6H_4OH$, **5**

m-$(SF_5CF_2CF_2)$-aniline (1.10 g, 3.4 mmol) was diazotized at 0 °C in dilute H_2SO_4 (1.8 ml concentration $H_2SO_4 + 8$ ml H_2O), by adding over a 20 min period a solution of 0.54 g of $NaNO_2$ (7.8 mmol) in 2 ml of H_2O. The pale yellow solution containing shiny crystalline platelets was stirred at 0 °C for another 20 min; it was then added at this temperature in small portions during a 30 min period to a stirred mixture of 7 ml of concentration H_2SO_4 and 11 ml H_2O heated at 120 °C in a 50 ml round-bottomed flask. Gas was evolved upon addition after which a dark oil separated. After addition was completed, a reflux condenser was attached and the oil bath temperature raised to 140–145 °C and held at this temperature for 1 h. The mixture was cooled and finally chilled in an ice bath. Ether extraction (4×25 ml) produced, after evaporation, an orange oil. Thin-layer chromatography (Kieselgel, methylene chloride) showed several products to be present. Column chromatography (75 g silica gel, 7 cm i.d., CH_2Cl_2) gave, after a pale yellow forerun, an orange fraction (A, $R_\mathrm{f} = 0.9$) and a pale yellow fraction (B, $R_\mathrm{f} = 0.6$). The intermediate fractions with additional components were discarded.

Fraction B was shown by GC–MS analysis to be the phenol ($M^+ = 320$). Fraction B was again chromatographed with 15 g of silica gel; 330 mg of an orange oil, pure by thin-layer chromatography and GC–MS, was obtained (yield = 30%). IR spectrum (neat, KBr, cm^{-1}): 3700 (w), 3622 (w), 3352 (m–s, br.), 3073 (vw), 3046 (vw), 1612 (m), 1597 (m–s), 1490 (w–m), 1458 (s), 1343 (w), 1299 (s–vs), 1242 (w–m), 1203 (s–vs), 1160 (s), 1116 (s–vs), 1071 (w), 1045 (w), 1001 (vw–w), 967 (vw), 944 (w–m), 875 (vs), 816 (m–s), 800 (s–vs), 768 (vs), 710 (w–m), 702 (w–m), 677 (m), 659 (vw), 611 (m–s).

Mass spectrum (DB5, 30 m, 50 °C: 2 min, then 11 °C min^{-1} → 280°C; mass, percent, fragment): 320, 21%, M^+; 193, 12, $(M–SF_5)^+$; 174, 7, $(M–SF_5–F)^+$; 143, 100, $(M–CF_2SF_5)^+$; 127, 3, SF_5^+; 114, 10, $(C_2F_3S + H)^+$; 89, 14, SF_3^+.

High resolution mass spectrum: $M^+ = 319.99145$. Calculated for $^{12}C_8{}^1H_5{}^{19}F_9{}^{16}O^{32}S$: M = 319.99174.

3.4.1. Fraction A

After evaporation, 230 mg of a dark-orange oil was obtained. The highest mass in the mass spectrum was $M^+ = 365$, 48%; $(M–SF_5)^+ = 238$, 23%; $(M–SF_5CF_2)^+ = 188$, 100%. The GC spectrum contained a single band with $R_\mathrm{f} = 6.7$ min. The oil was dissolved in aqueous NaOH (orange color solution); from this solution, acidification with HCl produced a pale yellow emulsion. The acetylation ($Ac_2O + H_2SO_4$) of the oil gave a pale yellow solid, $R_\mathrm{f} = 0.9$ (Kieselgel, CH_2Cl_2). The GC spectrum contained a single band, $R_\mathrm{f} = 13.5$ min, $M^+ = 407$, 3%; $(MH–SF_5)^+ = 281$, 10%; $CH_3CO^+ = 43$, 100%.

^{1}H NMR spectrum ($CDCl_3$, 500 MHz): $\delta = 7.24$ ppm, d (br.), $J \approx 8.8$ Hz, 1.0H; $\delta = 7.47$, s (br.), 1.0H; $\delta = 8.26$, d, $J \approx 8.8$, 1.0H; $\delta = 10.58$, s (sharp), 0.94H (chelated H).

This information suggests that the substance of fraction A is 2-nitro-5-(1,1,2,2-tetrafluoro-2-SF_5-ethyl)-phenol. Yield = 18%.

3.5. Preparation of *m*-($SF_5CF_2CF_2$)-acetanilide, **6**

m-$SF_5CF_2CF_2C_6H_4NH_2$ (≈100 mg), **3**, was stirred with a solution of 2 ml of acetic anhydride containing one drop of concentration H_2SO_4 at room temperature overnight. The mixture was poured into water (20 ml), stirred (30 min) and extracted (2 × 20 ml of ether). After washing with water (3 × 10 ml) and drying, the product was chromatographed on 15 g of silica gel (column i.d. = 3 cm). The column was first eluted with 150 ml of methylene chloride in order to wash out two fast-running weak bands, then with 140 ml of a mixture of methylene chloride (140 ml) and acetone (3 ml). Evaporation of the latter solution furnished 80 mg (≈70%) of a white, crystalline solid; re-crystallization (−12 °C) from aqueous alcohol gave 60.3 mg (m.p. = 119–120 °C).

Infrared spectrum (neat, KBr, cm^{-1}): 3315 (w), 3276 (w), 3222 (vw), 3106 (vw), 1671 (m–s), 1626 (w–m), 1600 (m), 1568 (m), 1560 (m), 1485 (w), 1445 (m), 1377 (w), 1328 (w), 1303 (w), 1279 (w–m), 1268 (w–m), 1204 (m–s), 1154 (m–s), 1116 (m–s), 1018 (vw), 896 (m–s), 866 (vs), 799 (s), 777 (s–vs), 717 (m), 677 (m–s).

Mass spectrum (DB5, 30 m, 50 °C: 2 min, then 11 °C min^{-1} → 280 °C; mass, percent, fragment): 361, 26%, M^+; 319, 76, $(M–CH_2{=}C{=}O)^+$; 214, 19, $(M–SF_5–HF)^+$; 172, 12, $(M–SF_5–HF–CH_2{=}C{=}O)^+$; 142, 100, $(M–CF_2SF_5–CH_2{=}C{=}O)^+$; 127, 2, SF_5^+; 114, 14, $(C_2F_3S + H)^+$; 89, 2, SF_3^+; 43, 34, CH_3CO^+.

High resolution mass spectrum: $M^+ = 361.01856$. Calculated for $^{12}C_{10}{}^1H_8{}^{19}F_9{}^{14}N^{16}O^{32}S$: M = 361.01829.

3.6. Preparation of *m*-$SF_5CF_2CF_2C_6H_4SO_2Cl$, **7**

Into a 100 ml three-necked flask equipped with trap-bubbler, thermometer, dropping funnel and a Teflon-coated stirring bar, 14.9 ml (225.1 mmol) of HSO_3Cl was added. The acid was cooled to 0 °C and then 2.5 g (8.2 mmol) of $SF_5CF_2CF_2C_6H_5$ (**1**) was added dropwise and at such a rate that the temperature of the stirred mixture did not rise above 5 °C. After complete addition of **1**, the chilled reaction mixture was stirred for 1 h, then warmed to room temperature and stirred for another 34 h; a GC–MS spectrum was taken in order to assure completion of the reaction. The liquid mixture was added dropwise to ice-cold water and the white oily liquid that formed was extracted with methylene chloride and dried over magnesium sulfate. The solvent was distilled away at atmospheric pressure; a low-pressure distillation of the residue gave 1.96 g (4.87 mmol) of a colorless liquid, boiling point 83–85 °C/1 Torr. The yield of the product was 59%.

The IR spectrum contains the following peaks (cm^{-1}): 3083 (w), 1985 (vw), 1935 (vw), 1725 (vw), 1606 (w), 1584 (w), 1480 (w), 1437 (m), 1387 (s), 1314 (w), 1295 (m), 1269 (ms), 1247 (m), 1201 (s), 1183 (s), 1123 (s), 1098 (m), 1076 (m), 1047 (mw), 1018 (vw), 998 (w), 960 (w), 939 (vw), 924 (mw), 878 (vs), 824 (vs), 806 (ms), 765 (mw), 748 (s), 699 (m), 685 (m), 675 (ms), 654 (m), 613 (ms), 591 (s), 572 (s), 552 (s), 510 (m), 466 (vw), 416 (mw).

The major mass spectra peaks include (*m*/*z*, molecular ion, relative percentage): 404, 402 (^{37,35}Cl, M^+, 1.4, 3.5%); 367 ($M–Cl^+$, 71%); 303 ($M–SO_2Cl^+$, 62%); 275 ($M–SF_5^+$, 25%); 225 ($M–SF_5CF_2^+$, 70%); 176 ($M–SF_5–SO_2Cl^+$, 56%); 174 ($CF_2C_6H_4SO^+$, 13%); 127 (SF_5^+, 31%); 126 ($CF_2C_6H_4^+$, 19%); 89 (SF_3^+, 25%); 75 ($CF_2C_2H^+$, 23%); 50 (CF_2^+, 17%).

Analysis: calculated for $SF_5CF_2CF_2C_6H_4SO_2Cl$: C, 23.85; H, 0.99; S, 15.90; F, 42.5%. Found: C, 24.01; H, 1.04; S, 15.80; F, 42.6%.

3.7. Preparation of $SF_5CF_2CF_2C_6H_4SO_3^-K^+$, **8**

Into a 50 ml round-bottomed flask equipped with a Teflon-coated stirring bar and a condenser, were added

$SF_5CF_2CF_2C_6H_4SO_2Cl$ (5.60 g, 17.9 mmol), KOH powder (0.59 g, 1.9 eq.) and 10 ml of water. The reaction mixture was heated under reflux overnight. The solution was acidified with a 10% HCl solution and passed through an ion-exchange column containing Amberlite (IR-120, 40 ml). The acid, after removal of water under vacuum, was then titrated with a standardized KOH solution. The water was then removed under vacuum; a dry white solid powder, $SF_5CF_2CF_2C_6H_4SO_3^-K^+$ (4.19 g, 9.9 mmol, decomposition at 250 °C) was formed in 55% yield.

The IR spectrum contains the following bands (cm^{-1}): 3079 (w), 2931 (vw), 2848 (vw), 1605 (vw), 1482 (vw), 1438 (w), 1293 (vw), 1277 (w), 1242 (w), 1216 (vs), 1197 (vs), 1162 (m), 1128 (m), 1115 (s), 1096 (w–m), 1078 (w), 1051 (m), 1043 (w–m), 1001 (vw), 925 (w), 902 (w), 885 (s), 874 (vs), 832 (s), 826 (s), 809 (m), 757 (m), 751 (s), 704 (w–m), 686 (w–m), 681 (w–m), 661 (w–m), 632 (w–m), 613 (w–m), 588 (m), 575 (w–m), 568 (w–m), 515 (w).

Analysis: calculated for $SF_5CF_2CF_2C_6H_4SO_3K$: C, 22.75; H, 0.95; S, 15.18; F, 40.5%. Found: C, 22.58; H, 1.05; S, 14.95; F, 40.1%.

3.8. Preparation of *m*-$SF_5CF_2CF_2C_6H_4SO_3H{\cdot}xH_2O$, **9**

A portion of the potassium salt (0.66 g in 10 ml of water) was passed through an Amberlite column. The water was removed from the eluent via vacuum drying; 0.68 g of the acid **9** was recovered as a soap-like white semi-solid.

The IR spectrum contained the following bands (cm^{-1}): 3499 (vs, b), 3000 (vw, b), 1740 (w), 1658 (m), 1432 (w), 1239 (vs), 1180 (m), 1045 (vs), 861 (vs, b), 777 (w), 605 (w), 575 (w).

The composition of the acid was established by conversion to the corresponding potassium salt. The spectral data agreed with those described above.

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