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Short communication

ω-Pentafluoro-λ^6-sulfanyl(SF_5)-*n*-perfluoroalkyl benzene derivatives

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Abstract

The reaction of pentafluoro-λ^6-sulfanyl(SF_5)-perfluoroalkyl iodides with benzene is a convenient route for preparing SF_5-perfluoroalkyl benzene derivatives, $SF_5(CF_2)_nC_6H_5$ ($n = 2$, 4, 6, 8), a new class of perfluoroalkylaromatic compounds. The preparation and characterization of these new materials are described. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The perfluoroalkylation of aromatic compounds has been accomplished through the thermolysis of perfluoroalkyl iodides in the presence of the appropriate aromatic compound. In 1960, G.V.D. Tiers described a general procedure for the direct introduction of a perfluoroalkyl group (R_f) into benzene and other aromatic compounds [1]. Other workers have extended the scope of this reaction using other aromatic compounds and iodides [2]. The introduction of an SF_5-group into an aromatic system was first reported in 1962 [3]; aryl disulfides or arylsulfur trifluorides are fluorinated using AgF_2. The parent compound, $SF_5C_6H_5$ (pentafluorothiobenzene or phenylsulfur pentafluoride or pentafluoro-λ^6-sulfanyl benzene) can also be prepared in low yields by the thermal reaction of S_2F_{10} with benzene [4]. In a more recent report, the use of elemental fluorine was described [5]. A multistep method involving $SF_5C{\equiv}CH$ has been reported as a pathway to $SF_5C_6H_5$ [6]. The photolysis of $SF_5C{\equiv}CH$ with SF_5Cl or the reaction of $SF_5C{\equiv}CH$ with $Co_2(CO)_8$ and bromine have produced SF_5-trisubstituted derivatives of benzene [7].

We have recently developed an interest in aromatic compounds containing the SF_5-group because of the unique properties that the SF_5-group can confer upon organic systems. These properties include high dielectric strength, high thermal stability, high chemical resistance, low refractive index and low surface free energy [6,8–14].

2. Results and discussion

The introduction of the $SF_5(CF_2)_n$ ($n = 2$, 4, 6, 8) group into benzene was accomplished via the following thermal reaction:

$$SF_5(CF_2)_nI + xsC_6H_6 \xrightarrow{\Delta} SF_5(CF_2)_nC_6H_5 + \text{by-products}$$

For $n = 2$ (**1**), the yield of the reaction and the amount of by-products (characterized by GC–MS) formed proved to be highly dependent upon reaction conditions.

In Section 3, the experimental conditions that minimize the production of by-products are given. The optimum conditions were 72 h at 145°C and resulted in a pure product with a yield of 39%. For the $n = 4$ (**2**) homologue, a yield of 50% was obtained. A GC–MS study of the reaction of $SF_5(CF_2)_6I$ with benzene showed that 51% of the starting iodide was converted to product, $SF_5(CF_2)_6C_6H_5$ (**3**). In one reaction, using $SF_5(CF_2)_nI$ (a mixture containing $n = 6$ and 8), both the $SF_5(CF_2)_6C_6H_5$ and $SF_5(CF_2)_8C_6H_5$ were obtained and characterized by GC–MS.

The infrared spectra of the new $SF_5(CF_2)_nC_6H_5$ compounds (for $n = 2$, 4) have in common the characteristic absorption bands of the SF_5-group. Cross and coworkers found that the most intense band attributed to the SF_5-group appears in the region 850–920 cm^{-1} (S–F stretching modes) with one of the S–F deformation modes in the region of 600 cm^{-1} [15]. For the new compounds reported in this paper, the stretching and deformation bands are found in the 808–888 cm^{-1} and 606–599 cm^{-1} ranges, respectively. The stretching vibrations for the CF_2-groups give rise to strong absorption bands in the 1105–1287 cm^{-1} region; these

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stretching modes are normally found in the 1100–1400 cm^{-1} region [16]. The ^{19}F-NMR spectra for the compounds ($n = 2, 4$) show an AB_4 pattern for the SF_5-group: A (distorted pentet or nine-line pattern) at $\varphi = 65.2$–66.1 ppm; B (doublet) at $\varphi = 45.1$ ppm. For $SF_5CF_2CF_2I$ and other SF_5-fluoroalkyl derivatives, the chemical shifts are located at $\varphi = 67.2$–64.0 and 44.2–47.3 ppm, respectively [17]. The chemical shifts of the CF_2 fluorines adjacent to the SF_5-group are located in the range $\varphi = -93.8$–96.5 ppm; for other $SF_5CF_2CF_2$-fluoroalkyl derivatives this range is -97.5 to -89.0 ppm [17]. The CF_2 fluorines adjacent to the benzene ring are present at -111.5 ppm for $n = 2$, at -112.0 ppm for $n = 4$; by comparison, the chemical shifts of the fluorines of the CF_2-group in m-$CF_3CF_2C_6H_4X$ ($X = F, NO_2, NH_2$) are found at -115.5 to -115.9 ppm [18].

The major mass spectral peaks as well as relative retention times for $SF_5(CF_2)_nC_6H_5$, ($n = 2, 4, 6, 8$) are listed in Section 3. Molecular ion peaks are observed for all new compounds. A GC–MS study allowed us to clearly separate and identify each new compound; for $n = 6, 8$ only GC–MS results are given.

3. Experimental

3.1. Starting materials

The SF_5-perfluoroalkyl iodides were prepared from S_2F_{10}, ICF_2CF_2I, and $CF_2{=}CF_2$ [17,19–21]; benzene was obtained from E. Merck and was used as received.

NMR-spectra were recorded with a Varian EM-390 spectrometer operating at 84.67 MHz for ^{19}F-analysis; a Bruker AMX-400 spectrometer operating at 400 MHz for ^{1}H-analysis, and 376.5 MHz for ^{19}F-analysis; CCl_3F and $(CH_3)_4Si$ were used as internal standards. The IR-spectra were obtained between potassium bromide plates using a Perkin-Elmer System 2000 FT-IR operating at 2 cm^{-1} resolution. Elemental analyses were determined by Beller, Mikroanalytisches Laboratorium, Göttingen, Germany. Mass spectra were obtained using a Hewlett-Packard HP5890 series II gas chromatograph (25 m, DB-5 column) with a HP5970 mass-selective detector operating at 70 eV. The temperature program was such that $t = 50$°C for 2 min, then the temperature was raised to 280°C at 11°C/min; injection port temperature was 250°C.

3.2. Synthesis of $SF_5CF_2CF_2C_6H_5$ (**1**)

Into a 350 ml Carius tube equipped with a Teflon coated stirring bar, 10.34 g (29.21 mmol) of $SF_5CF_2CF_2I$ and 110 g (1408.21 mmol) of C_6H_6 were added. The vessel was cooled to -196°C and evacuated to remove air. After the reaction mixture warmed to room temperature, the lower part of the vessel was heated for 72 h at 145°C. The top part of the Carius tube was covered with glass wool and aluminum foil, in order to avoid any condensation of the reagents. After cooling, the reaction mixture was poured into a separatory funnel and the vessel was rinsed with about 10 ml of diethyl ether. The mixture was washed with sodium bisulfite (three times, using about 40–50 ml of a saturated solution each time), sodium bicarbonate (three times, using about 40–50 ml of a saturated solution each time) and water (about 50–60 ml), then dried over magnesium sulfate. The lower boiling materials were distilled away at atmospheric pressure. Distillation of the residue at low pressure gave 3.42 g (11.25 mmol) of the colorless liquid $SF_5CF_2CF_2C_6H_5$, boiling point 85–87°C/44 Torr, yield was 39%. The retention time via GC–MS analysis was 6.10 min.

The infrared spectrum shows the following bands (cm^{-1}): 3075 (w); 3052, (vw), 1965, (vw), 1904 (vw), 1814 (vw), 1775 (vw), 1608 (w), 1500 (mw), 1457 (ms), 1325 (vw), 1276 (s), 1258 (m), 1243 (m), 1199 (s), 1167 (ms), 1116 (vs), 1095 (m), 1073 (ms), 1046 (mw), 1030 (mw), 1023 (mw), 1004 (vw), 947 (m), 933 (mw), 923 (mw), 875 (vs), 825 (s), 808 (vs), 758 (s), 701 (s), 677 (s), 660 (ms), 642 (w), 606, (s), 584 (m), 574 (s), 484 (w), 417 (mw).

A molecular ion peak and appropriate fragments were observed in the mass spectrum. Major peaks include (m/z, molecular ion, relative %): 304 (M^+, 18%), 177 ($SF_5CF_2{}^+$ or $(M–SF_5)^+$, 12%), 158 (SF_5CF^+or $C_6H_5CF_2CF^+$, 4%), 127 ($SF_5{}^+$ or $C_6H_5CF_2{}^+$, 100%), 107 [$(C_7H_4F)^+$, 3%), 89 [$SF_3{}^+$ or $(C_7H_5)^+$, 3%], 77 ($C_6H_5{}^+$, 10%), 51 (SF^+ or $C_4H_3{}^+$, 4%).

The ^{19}F-NMR ($CFCl_3$) of $F^a{-}SF_4^b{-}CF_2^c{-}CF_2^d{-}C_6H_5$ shows the following peaks: φ_a (66.1 ppm, p, m), φ_b (45.1 ppm, d, p), φ_c (-93.8 ppm, m), φ_d (-111.5 ppm, m). The coupling constants were as follows: $J_{a,b} = 146.3$ Hz, $J_{a,c} = 4.7$ Hz, $J_{c,d} = 12.2$ Hz, and $J_{b,c}$ and $J_{b,d}$ were between 13.4 and 14.5 Hz. The integration values for $FSF_4CF_2CF_2$ were $a = 1.0$; $b = 3.9$; $c = 2.0$; $d = 2.0$.

The ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of $\mathbf{SF_5CF_2CF_2\overline{CCH^eCH^fCH^gCH^hCH}^i}$ shows the following peaks: $\delta_{ei} = 7.57$ ppm (d), $\delta_{fh} = 7.43$ ppm (t), $\delta_g = 7.51$ ppm (t), and the coupling constants were as follows: $J_{e,f} \cong J_{h,i} = 7.76$ Hz, and $J_{f,g} \cong J_{g,h} = 7.31$ Hz.

Analysis: calculated for $C_8H_5F_9S$: C, 31.58; H, 1.64; F, 56.3; S, 10.53%. Found: C, 31.41; H, 1.70; F, 55.8; S, 10.37%.

3.3. Preparation of $SF_5(CF_2)_4C_6H_5$ (**2**)

Into 210 ml Pyrex-glass Carius tube equipped with a Kontes Teflon stopcock, 10.45 g (23.01 mmol) of $SF_5(CF_2)_4I$, and 91 g (1166.7 mmol) of C_6H_6 were added. The reaction vessel was cooled to -196°C and evacuated. The reaction mixture was heated at 180–185°C for 16 days during which time periodic measurements of the progress of the reaction were checked via GC–MS. At the end of the reaction time, the contents of the Carius tube were transferred into a 500 ml beaker and washed in a similar fashion to that described above with saturated solutions of sodium bisulfite and sodium bicarbonate in order to remove iodine and HI, then dried over magnesium sulfate; lower boiling materials were removed via distillation at atmospheric pressure. Distillation of the residue, at reduced pressure, gave 4.63 g (11.5 mmol) of $SF_5(CF_2)_4C_6H_5$, boiling point 90–95°C/20 Torr, yield was 50%. The retention time via GC–MS analysis was 7.59 min.

The infrared spectrum of $SF_5(CF_2)_4C_6H_5$ shows the following bands (cm^{-1}): 3080 (w), 3050 (vw), 1988 (vw), 1967 (vw), 1912 (vw), 1897 (vw), 1612 (w), 1502 (mw), 1457 (ms), 1313 (w), 1287 (s), 1218 (vs), 1175 (s), 1151 (vs), 1105 (s), 1074 (ms), 1033 (mw), 1054 (mw), 963 (s), 952 (s), 922 (s), 888 (vs), 859 (vs), 808 (mw), 787 (s), 768 (vs), 741 (s), 727 (s), 711 (s), 698 (vs), 685 (s), 676 (s), 640 (s), 599 (s).

A molecular ion peak and appropriate fragments were observed in the mass spectrum. Major peaks include (*m*/*z*, molecular ion, relative %): 404 (M^+, 10%), 277 [$M–SF_5^+$ or $SF_5(CF_2)_3^+$, 13%], 257 ($M–SF_5–HF^+$, 4%), 227 [$SF_5(CF_2)_2^+$ or $M–SF_5CF_2^+$, 3%], 177 [$SF_5CF_2^+$ or $C_6H_5(CF_2)_2^+$, 2%], 158 ($C_6H_5C_2F_3^+$ or SF_5CF^+), 127 (SF_5^+or $C_6H_5CF_2^+$, 100%), 107 ($C_7H_4F^+$, 2%), 89 (SF_3^+ or $C_7H_5^+$, 3%), 77 ($C_6H_5^+$, 8%), 51 (SF^+, 3%).

The ^{19}F-NMR ($CFCl_3$) of $F^a{-}SF_4^b{-}CF_2^c{-}CF_2^d{-}CF_2^e{-}CF_2^f{-}C_6H_5$ shows the following peaks: φ_a (65.2 ppm, m), φ_b (45.1 ppm, d), φ_c (−96.5 ppm, m), φ_d and φ_e (122.5–123.5 ppm, m), and φ_f (112.0 ppm, m). The relative integration areas for $FSF_4CF_2(CF_2CF_2)CF_2$ were $a = 1.0$; $b = 4.0$; $c = 2.0$; $d + e = 3.8$; $f = 2.0$.

Analysis: calculated for $C_{10}H_5F_{13}S$: C, 29.72; H, 1.25; F, 61.1; S, 7.94%. Found: C, 29.52; H, 1.10; F, 60.7; S, 8.04%.

3.4. Preparation of $SF_5(CF_2)_6C_6H_5$ (**3**)

Into a 50 ml Pyrex-glass Carius tube equipped with a Kontes Teflon stopcock, 0.58 g (1.05 mmol) of $SF_5(CF_2)_6I$, and 3.1 g (39.74 mmol) of C_6H_6 were added. The reaction vessel was cooled to −196°C and evacuated. The reaction mixture was heated at 160–165°C for 14 days during which time periodic GC–MS measurements were made in order to determine the progress of the reaction. After 14 days, the volatile materials were pumped through a −196°C trap; excess benzene was removed by distillation at atmospheric pressure. A GC–MS study of the pot residue showed 51% conversion into $SF_5(CF_2)_6C_6H_5$; retention time was 9.20 min.

A molecular ion peak and appropriate fragments were observed in the mass spectrum of $SF_5(CF_2)_6C_6H_5$. Major peaks include (*m*/*z*, molecular ion, relative %): 504 (M^+, 3%), 377 [$SF_5(CF_2)_5^+$ or $M–SF_5^+$, 3%], 357 ($M–SF_5–HF^+$, 1%), 327 [$SF_5(CF_2)_4^+$ or $C_6H_5(CF_2)_5^+$, 1%], 257 [$M–SF_5(CF_2)_2–HF^+$, <1%], 227 [$SF_5C_2F_4^+$ or $C_6H_5(CF_2)_3^+$, <1%], 177 [$SF_5CF_2^+$ or $C_6H_5(CF_2)_2^+$, 2%], 158 (SF_5CF^+ or $C_6H_5C_2F_3^+$), 127 (SF_5^+ or $C_6H_5CF_2^+$, 100%), 107 ($C_7H_4F^+$, 1%), 89 (SF_3^+ or $C_7H_5^+$, 3%), 77 ($C_6H_5^+$, 6%), 51 (SF^+, 2%).

3.5. Preparation of $SF_5(CF_2)_6C_6H_5$ (**3**) and $SF_5(CF_2)_8C_6H_5$ (**4**)

Into a 50 ml Pyrex-glass Carius tube equipped with a Kontes Teflon stopcock, 0.53 g mixture of $SF_5(CF_2)_6I$ and $SF_5(CF_2)_8I$, and 2.34 g (30.0 mmol) of C_6H_6 were added. The reaction vessel was cooled to −196°C and evacuated. The reaction mixture was then heated at 160–165°C for 14 days during which time periodic measurements of the reaction completion were checked by GC–MS. At the end of the reaction time, the volatile materials of the reaction were pumped through a trap at −196°C and the excess amount of benzene was removed through distillation at atmospheric pressure. A representative sample of the pot residue was analyzed via GC–MS and $SF_5(CF_2)_6C_6H_5$ (retention time of 9.20 min) and $SF_5(CF_2)_8C_6H_5$ (retention time of 10.59 min) were found to be present.

The molecular ion peak and appropriate fragments were observed in the mass spectrum for $SF_5(CF_2)_6C_6H_5$; these values are reported above. A molecular ion peak and appropriate fragments were observed in the mass spectrum of $SF_5(CF_2)_8C_6H_5$. Major peaks include (*m*/*z*, molecular ion, relative %): 604 (M^+, 2%), 585 ($M–F^+$, 2%), 477 [$SF_5(CF_2)_7^+$ or $M–SF_5^+$, 3%], 457 ($M–SF_5–HF^+$, 1%), 427 [$SF_5(CF_2)_6^+$ or $M–SF_5CF_2^+$, 1%], 358 [$M–SF_5–C_2F_5^+$, $SF_5(CF_2)_4CF^+$, <1%], 208 [$SF_5CF_2CF^+$, $C_6H_5(CF_2)_2CF^+$, 2%], 177 [$SF_5CF_2^+$ or $C_6H_5(CF_2)_2^+$, 3%], 158 (SF_5CF^+, $C_6H_5CF_2CF^+$, 5%), 127 (SF_5^+or $C_6H_5CF_2^+$, 100%), 107 ($C_7H_4F^+$, 1%), 77 ($C_6H_5^+$, 4%), 51 (SF^+, 1%).

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