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Short communication

An improved and facile preparation of ω-SF_5-(perfluoroethyl)benzene ($SF_5CF_2CF_2C_6H_5$)

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Abstract

A high-yield preparation of $SF_5CF_2CF_2C_6H_5$ has been achieved via a two-step process: α,β,β-trifluorostyrene reacts with SF_5Br to give the intermediate product $SF_5CF_2CFBrC_6H_5$ (**1**) which, when treated with $AgBF_4$ in methylene chloride, produces $SF_5CF_2CF_2C_6H_5$ (**2**) in high yield.

Keywords: SF_5-fluoroalkyl aromatics; Sulfur hexafluoride derivatives

1. Introduction

The replacement of fluorine in SF_6 with organic substituents leads to compounds of the general formula RSF_5. Organosulfur pentafluorides (RSF_5) have a number of useful properties that include low wettability, low dielectric constant, high thermal stability, high chemical resistance, low refractive index and low surface energy [1–4]. The interest in RSF_5 chemistry, where R is an aromatic group, has extended to the fine chemical industry [5]; for example, Aldrich Chemical Company, Oakwood Products Inc., Fluorochem, USA, and Lancaster Synthesis Inc. now sell 3(4)-nitrophenylsulfur pentafluoride. Also, patents incorporating the phenylsulfur pentafluoride group have been issued [6].

A starting point for preparing SF_5-aromatic derivatives involves using one of the primary reagents, $SF_5C_6H_5$, $SF_5OC_6H_5$ and more recently, $SF_5(CF_2)_nC_6H_5$ ($n = 2$, 4, 6, 8) [7–9]. In addition to the synthesis of $SF_5(CF_2)_nC_6H_5$ ($n = 2$, 4, 6, 8), our laboratories have successfully prepared a number of derivatives of $SF_5CF_2CF_2C_6H_5$ (**2**); *m*-$SF_5CF_2CF_2C_6H_4X$ (X: NO_2, NH_2, N_3, $NHC(O)CH_3$, OH, I, Br, SO_2Cl, SO_3H, SO_3Na) [10,11]. Also, the preparation and polymerization of *m*-$SF_5CF_2CF_2C_6H_4Z$ (Z: $OC(O)CH{=}CH_2$ and $CH{=}CH_2$) have been achieved [11].

Previously, we reported a multi-step and time-consuming method for preparing $SF_5CF_2CF_2C_6H_5$ (**2**) that involved heating $SF_5CF_2CF_2I$ with a large excess of benzene for 14 days (145 °C in a 300 ml stirred Parr Bomb reactor); yield 74.4% [9,11]. The $SF_5CF_2CF_2I$ was prepared from S_2F_{10}, ICF_2CF_2I and $F_2C{=}CF_2$ [12] and the S_2F_{10} in turn from SF_5Br [13].

Therefore, in order to prepare $SF_5CF_2CF_2C_6H_5$ (**2**), it is advantageous to have a method that directly uses SF_5Br to give an intermediate precursor that is easily and quickly converted to the desired product.

2. Results

The preparation of $SF_5CF_2CF_2C_6H_5$ is carried out in the following two steps (Eqs. (1) and (2)):

$$SF_5Br + CF_2{=}CFC_6H_5 \xrightarrow{h\nu} \underset{(\mathbf{1})}{SF_5CF_2CFBrC_6H_5} \tag{1}$$

$$SF_5CF_2CFBrC_6H_5 + AgBF_4 \xrightarrow{CH_2Cl_2} \underset{(\mathbf{2})}{SF_5CF_2CF_2C_6H_5} + AgBr + BF_3 \tag{2}$$

In Eq. (2), the reaction is accompanied by the formation of AgBr precipitate and a vigorous evolution of gaseous BF_3.

The intermediate product (**1**) is a liquid at room temperature. Bromine in a benzylic position shows increased activity that promotes halogen exchange. The infrared spectrum contains the characteristic absorption bands for the SF_5-group (stretching bands at 853–917 cm^{-1} and one of the deformation bands at 597 cm^{-1}) along with additional bands

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that support the assigned structure. The stretching bands for the CF_2CF-group gives rise to strong absorption bands in the 1095–1195 cm^{-1} region. The ^{19}F NMR spectrum for (**1**) shows for the SF_5-group the expected AB_4 pattern. The axial fluorine atom (A) of the SF_5 is a triplet of a nine-line pattern (φ_A, 70.6 ppm) and the equatorial fluorine atoms (B) is a skewed doublet (φ_B, 47.3 ppm). The ^{19}F NMR spectrum for the CF_2-group is a complex AB pattern from which the appropriate SF_4F_A–CF_2 coupling ($J_{ACF_2} \sim 5.4$ Hz) has been determined. This result along with integration of peak areas provide evidence that the SF_5-group is attached to CF_2 as would be expected for a radical chain type addition product.

The major mass spectral peaks for (**1**) contain the parent ion; additional peaks are found supporting the assigned structure; in particular, the strong $(M–Br)^+$ peak (56%) and the strong $(SF_5CF_2)^+$ peak (45%) are found. The molecular weight of compound (**1**) was determined to seven significant places by high-resolution mass spectrometry (HRMS).

The spectral properties of $SF_5CF_2CF_2C_6H_5$ (^{19}F, ^1H, IR) and GC–MS (R_f value and ion spectrum) matched an authentic sample [9].

3. Experimental

The reactant SF_5Br was prepared using SF_4, BrF_3, Br_2 and CsF [14]. The α,β,β-trifluorostyrene was obtained from the SynQuest laboratories and was used as received. This material is also readily prepared by the method of Burton [15]; additional syntheses are found in a review article by Nikitina [16]. $AgBF_4$ was prepared from AgF and BF_3 in benzene [17]. The infrared spectra of the reactants and products were obtained on a Perkin-Elmer 2000 FTIR operating at 1.0 cm^{-1} resolution using KBr windows, ^{19}F NMR spectra on a Varian EM-390 spectrometer operating at 84.67 MHz, and ^1H NMR spectra on a Nicolet NM-500 (500 MHz). Mass spectra were obtained using a Hewlett-Packard HP5890 series II Gas Chromatograph equipped with a HP5970 mass selective detector operating at 70 eV and a 30 m DB-5 column. The precise molecular weight was determined on a Kratos MS 50TC; chemical ionization with methane.

3.1. Preparation of $SF_5CF_2CFBrC_6H_5$ (1)

To a 150 ml Carius vessel equipped with a Teflon stirring bar and a Kontes Teflon valve, 4.80 g (30.3 mmol) of $F_2C{=}CFC_6H_5$ in 45 ml of CH_2Cl_2, and 11.6 g (56 mmol) of SF_5Br were added via a vacuum transfer. This mixture was stirred and irradiated (250-W sunlamp at a distance of 35 cm) in an ice-bath. During irradiation, one-half of the solution level was above the ice-bath. After 1.5 h, the mixture turned brownish. The solution was irradiated for an additional 1.0 h; GC–MS analysis showed the reaction to be complete. The solvent was removed at atmospheric pressure; distillation of the residue gave 7.89 g (21.6 mmol) of a clear, light peach-color, product (**1**); bp 82–85 °C/11–12 Torr (71% yield).

The IR spectrum contained the following bands (cm^{-1}): 3070 (w), 3040 (vw), 1500 (w), 1453 (m), 1210 (ms, sh), 1195 (s), 1121 (m), 1095 (m), 1072 (ms), 1026 (wm), 917 (s), 876 (vs), 853 (s), 793 (m), 773 (m), 735 (m), 708 (vs), 694 (wm), 682 (m), 673 (ms), 640 (m), 624 (m), 597 (vs).

The ^1H NMR spectrum ($CDCl_3$) showed the following peaks: $\delta = 7.60$ ppm (center of multiplet), 2H; $\delta = 7.42$ ppm (center of multiplet), 3H. ^{19}F NMR spectrum ($CDCl_3$): $SF_5(AB_4)$: $\varphi_A = 70.6$ ppm (triplet of a nine-line pattern), 1.0F; $\varphi_B = 47.3$ ppm (skewed doublet), 4.0F; $J_{AB} = 149$ Hz, $J_{ACF_2} \approx 5.4$ Hz. $\varphi_{CF_2} = -85.8$ ppm, center (AB system of multiplet), 2.0F; $\varphi = -84.3$ and -87.3 ppm; $J_{AB} = 200$ Hz, doublet splitting is present in multiplets, $J \approx 5.5\ \text{Hz} = J_{FSF_4CF_2}$; $\varphi_{CFBr} = -131.0$ ppm (poorly resolv. multiplet), 1.0F, $J \approx 11$ Hz.

The major mass spectral peaks include (*m/z*, ion, rel.%): 366/364, $(M)^+$, 0.5%; 285, $(M–Br)^+$, 56%; 237/239, $(M–SF_5)^+$, 9.1/8.8%; 177, $(SF_5CF_2)^+$, 45%; 159, $(MH–Br–SF_5)^+$, 9%; 158, $(M–Br–SF_5)^+$, 100%; 157, $(M–H–Br–SF_5)^+$, 8%; 127, $(SF_5)^+$, 72%; 108, $(CFC_6H_5)^+$, 16%; 107, $(CFC_6H_4)^+$, 21%; 89, $(SF_3)^+$, 11%.

High-resolution mass spectrum: $m^+ = 363.91706$. Calculated for $^{12}C_8{}^1H_5{}^{19}F_8{}^{32}S^{79}Br$: $m = 363.91676$.

3.2. Preparation of $SF_5CF_2CF_2C_6H_5$ (2)

To a 150 ml Carius vessel equipped with a Teflon stirring bar and a Kontes Teflon valve, containing 2.51 g (12.9 mmol) of $AgBF_4$, 4.31 g (11.8 mmol) of (**1**) in 20.0 ml of CH_2Cl_2 was added with stirring. A vigorous reaction occurred with the release of BF_3. The reaction, after stirring for 45 min in an ambient-temperature water bath, was found to be complete (GC–MS spectrum showed only (**2**) to be present). The reaction mixture was suction-filtered and the filter cake washed with 20 ml of CH_2Cl_2; the filtrate was passed through a short column of Kieselgel (10 g) and eluted with CH_2Cl_2. The bulk of the solvent was removed using a rotary evaporator; the residue was transferred into a cold trap at −196 °C which when warmed from −35 to −40 °C is pumped on in order to remove any remaining solvent. The product residue (3.32 g, 10.9 mmol, yield of 92%) was found to be identical in all aspects (^{19}F, ^1H NMR, IR spectrum, GC–MS-identical R_f values and spectra) with an authentic sample of $SF_5CF_2CF_2C_6H_5$ [9].

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