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New acrylate systems: derivatives of β-SF_5-acrylic acid

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Dedicated to Professor Jean'ne M. Shreeve on the occasion of her 70th birthday.

Abstract

Addition of pentafluorothio bromide, SF_5Br, to ethyl propiolate results in an 1:1 adduct, $SF_5CH{=}CBrC(O)OC_2H_5$, and a small amount of a 1:2 adduct. The former is converted by reduction to the corresponding β-SF_5-acrylic ester, $SF_5CH{=}CHC(O)OC_2H_5$. Treatment of $SF_5CH_2CBr(CH_3)C(O)OCH_3$ with base produces methyl-β-SF_5-methacrylate, $SF_5CH{=}C(CH_3)C(O)OCH_3$. The preparation and characterization of these new compounds are described.
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Keywords: β-SF_5-acrylates; Pentafluorothio (SF_5); Sulfur hexafluoride derivatives

1. Introduction

While a significant number of fluorinated acrylates are known only a limited number containing the SF_5-group have been reported. In all but one of the cases, the SF_5-group is located in the alcohol portion of the acrylate ester. The first SF_5-containing acrylate monomer and bulk polymer system, $SF_5(CF_2)_4CH_2OC(O)CH{=}CH_2$ were reported in 1992 [1,2]. More recently, in our laboratories, we have prepared the monomer $SF_5(CF_2)_2(CH_2)_2OC(O)CH{=}CH_2$ and copolymers with HEMA [3], and the monomer $SF_5(CF_2)_6(CH_2)_2$-$OC(O)CH{=}CH_2$ and its bulk polymer [4]. The new polymers with terminal SF_5-groups gave fluorinated surfaces with low wettability [3,4]. In addition, the monomer/polymer acrylate $SF_5(CF_2)_2(CH_2)_2OCH_2C(C(O)OCH_2CH_3){=}CH_2$ was prepared; this system may be regarded as a derivative of methacrylic acid in which the SF_5 is present in the acid moiety [3].

In this report, we describe the successful synthesis of three derivatives of β-SF_5-acrylic acid and some of their reactions.

2. Results and discussion

The addition of SF_5-halides to carbon compounds with varying degree of unsaturation has the broadest applicability for the production of primary SF_5-compounds.

It has been shown that SF_5X (X = Cl, Br) will add to alkynes; SF_5Cl was added to acetylene and propyne [5] and to $RC{\equiv}COR'$ (R=CH_3, H; R′=CH_3, CH_3CH_2) [6,7] while in separate reports, SF_5Br was added to $YC{\equiv}CH$ (Y = SF_5, CF_3) and to $CF_3C{\equiv}CH$ or $CH_3C{\equiv}CH$ [8,9]. In all cases, the SF_5 group was attached to the olefinic carbon with the most hydrogen. Our studies with SF_5Br have shown that it is generally much more reactive than SF_5Cl and undergoes addition, under mild conditions, to acrylic esters [10].

The addition of SF_5Br to ethyl propiolate readily occurs leading to two products

$$SF_5Br + HC{\equiv}CCO_2C_2H_5 \rightarrow \underset{(\mathbf{1})}{SF_5CH{=}CBrC(O)OC_2H_5} + \text{1:2 adduct} \quad (1)$$

The main product (**1**) contains two isomers as evidenced in the GC–MS; two bands (ratio ≈ 95 : 5) having very similar mass spectra are obtained. The ^1H and ^{19}F NMR spectra could not differentiate the two isomers. The second product is a high-boiling residue and based on our analysis is considered to be a mixture of the various possible geometric isomers of the structure $SF_5CH{=}C(C(O)OC_2H_5)CH{=}CBrC(O)OC_2H_5$. The addition of SF_5Br to $HC{\equiv}CC(O)OC_2H_5$ conceivably leads to four isomers, *cis*, *trans* and the structural isomers (also *cis* and *trans*) produced by reversed addition. This has been observed in the case of hydroplumbation and hydrostannation where, dependent upon the reaction conditions, the ratio of α- to β-additions may be changed. β-Addition is attributed to radical-type reaction and α-addition to a polar-type reaction [11–14]. While neither NMR, IR nor mass

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spectral data unambiguously support one or the other possibility, the subsequent reduction indicates the orientation:

$$SF_5CH{=}CBrCO_2C_2H_5 + (n\text{-}C_4H_9)_3SnH \rightarrow \underset{(\mathbf{2})}{SF_5CH{=}CHCO_2C_2H_5} + (n\text{-}C_4H_9)_3SnBr \quad (2)$$

The product (**2**) may be distinguished, by ^{1}H NMR spectroscopy, as a mixture of *cis*- and *trans*-ethyl β-SF_5-acrylate; the *cis*-isomer was obtained in the pure state. For these isomers, the direct precursors would be *cis*- and *trans*-ethyl α-bromo-β-SF_5-acrylate. The yield in this reduction in ether is poor, and is attributed to losses that occurred during isolation. If the solvent is tetraglymedimethyl ether (bp: 275 °C), the product can be transferred under vacuum into a cold-trap and obtained in nearly 90% yield.

In an attempt to obtain ethyl β-SF_5-acrylate, from the readily accessible ethyl α-bromo-β-SF_5-propionate by HBr-elimination with base, only the α-bromoacrylate was produced [15].

As previously reported, SF_5Br adds to methyl methacrylate [10]; however, unlike ethyl α-bromo-β-SF_5-propionate, the adduct formed from methyl methacrylate (methyl α-bromo-β-SF_5-isobutyrate) undergoes HBr elimination giving methyl β-SF_5-methacrylate:

$$SF_5CH_2CBr(CH_3)CO_2CH_3 \xrightarrow[O\,^\circ C]{NaOCH_3} \underset{(\mathbf{3})}{SF_5CH{=}C(CH_3)C(O)OCH_3} + NaBr \quad (4)$$

In the above reaction (4) two isomers are obtained in the ratio of 3:97.

Attempts to polymerize compound (**2**) using several different initiators (benzoyl peroxide, t-butyl peroxide and potassium persulfate) with heat were unsuccessful. β-SF_5-acrylate (**2**) is a structure analog to γ,γ,γ-trifluorocrotonate.

The infrared spectra for all new compounds have in common the characteristic absorption bands of the SF_5-group. Cross and coworkers reported that the most intense band for compounds containing the SF_5-grouping appears in the 850–920 cm^{-1} region (S–F stretching modes) and in the 600 cm^{-1} region (S–F deformation modes) [16]. For the new compounds reported in this paper, the S–F stretching bands and one of the deformation bands are found in the 878–830 and 601–600 cm^{-1} ranges, respectively. The C–H, C=O, and C=C vibrations were found, respectively, in the 3110–2851, 1748–1737 and 1656–1635 cm^{-1} regions.

The ^{19}F NMR spectra for the apical fluorine atom (ϕ_A) in the SF_5-group were in the range of 77.9–82.3 ppm, while the basal fluorine atoms (ϕ_B) were observed at 65.0–66.6 ppm; these chemical shifts agree with those of other SF_5-alkenes [9].

It is known from previous NMR spectral studies with the following SF_5-olefinic systems, $SF_5CH{=}CH_2$ [17], $SF_5CH{=}C(CH_3)Br$ [9], $SF_5CH{=}CHCl$ [18], *cis*/*trans*-$SF_5CH{=}CH(OCH_3)$ [18] and *trans*-$SF_5CH{=}CHCH_3$ [19] that the $J_{SF5\text{-}CH}$ geminal coupling values are in the 6.1, 8.1, 5, 8.7/6 and 5 Hz, respectively. The $J_{SF5\text{-}CH}$ *cis* coupling values are near 0 or absent for $SF_5CH{=}CH_2$ [17], $SF_5CBr{=}CHCl$ [19], $SF_5CH{=}CHCl$ [18], $SF_5CH{=}CHOCH_3$ [18], $SF_5CBr{=}CHBr$ [20], $SF_5CCl{=}CH_2$ [21] and $SF_5CBr{=}CHCl$ [16]. Also of interest is the $J_{SF5\text{-}CH}$ *trans* interaction; for $SF_5CH{=}CH_2$ [17], $SF_5CH{=}CHOCH_3$ [18], $SF_5CBr{=}CHBr$ [20], and $SF_5CCl{=}CH_2$ [21], and *trans*-$SF_5CBr{=}CHCl$ [19] the coupling values are 2.3, 3, 3.0, 3.3 and 2.2 Hz, respectively. It is clear from our data that all new compounds (**1**–**3**) have $SF_5CH{=}$ arrangement based on the values for the geminal coupling. For compound (**2**), the main isomer is the *cis*-isomer as both hydrogens are coupled to the SF_4(F) group while the minor product has the *trans* structure; this is demonstrated by the lack of any coupling between the SF_4(F) group and the adjoining *cis* H and by $J_{\alpha\beta}$ coupling equals 10.94 Hz (*cis*) and 15 (*trans*). By comparison, the $J_{\alpha\beta}$ coupling for *cis*-$CF_3CH{=}CHC(O)OCH_2CH_3$ is 12.3 Hz [22].

In an attempt to obtain additional structural information the ^{13}C NMR spectra of compounds **1**, *cis*-**2**, and **3** were obtained and analyzed. The following carbon-13 chemical shifts for these compounds were obtained: C_β = 139.3, 142.3, 152.3 ppm; C_α = 120.2, 125.8, 128.1 ppm; –C(O) = 161.2, 163.4, 166.0 ppm; CH_2 = 62.8, 62.4 ppm; $-CH_3$ = 12.5, 14.0, 14.3 and 52.8 (OCH_3) ppm. The chemical shift values for the *trans*-**2** compound were C_β = 152.3 ppm and C_α = 128.1 ppm; due to overlap of the more concentrated *cis*-isomer the remaining chemical shifts were not obtained. While a number of coupling constants were obtained it was not possible to make a definite assignment of compound **3** using these values; the carbonyl signal appears as a broad multiplet which prevents further analyses and the coupling of H_β with α-CH_3 (4.8 Hz) did not allow for a clear distinction between the geometric isomers. A NOESY spectrum of compound **3** at 600 ms mixing time gave nearly the same intensity cross-peaks for both methyl groups in the compound. This result would not be expected if the olefinic methyl group were *cis* to the olefinic hydrogen and would suggest a structure in which the olefinic hydrogen is *cis* to the ester group. Therefore, we believe that the main product in the isomer mixture of (**3**) is the one expected by HBr elimination from the most favorable rotational isomer, that is, the one where the olefinic hydrogen is *trans* to the methyl group.

The mass spectrum contained the parent peak and other appropriate fragments that supported the assigned structure.

3. Experimental details

The reactant SF_5Br was prepared from SF_4, BrF_3, and CsF [23]. The following compounds were obtained from Aldrich Chemical Co. and used as received: $(n\text{-}C_4H_9)_3SnH$, $HC{\equiv}CC(O)OC_2H_5$, and diethyl ether. The infrared spectra were obtained on a Perkin-Elmer 2000 FTIR operating at 1 cm^{-1} resolution using KBr windows (vw, very weak; w, weak; m, medium; s, strong; vs, very strong.

For NMR spectroscopy: ^{1}H Bruker (500 MHz), Varian EM-390 (90 MHz), ^{19}F Varian EM-390 (84.7 MHz), ^{13}C Bruker AMX-400 (100.6 MHz) in $CDCl_3$, with $Si(CH_3)_4$ and CCl_3F as internal standards. Gas-chromatography–mass spectroscopy results 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 DB5 column; the temperature profile used was 50 °C for 2 min, then at 11 °C/min. up to 280 °C. Elemental analyses were completed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

3.1. Preparation of ethyl α-bromo-β-SF_5-acrylate (**1**)

A 75 ml steel bomb tube was charged with ethyl propiolate (5.08 g, 51.8 mmol) and 10 ml of freon 113; after sealing and evacuating (−196 °C), SF_5Br (10.48 g, 50.6 mmol) was condensed into the vessel, and the mixture was allowed to warm up slowly; it was then heated at 38–40 °C (1 day), then at 65 °C (1 day). After cooling, the product was pipetted out. The main product (10.87 g, 70%) was obtained as a single fraction by short-path distillation at 61–62 °C/10.5 Torr. A residue (0.87 g, pale yellow oil) was obtained, boiling at 96–97 °C/120 μ.

3.1.1. Primary product

^{1}H NMR spectrum (90 MHz): $\delta = 1.35$ ppm, t, $J = 7.25$ Hz, 3 H, CH_3. $\delta = 4.39$ ppm, q, $J = 7.25$ Hz, 2.1 H, CH_2. $\delta = 6.97$ ppm, p, $J_{HFB} = 7.70$ Hz, 1 H, CH.

^{19}F NMR spectrum: AB_4 spectrum: $\varphi_A = 77.9$ ppm, nine lines, 1.0 F. $\varphi_B = 66.6$ ppm, skewed d-m, $J_{AB} = 154$ Hz, 3.8 F.

Infrared spectrum (neat, KBr, cm^{-1}): 3084, w; 2990, w; 2944, w-vw; 2900, vw; 1748, s-vs, sh; 1635, w-m; 1467, w; 1450, w; 1393, w-vw; 1371, w-m; 1311, s; 1222, s-vs; 1173, w, sh; 1116, w-vw; 1097, w; 1022, m; 965, w-m; 855 vs; 791, w; 735, w; 700, w; 639, m; 600, m-s; 573, w-m; 551, vw.

GC–MS, R_t	7.22	7.67 min	Two bands
Area (%)	>95	<5	
Mass (%) assignment			
304, 306	0.08, 0.09	0.39, 0.28	M^+
259, 261	34.2, 31.5	24.8, 22.7	$(M–C_2H_5O)^+$
225	25	22	$(M–Br)^+$
177, 179	3.9, 3.7	12.9, 11.7	$(M–SF_5)^+$
127	16.5	13.6	SF_5^+
123, 125	19.5, 19.1	9.3, 8.2	$(C_2HBrF?)^+$
104, 106	15.2, 14.9	10.9, 10.7	C_2HBr^+
89	47	50	SF_3^+
53	75	52	C_3HO^+
29	100	100	$C_2H_5^+$

Anal. calcd. for $C_5H_6BrF_5O_2S$: C, 19.68; H, 1.98; F, 31.1. Found: C, 19.74; H, 2.13; F, 31.4%.

3.1.2. Residue

The distillation residue had the following characteristics: Three bands in the gas chromatogram, $R_{t1} = 11.97$ min (major), $R_{t2} = 12.75$ min (minor), $R_{t3} = 12.75$ min (very feeble). The major and minor bands show two peaks of equal intensity (357, 359, 1:1) in the mass spectrum, the smallest band is too weak to make meaningful comparisons with the other two bands. The major identifying bands in the infrared spectrum were (neat, KBr, cm^{-1}): $\nu = 1737$ (s-vs), 1606 (w-m), 1237 (s), 856 (vs). The ^{19}F NMR spectrum (84.7 MHz, $CDCl_3$): two overlapping SF_5-signals (AB_4 spectra): major component: $\varphi_{A1} = 77.8$ ppm, nine lines. $\varphi_{B1} = 66.8$ ppm, skewed d-m, $J_{AB} \approx 153$ Hz; minor component: $\varphi_{A2} = 77.3$ ppm, nine lines. $\varphi_{B2} \approx 67$ ppm, skewed d-m, $J_{AB} \approx 153$ Hz. Area $\varphi_{A1+A2} = 0.9$ F; $\varphi_{B1+B2} = 4.1$ F.

Elemental analysis: Found: C, 29.43; H, 2.89; F, 24.2; S, 7.85. Calculated for $SF_5(HC{\equiv}CCOOC_2H_5)_2Br$, $C_{10}H_{12}BrF_5O_4S$: C, 29.79; H, 3.00; F, 23.6; S, 7.95%.

Therefore, the residue is the 2:1 adduct of ethyl propiolate and SF_5Br; which is most likely a 1,3-butadiene derivative, and would allow for several geometric isomers. The two peaks of equal intensity in the mass spectrum (357, 359, 1:1) is in line with the general ester fragmentation pattern $(M–OR)^+$, therefore, $M^+ = 403$ (402, 404, 1:1), the molecular weight of the above bis-adduct.

3.2. Preparation of ethyl β-SF_5-acrylate (**2**)

Ethyl α-bromo-β-SF_5-acrylate (10.6 g, 34.8 mmol) in ether 100 ml was reduced with $(n\text{-}C_4H_9)_3SnH$ (11.00 g, 37.5 mmol, added dropwise) while cooling was maintained using a room-temperature water bath. After 24 h, another gram of reductant was added (since the reaction had not gone to completion). After stirring overnight, all starting material was consumed and the ether was pumped off through a −196 °C cold trap. Since this also led to the transfer of the product, pumping was maintained for several hours, and the ether was then distilled off at atmospheric pressure from the material collected in the cold trap. The residue was distilled at 67–74 °C/19.5 Torr. Yield = 1.56 g of a clear, colorless liquid with an overpowering sweet odor, showing two bands in GC–MS, apparently *cis*- and *trans*-product. The pot residue was collected by vacuum-transfer and consisted of the major component of the above mixture. Total yield = 1.83 g (23.6%).

In an improved process, the yields are increased to ∼90% when the reduction is carried out in tetraglymedimethyl ether; the pure product is isolated by heating the reaction flask to ∼100 °C and pumping away the volatile materials through a trap cooled to −196 °C.

^{1}H NMR spectrum: Main product was obtained pure: $\delta = 1.32$ ppm, t, $J = 7.23$ Hz, 2.9 H, CH_3. $\delta = 4.29$ ppm, q, $J = 7.25$ Hz, 2.0 H, CH_2. $\delta_\alpha = 6.24$ ppm, d-p, $J_{\alpha\beta} = 10.94$ Hz, $J_{SF4H\alpha} = 2.34$ Hz, 1.2 H. $\delta_\beta = 6.52$ ppm, d-p, $J_{\alpha\beta} = 10.94$ Hz, $J_{SF4H\beta} = 8.4$ Hz, 1.0H; *cis*-isomer.

For the minor product, which was obtained in mixture with the major component: $\delta = 1.33$ ppm, t, $J = 7.0$ Hz, CH_3. $\delta = 4.19$ ppm, q, $J = 7.0$ Hz, CH_2. $\delta_\alpha = 6.56$, skewed d, broadened lines, $J_{\alpha\beta} \approx 15$ Hz. $\delta_\beta = 7.42$ ppm, d-p, $J_{\alpha\beta} = 14.46$ Hz, $J_{SF4H\beta} = 6.83$ Hz; *trans*-isomer. *Cis*:*trans* for this mixture ≈4:1.

^{19}F NMR spectrum (ppm): Two overlapping AB_4 spectra in the above mixture; combined integration: $\varphi_A + \varphi_B = 1 : 4$.

	Minor	Major
φ_A	80	79.7
φ_B	≈65.5	65.0
J_{AB}	Probably 144	144

Minor:Major=22:78 (extrapolated from overlapping B_4-resonances).

Infrared spectrum (mixture, neat, KBr): 3094, w; 3045, w-vw; 2990, w-m; 2946, w; 2911, w-vw; 2882, vw; 1744, s-vs; 1656, w-m; 1469, w-m; 1456, w-m; 1394, -m; 1374, s; 1350, m-s; 1313, m; 1302, w-m; 1251, s; 1233, s; 1205, s; 1116, vw; 1096, w; 1024,s; 953, w-m; 850, vs; 830, s-vs; 793, vw; 737, w-m; 695, vw; 653,w; 601, s; 578, w-m; 561, m; 467, w-m.

GC–MS, R_t,	2.65		4.89 min	Two bands
Area %	23		77	
Mass, %	181	77	89	$(M–C_2H_5O)^+$
	159	–	20.3	$(M–C_2H_5–2F)^+$
	127	15.7	15.1	SF_5^+
	99	9.5	3.5	$(M–SF_5)^+$
	89	47	50	SF_3^+
	73	54.2	35.8	$(COOC_2H_5)^+$
	54	48	73	$C_3H_2O^+$
	53	17	14.7	C_3HO^+
	45	31.8	56.6	$C_2H_5O^+$
	29	100	100	$C_2H_5^+$

Anal. calcd. for $C_5H_7F_5O_2S$:

Calculated	Found:pure isomer (*cis*)	Found:isomer mixture
C, 26.55	27.12	26.96
H, 3.12	3.23	3.11
F, 42.0	41.7	41.8
S, 14.18	13.94	13.93

3.3. Preparation of methyl β-SF_5-methacrylate (**3**)

An ice-cold solution of sodium (0.45 g,19.6 mmol) in methanol (10 ml) was added dropwise over 5 min to a solution of methyl α-bromo-β-SF_5-isobutyrate (19.6 mmol) in methanol (5 ml) while being stirred in an ice bath. After standing overnight at room temperature, the solvent was distilled off at atmospheric pressure and the product was obtained at 53–56 °C/13 Torr as a clear, colorless liquid. Yield = 3.14 g or 71% of theory.

^{1}H NMR spectrum: Multiplets were observed at $\delta_1 = 2.19$ ppm, d-p, $J_{HFB} \approx 2$ Hz, $J_{HH} \approx 1.8$ Hz, 3 H (α-CH_3). $\delta_2 = 3.83$, s, 3 H (OCH_3). $\delta_3 \approx 7.32$, p-q, broadened, $J_{HFB} \approx 1.7$ Hz, 0.9 H (H_β). A minor component was also observed at $\delta_{1'} = 2.17$ ppm, s, br, very feeble. $\delta_{2'} = 3.86$, s, very feeble.

^{19}F NMR spectrum: AB_4-spectrum: $\varphi_A = 82.3$ ppm, nine lines, 1 F. $\varphi_B = 65.0$ ppm, skewed d-m, 4 F, $J_{AB} = 151$ Hz. A minor signal was observed at 68 ppm (B_4-portion of an AB_4-spectrum, the A-part of which was not detected; it had ≈3% of the intensity of the B_4-portion of the major component).

Infrared spectrum (neat sample, KBr): 3450, vw; 3110, vw; 3093, vw; 3044, vvw; 3014, vw; 2962, w; 2906, vvw; 2851, vvw; 1737, s-vs; 1649, w-m; 1449, w-m; 1439, m; 1334, w-m; 1260, s; 1195, w; 1127, m-s; 1070, vvw; 1027, w; 963, vvw; 878, s-vs,sh; 836, vs; 784, vvw; 745, m; 739, m, sh; 690, vvw; 636, m; 627, w-m, sh; 601, m-s; 575, w-m; 568, m; 556, w; 518, vvw.

GC–MS: $R_t = 3.59$ min: 226, 0.6%, M^+; 206, 19.3%, $(M–HF)^+$; 195, 25.5%, $(M–OCH_3)^+$;167, 5.1%, $(M–CO_2CH_3)^+$; 127, 9.3%, SF_5^+; 101, 3.1%, SF_3C^+; 99, 17.6%, $(M–SF_5)^+$; 89, 67%, SF_3^+; 71, 2.3%, $CCO_2CH_3^+$; 70, 4.8%, SF_2^+; 59, 100%, $CO_2CH_3^+$. The minor component identified by NMR spectroscopy was not observed in the gas chromatogram.

Anal. calcd. for $C_5H_7F_5O_2S$: C, 26.55; H, 3.12; F, 42.0; S, 14.18. Found: C, 26.43; H, 3.06; F, 42.3; S, 13.67%.

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