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New polyfluoroalkoxysulfonyl fluorides
Part VI. Heterocyclic ether derivatives

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Abstract

The reaction of $\overline{CF_2CF_2OS}O_2$ with heterocyclic haloalkanes in the presence of silver fluoride has been used to prepare two novel reactive polyfluorosulfonyl fluoride derivatives, i.e. $ROCF_2CF_2SO_2F$ ($R=\overline{O(CH_2)_3OC}HCH_2CH_2$ and $\overline{O(CH_2)_4C}HCH_2$). Infrared, mass and NMR spectra are presented in order to support the assigned structures.

Introduction

Previously, we have reported a method which involves the use of metal fluorides (KF, CsF, AgF), fluorosultones ($\overline{CF_2CF_2OS}O_2$, $\overline{CF_3CFCF_2OS}O_2$) and aliphatic haloalkanes or aromatic haloalkanes (RX, X = Br, I) for preparing fluorocarbon ether-containing sulfonyl fluorides [1–4]. In this paper we wish to report the reaction of several heterocyclic haloalkanes with the $\overline{CF_2CF_2OS}O_2$ sultone in the presence of silver fluoride. The new fluorocarbon derivatives contain not only the SO_2F grouping but a reactive heterocyclic grouping as well. There is considerable interest in the fluorocarbon sulfonyl fluorides (RSO_2F) precursors because of their utilization as ion-exchange resins, surface-active agents and in the preparation of strong sulfonic acids [5–10]. The fluoroheterocyclic ethers discussed in this paper may also find use as potential monomers for polymerization [11].

Results and discussion

The reactions of $\overline{CF_2CF_2OS}O_2$ with heterocyclic haloalkanes were carried out according to the following equations:

$$\overline{CF_2CF_2OS}O_2 \xrightarrow[\text{diglyme}]{\text{AgF}} FC(O)CF_2SO_2F \quad (1)$$

$$FC(O)CF_2SO_2F \xrightarrow{\text{AgF}} AgOCF_2CF_2SO_2F \quad (2)$$

$$AgOCF_2CF_2SO_2F + RX \longrightarrow ROCF_2CF_2SO_2F + AgX \quad (3)$$

$R=\overline{O(CH_2)_3OC}HCH_2CH_2$, **1**; $R=\overline{O(CH_2)_4C}HCH_2$, **2**

In general, the reaction is carried out in two stages: in the first stage the $\overline{CF_2CF_2OSO_2}$ sultone undergoes rearrangement [eqn. (1)], followed by formation of the silver alkoxide [eqn. (2)]. In the second stage, a nucleophilic substitution of RX by $^-OCF_2CF_2SO_2F$ from $AgOCF_2CF_2SO_2F$ occurred [eqn. (3)]. The two new compounds are clear colorless liquids; product **1** decomposes slowly at room temperature.

The infrared spectra of the two new products, **1** and **2**, have several common features. The characteristic SO_2(asym), SO_2(sym) and S–F (stretching) frequencies are found in the 1463–1457, 1242 and 800–793 cm^{-1} regions, respectively. The C–H absorption bands are located in the 2946–2857 cm^{-1} region. These assignments agree with the results previously obtained [1–4].

In the EI mass spectra, MH^+, M^+ and $M-H^+$ ions were found. In the CI^- and EI^+ spectra, cracking patterns were obtained that were supportive of the assigned structure.

The structures of the new products were determined from their respective ^1H and ^{19}F NMR spectra. In the ^{19}F NMR spectra, chemical shifts consistent with similar groupings in other polyfluoroalkyl sulfonyl fluorides were found. For $ROCF_2CF_2SO_2F$, the chemical shift values found for OCF_2, CF_2 and SO_2F range from -86.2 to -84.8, -113.8 to -112.5 and 43.0 to 44.5 ppm, respectively. The coupling constants $J_{OCF_2-SO_2F}$, $J_{OCF_2CF_2}$ and $J_{CF_2SO_2F}$ range from 5.9–6.3, 5.1–5.2 and 5.1–6.8 Hz, respectively. The values are in excellent agreement with those for other $ROCF_2CF_2SO_2F$ derivatives [1–4].

Experimental

The sultone $\overline{CF_2CF_2OSO_2}$ was prepared according to a modified literature method [12]. Silver fluoride was dried under vacuum before use. All other chemicals were obtained from commercial sources and used as received.

General procedure

Gases were manipulated in a conventional Pyrex glass vacuum apparatus equipped with a Heise–Bourdon tube gauge and televac thermocouple gauge. Infrared spectra were obtained by using a Pyrex glass cell with KBr windows on a Nicolet 20DX spectrometer. The NMR spectra were recorded with a Varian model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for the fluorine resonance. TMS and F-11 ($CFCl_3$) were used as external standards. By convention, fluorine resonances appearing downfield from $CFCl_3$ are assigned positive values; upfield resonances are assigned negative values. In some cases, compounds were purified via gas chromatography using an Aerograph Autoprep (model A-700) gas chromatograph. The mass spectra were taken on a VG-7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluorokerosene was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Germany.

Preparation of 2-(2-fluorosulfonyltetrafluoroethoxy)1,3-dioxan

Into a 125 ml Pyrex glass vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 3.70 g (29.1 mmol) of dried silver fluoride, 5.0 ml diglyme and 7.50 g (41.7 mmol) of $\overline{\mathrm{CF_2CF_2OSO_2}}$. The reaction mixture was warmed to room temperature and stirred at 35–37 °C for 3 h. After heating, 5.00 g (25.6 mmol) of 2-(2-bromoethyl)-1,3-dioxan was added via vacuum transfer. The reaction mixture was stirred at 37–40 °C for 68 h.

The products were filtered in order to remove AgBr. The filtrate was washed three times with water (60 ml total), dried over P_4O_{10} and distilled to give 2.96 g of product, 37.0% yield, b.p. 90–92 °C/30 mmHg.

The infrared spectrum of **1** had the following bands (cm^{-1}): 2945 (w); 2932 (w); 2862 (w); 1463 (s); 1452 (s); 1339 (m); 1242 (s); 1204 (m); 1143 (s); 1110 (m); 1022 (m); 981 (m); 930 (w); 914 (w); 895 (w); 825 (s); 793 (vs); 656 (w); 610 (s).

^{19}F NMR: $\phi_{\mathrm{OCF_2}} = -86.2$ (d, t); $\phi_{\underline{\mathit{CF}}_2\mathrm{SO_2F}} = -113.8$ (d, t); $\phi_{\mathrm{SO_2F}} = 43.0$ (t, t) ppm; coupling constants are $J_{\mathrm{OCF_2-SO_2F}} = 5.9$, $J_{\mathrm{OCF_2CF_2}} = 5.2$ and $J_{\mathrm{CF_2SO_2F}} = 5.10$ Hz.

^{1}H NMR: $\delta_{\mathrm{C}\mathit{H}} = 5.0$ (t); $\delta_{\mathrm{CH}\underline{\mathit{CH}_2}} = 1.5$–$2.2$ (overlap); $\delta_{\mathrm{CHCH_2}\underline{\mathit{CH}_2}} = 4.5$ (t); $\delta_{\mathrm{CHO}\underline{\mathit{CH}_2}} = 4.0$ (t), 4.3 (t); $\delta_{\mathrm{CHOCH_2}\underline{\mathit{CH}_2}} = 2.2$ (m) ppm.

MS (m/z) $(EI)^+$: 315, MH^+; 314, M^+; 313, $(M-H)^+$; 284, $(M-CH_2O)^+$; 257 $(MH-(CH_2)_3O)^+$; 256, $(M-(CH_2)_3O)^+$; 255, $(M-H(CH_2)_3O)^+$; 181, $(M-CF_2SO_2F)^+$; 151, $(M-CF_2SO_2F, CH_2O)^+$, $C_2F_4SF^+$; 131, $(M-CF_2CF_2SO_2F)^+$; 115, $(M-OCF_2CF_2SO_2F)^+$; 114, $CFSO_2F^+$; 113, $(M-H_2OCF_2CF_2SO_2F)^+$; 109, $(M-H_6OCF_2CF_2SO_2F)^+$; 100, $(C_2F_4^+, C_5H_8O_2)^+$; 97, $C_5H_5O_2^+$; 88, $C_2SO_2^+$; 87, $C_4H_7O_2^+$; 85, $C_4H_5O_2^+$; 83, SO_2F^+; 81, CF_2CF^+; 75, C_2FS^+; 73, $C_3H_5O_2^+$; 69, $C_4H_5O^+$; 67, $C_4H_3O^+$; 64, SO_2^+; 61, $C_2H_2OF^+$; 60, C_2HOF^+.

MS (m/z) $(CI)^-$: 299, $(MH-O)^-$; 199, $OC_2F_4SO_2F^-$, $C_7H_7O_2F_4^-$; 185, $C_6H_5O_2F_4^-$; 177, $C_7H_4O_2F_3^-$; 155, $C_3HO_3SF_2^-$, $C_5H_3OF_4^-$; 135, $COCCFSO_2^-$; 123, $OCCFSO_2^-$; 85, $C_4H_5O_2^-$; 83, SO_2F^-.

Analysis: Calc. for $C_8H_{11}F_5O_5S$: C, 30.57; H, 3.54; F, 30.2; S, 10.20%. Found: C, 30.33; H, 3.60; F, 26.5; S, 10.35%.

*Preparation of 2-(fluorosulfonyltetrafluoroethoxy)tetrahydro-2*H-pyran

In a similar procedure to that previously described, 3.40 g (26.8 mmol) of dried silver fluoride, 7.0 ml of diglyme and 6.00 g (33.3 mmol) of $\overline{\mathrm{CF_2CF_2OSO_2}}$ were heated at 37–39 °C for 3 h. After heating, 4.00 g (22.3 mmol) of 2-(bromomethyl)tetrahydro-2*H*-pyran was added and heated at 36–40 °C for 24 h. The reaction products were filtered in order to remove AgBr. The liquid was washed three times with H_2O (60 ml total), dried over P_4O_{10} and distilled to give 1.18 g of product 17.7% yield, b.p. 70–71 °C/4 mmHg.

The infrared spectrum of **2** had the following bands (cm^{-1}): 2946 (s); 2857 (s); 1457 (vs); 1338 (m); 1242 (vs); 1205 (s); 1138 (s); 1105 (vs);

1049 (m); 1001 (m); 952 (m); 897 (w); 863 (w); 800 (vs); 785 (vs); 655 (m); 611 (s); 544 (m); 488 (w).

^{19}F NMR: $\phi_{OCF_2} = -84.8$ (d, t); $\phi_{\underline{CF}_2SO_2F} = -112.5$ (d, t); $\phi_{SO_2F} = 44.5$ (t, t) ppm; coupling constants are $J_{OCF_2-SO_2F} = 6.3$, $J_{OCF_2CF_2} = 5.1$ and $J_{CF_2SO_2F} = 6.8$ Hz.

^{1}H NMR: $\delta_{CH} = 4.6$ (br); $\delta_{CH(\underline{CH}_2)_3} = 2.1$ (br); $\delta_{\underline{CH}_2OCH\underline{CH}_2} = 4.95$ (br) ppm.

MS (*m/z*) (EI)$^+$: 299, MH$^+$; 298, M$^+$; 297, (M−H)$^+$; 279, (M−F)$^+$; 259, (M−HF$_2$)$^+$; 181, $C_3H_2F_5OS^+$; 179, $C_3F_5OS^+$; 101, $C_5H_9O_2{}^+$; 99, $C_6H_{11}O^+$, $C_5H_7O_2{}^+$; 93, $C_6H_5O^+$; 85, (M−$CH_2OC_2F_4SO_2F$)$^+$; 83, SO_2F^+; 81, $C_5H_5O^+$, $CFCF_2{}^+$; 75, $C_6H_3{}^+$; 67, $C_4H_3O^+$; 65, C_4HO^+.

MS (*m/z*) (CI)$^-$: 249, (M−CH_2OF)$^-$; 206, (M−$H(CH_2)_4OF$)$^-$; 199, $OC_2F_4SO_2F^-$; 183, $OC_2F_4SOF^-$; 155, $CHOCCFSO_2F^-$; 146, $O(CH_2)_4CHCH_2OCF^-$; 128, $C_7H_9OF^-$; 111, $C_6H_4OF^-$; 85, $O(CH_2)_4CH^-$; 83, SO_2F^-.

Analysis: Calc. for $C_8H_{11}F_5O_4S$: C, 32.21; H, 3.72; F, 31.9; S, 10.75%. Found: C, 32.70; H, 3.80; F, 31.2; S, 10.52%.

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