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A new route to polyfluorinated trifluoromethanesulfonates. Synthesis of perfluoroallyl and perfluorobenzyl triflates ☆

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Abstract

Polyfluoroalkyl trifluoromethanesulfonates (triflates) can be prepared in good to excellent yields by the reaction of halofluoroalkanes such as CFC-11, CFC-113 and CFC-112 with boron triflate at 20–25 °C. Hexafluoropropene (HFP) is more active and reacts with $B(OSO_2CF_3)_3$ even at 0 °C to give perfluoroallyl triflate in 68% yield. Octafluorotoluene, 1,1,2-trichloro-3,3,3-trifluoroprop-1-ene and hexafluoro-2,3-dichloro-but-2-ene also produce the corresponding triflates in 30–60% yields on reaction with boron triflate.

Keywords: Polyfluorinated trifluoromethanesulfonates; Perfluoroallyl triflates; Perfluorobenzyl triflates; NMR spectroscopy; Mass spectrometry; IR spectroscopy

1. Introduction

Boron trifluoromethanesulfonate (**1**), first described by DesMarteau et al. [1] and isolated by Olah et al. [2], is a strong Lewis acid capable of generating stable carbocations [2,3] and catalyzing Friedel–Crafts aromatic substitution. This paper describes a new use of **1** for preparing polyfluoroalkyl and polyfluoroalkenyl triflates from polyfluorinated compounds having 'activated' fluorine atoms.

$$X_3C{-}F + 1/3B(OSO_2CF_3)_3 \longrightarrow \atop \textbf{(1)} \qquad X_3C{-}OSO_2CF_3 + 1/3BF_3$$

2. Results and discussion

The reaction between trichlorofluoromethane (CFC-11) and **1** proceeded smoothly at 25 °C to give triflate **2** and BF_3 (Eq. (1)].

$$CFCl_3 + \mathbf{1} \xrightarrow{25\,^\circ C,\ 5\ h} \underset{\textbf{(2)}\ 90\%}{CCl_3OSO_2CF_3} + BF_3 \qquad (1)$$

Although it has been reported [3] that 1,1,2-trichlorotrifluoroethane (CFC-113) can be used as a solvent for **1**, it reacted slowly with **1** at 25 °C to give triflate **3** [4] isolated in 44% yield [(Eq. (2)].

$$CF_2ClCCl_2F + \mathbf{1} \xrightarrow{25\,^\circ C,\ 20\ h} \underset{\textbf{(3)}\ 44\%}{CF_2ClCCl_2OSO_2CF_3} \qquad (2)$$

1,2-Dichlorotetrafluoroethane (CFC-114) did not react with **1** under similar conditions (25 °C, 24 h). Both $CF_2BrCFClBr$ and $CFCl_2CCl_2F$ (CFC-112) were more reactive towards **1**, but the formation of triflates **4** and **5** was accompanied by halogen migration [Eqs. (3) and (4)].

$$CF_2BrCFClBr + \mathbf{1} \xrightarrow{25\,^\circ C,\ 6\ h} \underset{\textbf{(4)}\ 56\%}{CF_3SO_2OCF_2CBr_2Cl} \qquad (3)$$

$$CFCl_2CCl_2F + \mathbf{1} \xrightarrow{25\,^\circ C,\ 8\ h} \underset{\textbf{(5)}\ 71\%}{CF_3SO_2OCFClCCl_3} \qquad (4)$$

Interestingly, the reaction of the isomeric CFC-112a with **1** was much slower and even after 72 h at 25 °C conversion of F-112a into **5** according to ^{19}F NMR spectroscopy was not greater than 30%.

Fluoro-olefins with activated allylic fluorines are more reactive than haloalkanes towards **1**. Thus hexafluoropropene (HFP), for example, interacted with boron triflate even at 0 °C to give perfluoroallyl triflate (**6**) in 68% isolated yield [Eq. (5)].

$$CF_2{=}CFCF_3 + \mathbf{1} \xrightarrow{0\,^\circ C,\ 5\ h} \underset{\textbf{(6)}\ 68\%}{CF_2{=}CFCF_2OSO_2CF_3} \qquad (5)$$

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Under similar conditions, octafluorotoluene was converted to perfluorobenzyl triflate **7** [Eq. (6)].

$$\mathrm{C_6F_5CF_3} + \mathbf{1} \xrightarrow{0\,^\circ\mathrm{C},\ 4\ \mathrm{h}} \underset{(\mathbf{7})\ 30\%}{\mathrm{C_6F_5CF_2OSO_2CF_3}} \tag{6}$$

while 1,1,2-trichlorotrifluoroprop-1-ene and hexafluoro-2,3-dichlorobut-2-ene reacted with **1** at room temperature giving triflates **8** and **9**, respectively [(eq. (7)].

$$\begin{array}{l} \mathrm{XCCl{=}CClCF_3} \\ \qquad + \mathbf{1} \xrightarrow{25\,^\circ\mathrm{C},\ 2\text{–}4\ \mathrm{h}} \mathrm{XCCl{=}CClCF_2OSO_2CF_3} \\ \qquad\qquad\qquad\quad (\mathbf{8})\ \mathrm{X{=}Cl},\ 63\% \\ \qquad\qquad\qquad\quad (\mathbf{9})\ \mathrm{X{=}CF_3},\ 55\% \end{array} \tag{7}$$

As with the analogous perfluoroallyl [5] and perfluorobenzyl [6] fluorosulfates, sulfonyl groups in **6** and **7** are easily displaced by nucleophiles [Eqs. (8) and (9)]. Both reactions are exothermic and produce the substitutional products **10**–**12** in high yield.

$$\begin{array}{l} \mathbf{6} + \mathrm{KX} \xrightarrow[\text{diglyme}]{0\text{–}25\,^\circ\mathrm{C},\ 1\ \mathrm{h}} \mathrm{CF_2{=}CFCF_2X} \\ \qquad\qquad\qquad (\mathbf{10})\ \mathrm{X{=}I},\ 81\% \\ \qquad\qquad\qquad (\mathbf{11})\ \mathrm{X{=}OCF(CF_3)_2},\ 88\% \end{array} \tag{8}$$

$$\mathbf{7} + \mathrm{KI} \xrightarrow[\text{diglyme}]{0\text{–}25\,^\circ\mathrm{C},\ 1\ \mathrm{h}} \underset{(\mathbf{12})\ 92\%}{\mathrm{C_6F_5CF_2I}} \tag{9}$$

3. Experimental details

3.1. General procedures

^{19}F NMR spectra were recorded on a QE-300 (General Electric) instrument using $\mathrm{CFCl_3}$ as internal standard and $\mathrm{CDCl_3}$ as a lock solvent. IR spectra were recorded on a Perkin-Elmer Model 983G spectrometer using $\mathrm{CH_2Cl_2}$ as a solvent. Compound **1** was prepared by a literature method [2] and stored at 0 °C. Compounds **3** [4], **10** [5], **11** [6] and **12** [7] were identified by comparison of their ^{19}F NMR, IR and mass spectral data with literature values.

3.2. Preparation of triflates 2–9

In a typical experiment, a glass flask equipped with a condenser, thermometer and magnetic stir bar was protected against atmospheric moisture and charged with 0.02–0.035 mol of solid **1**. The substrate was then added in one portion (molar ratio **1** to substrate = 1:3). The reaction mixture was stirred at 20–25 °C and monitored by GC. After the reaction was complete, the resulting mixture was poured into iced water, the product (lower layer) separated, dried over $\mathrm{P_2O_5}$ and distilled.

Reaction of HFP with **1** was performed in a 75 ml Hoke cylinder using a 3:1 ratio of HFP to **1** and 30–210 mmol of HFP. Compound **1** was loaded into the cylinder inside a dry box and the calculated amount of HFP introduced into an evacuated cylinder at −196 °C. The cylinder was stored at 0 °C for 5 h and then unloaded under vacuum. The crude product [mixture of **6** and 10%–15% of $\mathrm{(CF_3SO_2)_2O}$] was poured into water and stirred for 30 min at 25 °C to completely remove triflic anhydride. The product was separated, dried with $\mathrm{P_2O_5}$ and distilled.

Compound **2**: b.p. 117–120 °C. IR (cm^{-1}) 1439 ($\mathrm{SO_2}$). ^{19}F NMR δ: −73.80 (s) ppm. Analysis: Found: C, 8.94; F, 21.28%. $\mathrm{C_3F_3Cl_3SO_3}$ requires: C, 8.97; F, 21.31%.

Compound **4**: b.p. 125–126 °C/200 mmHg. IR (cm^{-1}): 1451 ($\mathrm{SO_2}$). ^{19}F NMR δ: −77.90 (2F, q); −73.6 (3F, t, J=6 Hz) ppm. MS (EI) m/z: 403.7532 ($\mathrm{M^+}$, $\mathrm{C_3F_5ClBr_2SO_3{}^+}$, calc. 403.7544).

Compound **5**: b.p. 123–124 °C/200 mmHg. IR (cm^{-1}): 1448 ($\mathrm{SO_2}$). ^{19}F NMR δ: −68.3 (1F, q); −73.7 (3F, d, J=6 Hz) ppm. MS (Cl) m/z: 182.8757 [$\mathrm{(M-CF_3SO_2)^+}$, $\mathrm{C_2Cl_4F^+}$, calc. 182.8738]; 69.0448 ($\mathrm{CF_3{}^+}$, calc. 68.9952).

Compound **6**: b.p. 64–65 °C. IR (cm^{-1}): 1789 (C=C); 1448 ($\mathrm{SO_2}$). ^{19}F NMR, $\mathrm{CF^AF^B{=}CF^CCF_2{}^DSO_2CF_3{}^E}$, δ A −88.3 (1F, ddt); B −102.3 (1F, ddt); C −190.1 (1F, ddt); D −68.4 (2F, m); E −74.4 (3F, t) ppm; J(A–B) = 47, J[A–C(*cis*)] = 40, J[B–C(*trans*)] = 118, J(A–D) = 7, J(B–D) = 25, J(C–D) = 14, J(D–E) = 5 Hz (cf. Ref. [5]). MS (EI) m/z: 279.9475 ($\mathrm{M^+}$, $\mathrm{C_4F_8SO_3{}^+}$, calc. 279.9440).

Compound **7**: b.p. 31–33 °C/0.04 mmHg. IR (cm^{-1}): 1659, 1531, 1516 ($\mathrm{Ph_f}$); 1445 ($\mathrm{SO_2}$). ^{19}F NMR, $\mathrm{C_6F_5CF_2{}^AOSO_2CF_2{}^B}$, δ: A −57.4 (2F, t, q); B −74.4 (3F, t) *o* −157.6 (2F, m), *m* −138.7 (2F, m), *p* −144.8 (1F, tt) ppm; J(A–B) = 5, J(A–*o*) = 29, J(*o*–*p*) = 7, J(*p*–*m*) = J(*o*–*m*) = 21 Hz (cf. Ref. [6]). MS (EI) m/z: 365.9397 ($\mathrm{M^+}$, $\mathrm{C_8F_{10}SO_3{}^+}$, calc. 365.9408).

Compound **8**: b.p. 125–127 °C. IR (cm^{-1}): 1584 (C=C); 1447 ($\mathrm{SO_2}$). ^{19}F NMR δ: −59.4 (2F, q); −74.1 (3F, t, J=5 Hz) ppm. MS (EI) m/z: 327.8560 ($\mathrm{M^+}$, $\mathrm{C_4F_5Cl_3SO_3{}^+}$, calc. 327.8554).

Compound **9**: b.p. 105–107 °C/150 mmHg. IR (cm^{-1}): 1604 (C=C); 1446 ($\mathrm{SO_2}$). ^{19}F NMR, $\mathrm{CF_3{}^ASO_2CF_2{}^B\text{-}CCl{=}CClCF_3{}^C}$; δ: A −74.1 (3F, t); B −61.8 (2F, q); C −63.6 (3F, s) ppm; J(A–B) = 5 Hz. MS (EI) m/z: 361.8773 ($\mathrm{M^+}$, $\mathrm{C_5F_8Cl_2SO_3{}^+}$, calc. 361.8816).

3.3. Reaction of 6 and 7 with nucleophiles

In a typical experiment, the triflate (10–20 mmol) was added dropwise to a stirred, equimolar solution of KI or $\mathrm{KOCF(CF_3)_2}$ [prepared from $\mathrm{(CF_3)_2C{=}O}$ and KF] in diglyme at 0 °C at a rate sufficient to keep the temperature below 25 °C. After 1 h at room temperature, the reaction mixture was poured into water, the product was separated, dried over $\mathrm{P_2O_5}$ and distilled.

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