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# A new route to polyfluorinated trifluoromethanesulfonates. Synthesis of perfluoroallyl and perfluorobenzyl triflates <sup>☆</sup>

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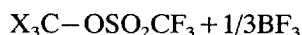
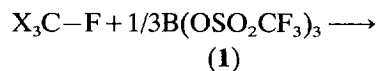
## Abstract

Polyfluoroalkyl trifluoromethanesulfonates (triflates) can be prepared in good to excellent yields by the reaction of halo-fluoroalkanes 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<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> 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; Perfluoroalkyl triflates; Perfluorobenzyl triflates; NMR spectroscopy; Mass spectrometry; IR spectroscopy

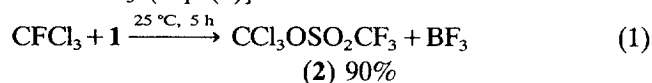
## 1. Introduction

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.



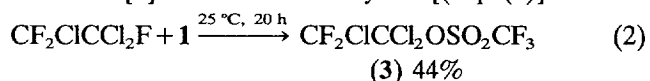
## 2. Results and discussion

The reaction between trichlorofluoromethane (CFC-11) and **1** proceeded smoothly at 25 °C to give triflate **2** and BF<sub>3</sub> (Eq. (1)).

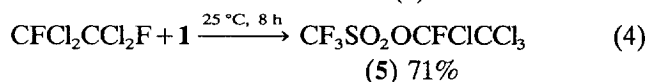
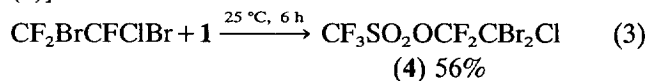


Although it has been reported [3] that 1,1,2-trichlorotrifluoroethane (CFC-113) can be used as a sol-

vent for **1**, it reacted slowly with **1** at 25 °C to give triflate **3** [4] isolated in 44% yield [Eq. (2)].

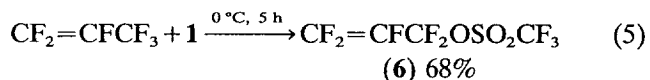


1,2-Dichlorotetrafluoroethane (CFC-114) did not react with **1** under similar conditions (25 °C, 24 h). Both CF<sub>2</sub>BrCFClBr and CFCl<sub>2</sub>CCl<sub>2</sub>F (CFC-112) were more reactive towards **1**, but the formation of triflates **4** and **5** was accompanied by halogen migration [Eqs. (3) and (4)].



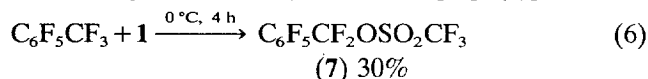
Interestingly, the reaction of the isomeric CFC-112a with **1** was much slower and even after 72 h at 25 °C conversion of F-112a into **5** according to <sup>19</sup>F NMR spectroscopy was not greater than 30%.

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)].

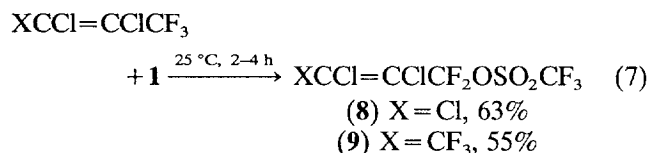


<sup>☆</sup> Contribution No. 6823.

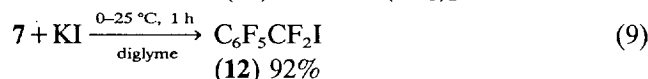
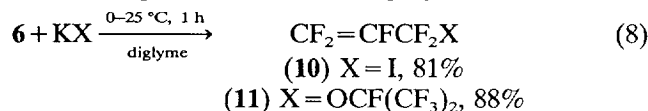
Under similar conditions, octafluorotoluene was converted to perfluorobenzyl triflate **7** [Eq. (6)].



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))].



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.



### 3. Experimental details

#### 3.1. General procedures

<sup>19</sup>F NMR spectra were recorded on a QE-300 (General Electric) instrument using CFCl<sub>3</sub> as internal standard and CDCl<sub>3</sub> as a lock solvent. IR spectra were recorded on a Perkin-Elmer Model 983G spectrometer using CH<sub>2</sub>Cl<sub>2</sub> 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 <sup>19</sup>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 P<sub>2</sub>O<sub>5</sub> 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 (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O] was poured into water and stirred for 30 min at 25 °C to completely remove triflic anhydride. The product was separated, dried with P<sub>2</sub>O<sub>5</sub> and distilled.

Compound **2**: b.p. 117–120 °C. IR (cm<sup>-1</sup>) 1439 (SO<sub>2</sub>). <sup>19</sup>F NMR δ: –73.80 (s) ppm. Analysis: Found: C, 8.94; F, 21.28%. C<sub>3</sub>F<sub>3</sub>Cl<sub>3</sub>SO<sub>3</sub> requires: C, 8.97; F, 21.31%.

Compound **4**: b.p. 125–126 °C/200 mmHg. IR (cm<sup>-1</sup>): 1451 (SO<sub>2</sub>). <sup>19</sup>F NMR δ: –77.90 (2F, q); –73.6 (3F, t, *J* = 6 Hz) ppm. MS (EI) *m/z*: 403.7532 (M<sup>+</sup>, C<sub>3</sub>F<sub>5</sub>ClBr<sub>2</sub>SO<sub>3</sub><sup>+</sup>, calc. 403.7544).

Compound **5**: b.p. 123–124 °C/200 mmHg. IR (cm<sup>-1</sup>): 1448 (SO<sub>2</sub>). <sup>19</sup>F NMR δ: –68.3 (1F, q); –73.7 (3F, d, *J* = 6 Hz) ppm. MS (CI) *m/z*: 182.8757 [(M–CF<sub>3</sub>SO<sub>2</sub>)<sup>+</sup>, C<sub>2</sub>Cl<sub>4</sub>F<sup>+</sup>, calc. 182.8738]; 69.0448 (CF<sub>3</sub><sup>+</sup>, calc. 68.9952).

Compound **6**: b.p. 64–65 °C. IR (cm<sup>-1</sup>): 1789 (C=C); 1448 (SO<sub>2</sub>). <sup>19</sup>F NMR, CF<sup>A</sup>F<sup>B</sup>=CF<sup>C</sup>CF<sub>2</sub><sup>D</sup>SO<sub>2</sub>CF<sub>3</sub><sup>E</sup>, 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 (M<sup>+</sup>, C<sub>4</sub>F<sub>8</sub>SO<sub>3</sub><sup>+</sup>, calc. 279.9440).

Compound **7**: b.p. 31–33 °C/0.04 mmHg. IR (cm<sup>-1</sup>): 1659, 1531, 1516 (Ph<sub>f</sub>); 1445 (SO<sub>2</sub>). <sup>19</sup>F NMR, C<sub>6</sub>F<sub>5</sub>CF<sub>2</sub><sup>A</sup>OSO<sub>2</sub>CF<sub>2</sub><sup>B</sup>, 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 (M<sup>+</sup>, C<sub>8</sub>F<sub>10</sub>SO<sub>3</sub><sup>+</sup>, calc. 365.9408).

Compound **8**: b.p. 125–127 °C. IR (cm<sup>-1</sup>): 1584 (C=C); 1447 (SO<sub>2</sub>). <sup>19</sup>F NMR δ: –59.4 (2F, q); –74.1 (3F, t, *J* = 5 Hz) ppm. MS (EI) *m/z*: 327.8560 (M<sup>+</sup>, C<sub>4</sub>F<sub>5</sub>Cl<sub>3</sub>SO<sub>3</sub><sup>+</sup>, calc. 327.8554).

Compound **9**: b.p. 105–107 °C/150 mmHg. IR (cm<sup>-1</sup>): 1604 (C=C); 1446 (SO<sub>2</sub>). <sup>19</sup>F NMR, CF<sub>3</sub><sup>A</sup>SO<sub>2</sub>CF<sub>2</sub><sup>B</sup>–CCl=CClCF<sub>3</sub><sup>C</sup>; 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 (M<sup>+</sup>, C<sub>5</sub>F<sub>8</sub>Cl<sub>2</sub>SO<sub>3</sub><sup>+</sup>, 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 KOCF(CF<sub>3</sub>)<sub>2</sub> [prepared from (CF<sub>3</sub>)<sub>2</sub>C=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 P<sub>2</sub>O<sub>5</sub> and distilled.

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