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

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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.

$$X_{3}C-F+\frac{1}{3}B(OSO_{2}CF_{3})_{3} \longrightarrow$$
(1)
$$X_{3}C-OSO_{2}CF_{3}+\frac{1}{3}BF_{3}$$

2. Results and discussion

The reaction between trichlorofluoromethane (CFC-11) and 1 proceeded smoothly at 25 °C to give triflate 2 and BF₃ (Eq. (1)].

$$CFCl_3 + 1 \xrightarrow{25 \, ^\circ C, 5 \, h} CCl_3 OSO_2 CF_3 + BF_3 \tag{1}$$

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)].

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

1,2-Dichlorotetrafluoroethane (CFC-114) did not react with 1 under similar conditions (25 °C, 24 h). Both CF₂BrCFClBr and CFCl₂CCl₂F (CFC-112) were more reactive towards 1, but the formation of triflates 4 and 5 was accompanied by halogen migration [Eqs. (3) and (4)].

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

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

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 ¹⁹F 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)].

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

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

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

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)].

$$XCCl=CClCF_{3}$$

$$+1 \xrightarrow{25 °C, 2-4 h} XCCl=CClCF_{2}OSO_{2}CF_{3} \quad (7)$$

$$(8) X=Cl, 63\%$$

$$(9) X=CF_{3}, 55\%$$

As with the analogous perfluoroally [5] and perfluorobenzy [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.

$$6 + KX \xrightarrow[diglyme]{\text{diglyme}} CF_2 = CFCF_2X$$
(8)
(10) $X = I, 81\%$
(11) $X = OCF(CF_3)_2, 88\%$
7 + KI $\xrightarrow[diglyme]{\text{diglyme}} C_6F_5CF_2I$ (9)
(12) 92%

3. Experimental details

3.1. General procedures

¹⁹F NMR spectra were recorded on a QE-300 (General Electric) instrument using CFCl₃ as internal standard and CDCl₃ as a lock solvent. IR spectra were recorded on a Perkin-Elmer Model 983G spectrometer using CH₂Cl₂ 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 ¹⁹F 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_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 (CF₃SO₂)₂O] was poured into water and stirred for 30 min at 25 °C to completely remove triflic anhydride. The product was separated, dried with P₂O₅ and distilled.

Compound 2: b.p. 117–120 °C. IR (cm⁻¹) 1439 (SO₂). ¹⁹F NMR δ : -73.80 (s) ppm. Analysis: Found: C, 8.94; F, 21.28%. C₃F₃Cl₃SO₃ requires: C, 8.97; F, 21.31%.

Compound 4: b.p. 125–126 °C/200 mmHg. IR (cm⁻¹): 1451 (SO₂). ¹⁹F NMR δ : -77.90 (2F, q); -73.6 (3F, t, J=6 Hz) ppm. MS (EI) *m/z*: 403.7532 (M⁺, C₃F₅ClBr₂SO₃⁺, calc. 403.7544).

Compound 5: b.p. 123–124 °C/200 mmHg. IR (cm⁻¹): 1448 (SO₂). ¹⁹F NMR δ : -68.3 (1F, q); -73.7 (3F, d, J=6 Hz) ppm. MS (Cl) *m*/z: 182.8757 [(M– CF₃SO₂)⁺, C₂Cl₄F⁺, calc. 182.8738]; 69.0448 (CF₃⁺, calc. 68.9952).

Compound 6: b.p. 64–65 °C. IR (cm⁻¹): 1789 (C=C); 1448 (SO₂). ¹⁹F NMR, CF^AF^B=CF^CCF₂^DSO₂CF₃^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 (M⁺, C₄F₈SO₃⁺, calc. 279.9440).

Compound 7: b.p. 31–33 °C/0.04 mmHg. IR (cm⁻¹): 1659, 1531, 1516 (Ph_t); 1445 (SO₂). ¹⁹F NMR, $C_6F_5CF_2^{A}OSO_2CF_2^{B}$, 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 (M⁺, $C_8F_{10}SO_3^{+}$, calc. 365.9408).

Compound 8: b.p. 125–127 °C. IR (cm⁻¹): 1584 (C=C); 1447 (SO₂). ¹⁹F NMR δ : -59.4 (2F, q); -74.1 (3F, t, *J*=5 Hz) ppm. MS (EI) *m/z*: 327.8560 (M⁺, C₄F₅Cl₃SO₃⁺, calc. 327.8554).

Compound 9: b.p. 105–107 °C/150 mmHg. IR (cm⁻¹): 1604 (C=C); 1446 (SO₂). ¹⁹F NMR, CF₃^ASO₂CF₂^B-CCl=CClCF₃^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 (M⁺, C₃F₈Cl₂SO₃⁺, 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(CF₃)₂ [prepared from (CF₃)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 P_2O_5 and distilled.

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References

[1] K.K. Johri, Y. Katsuhara and D.D. DesMarteau, J. Fluorine Chem., 19 (1982) 227.

- [2] G.A. Olah, K. Laali and O. Faroog, J. Org. Chem., 49 (1984) 45.
- [3] G.A. Olah, O. Faroog, S.M. Fornia and J. Olah, J. Am. Chem. Soc., 119 (1988) 2560.
- [4] Y. Katsuhara and D.D. DesMarteau, J. Org. Chem., 45 (1980) 2441.
- [5] K.C. Ramey and W.S. Brey, J. Chem. Phys., 40 (1964) 2349;
 C.G. Moreland and W.S. Brey, J. Chem. Phys., 45 (1966) 803.
- [6] C.G. Krespan and D.C. England, J. Am. Chem. Soc., 103 (1981) 5598.
- [7] L.S. German, I.L. Knunyants, S.R. Sterlin and V.F. Cherstkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 1933.