A Simple Preparation of Alkyl Trifluoromethanesulfonates (Triflates) from Alkyl Trimethylsilyl Ethers

Corinne Aubert, Jean-Pierre Bégué*

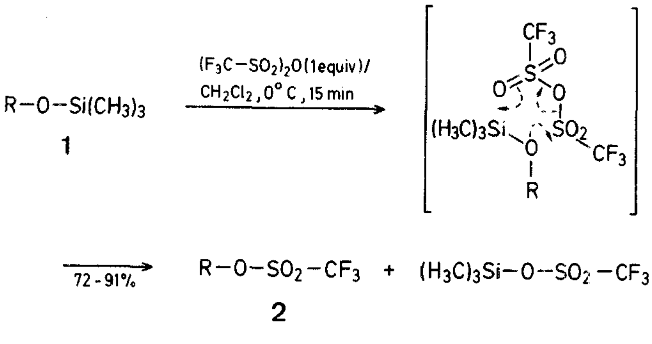
CERCOA, CNRS, 2 Rue Henri Dunant, F-94320 Thiais, France

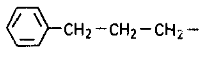
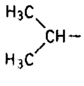
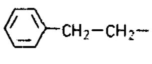
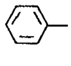
Several alkyl trifluoromethanesulfonates (triflates) **2** are prepared by reacting alkyl trimethylsilyl ethers **1** with trifluoromethanesulfonic anhydride. The triflates **2** can be used for further reactions without isolation, as illustrated in the preparation of the ether **3** and cumene (**4**).

Alkyl trifluoromethanesulfonates (triflates) are important reagents in both synthetic and physical organic chemistry[1,2,3]. These are usually prepared from trifluoromethanesulfonic (triflic) anhydride and the appropriate alcohol in the presence of a base[1-5], or via a displacement reaction from a primary halide using silver trifluoromethanesulfonate[1,2,3,5,6]. Most alkyl triflates are relatively unstable and they are used immediately after preparation[2].

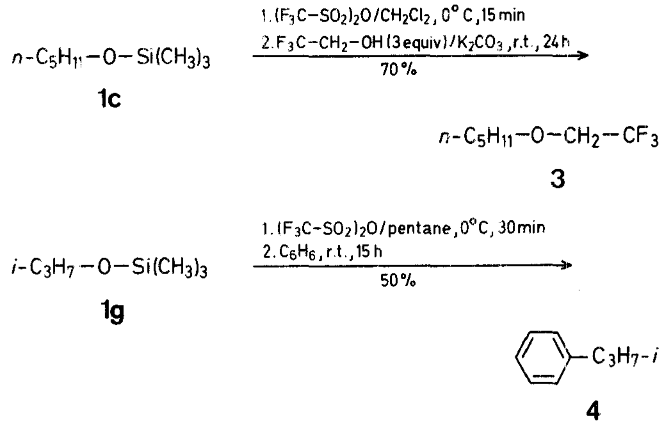
The reaction of aryl trimethylsilyl ethers and triflic anhydride (or trifluoromethanesulfonyl fluoride) with fluoride anion as catalyst[7] is one of several different methods for preparing aryl triflates[8,9,10]. This reaction has been also exemplified for the preparation of a vinyl triflate[11] but has never been reported in the case of alkyl triflates.

We report here a fast and very simple method for the preparation of alkyl triflates by reaction of alkyl trimethylsilyl ethers **1** with triflic anhydride. The trimethylsilyl ethers of primary and secondary alcohols react quickly with triflic anhydride, in an inert solvent (pentane or dichloromethane), without addition of a base or catalyst, leading quantitatively to the corresponding triflates. These can be isolated after a rapid work-up or used directly in the crude solution after reaction.



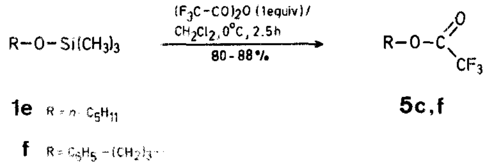
1,2	R	1,2	R
a	n-C_3H_7	f	
b	n-C_4H_9		
c	n-C_5H_{11}		
d	n-C_8H_{17}	g	 $\begin{matrix} H_3C & \\ & CH- \\ H_3C & \end{matrix}$
e		h	

In the latter case, only one equivalent of trimethylsilyl triflate is present in the reaction mixture, which is not damaging for some utilizations, as exemplified in our preparation of the ether **3** and cumene (**4**).



From a mechanistic point of view, it seems reasonable to assume that this reaction occurs by an electrophilic attack of the oxygen atom of the trimethylsilyl ether at triflic anhydride, followed by transfer of the triflate anion by a cyclic process[12].

It is interesting to note that the less electrophilic trifluoroacetic anhydride reacts slowly with trimethylsilyl ethers, leading to the corresponding trifluoroacetates **5** in very good yields.



In summary, the mild and efficient reaction reported here, which does not necessiate catalysis by fluoride ions or addition of a base is an useful variation for the preparation of alkyl triflates as compared to the classical method[2].

Alkyl Triflates 2a–g General Procedure:

Triflic anhydride (1.41 g, 5 mmol) is added by syringe through a septum cap to a stirred solution of the alkyl trimethylsilyl ether **1** (5 mmol) in pentane (10 ml) (or dichloromethane) at 0 °C. Stirring is continued for 15 min (if the solvent is dichloromethane) or 30 min (if the solvent is pentane). The crude solution is ready for most applications. If it is necessary to isolate the triflate, the mixture is hydrolyzed with ice, the organic phase is washed with water (2 × 10 ml), dried with sodium sulfate, and the solvent is evaporated under reduced pressure at room temperature. The residual oil obtained is the alkyl triflate **2**, pure according to ^{1}H-N.M.R. spectrometry (Table).

Pentyl 2,2,2-Trifluoroethyl Ether (3); Typical Procedure for One-Pot Preparation:

Triflic anhydride (1.21 g, 4.3 mmol) is added by syringe through a septum cap to a stirred solution of pentyl trimethylsilyl ether (**1c**; 0.68 g, 4.3 mmol) in dichloromethane (8 ml). After 15 min, 2,2,2-trifluoroethanol (1.55 g, 15.5 mmol) and anhydrous potassium carbonate (1.8 g, 13 mmol) are added to the mixture. Stirring is continued at room temperature for 24 h. After hydrolysis with water (10 ml) the organic layer is extracted with dichloromethane (3 × 20 ml). The combined organic layers are washed with water (4 × 10 ml), dried with magnesium sulfate, and evaporated. Chromatography of the residue on a silica gel columm using pentane as eluent gives ether **3** in a pure state as determined by G.L.C and ^{1}H-N.M.R. analysis; yield: 0.50 g (70%); b.p. 130–131 °C/760 torr (Lit.[16], b.p. 135.5–136.5 °C/760 torr.

^{1}H-N.M.R. ($CDCl_3$/TMS): $\delta = 3.76$ (q, 2H, $J_{HF} = 9$ Hz, OCH_2CF_3); 3.5 (t, 2H, $J = 6$ Hz, OCH_2); 1.13–1.90 [m, 6H, OCH_2—$(CH_2)_3$—]; 0.9 ppm (m, 3H, CH_3); cf. Lit.[4].
^{19}F-N.M.R. ($CDCl_3/CFCl_3$): $\delta = 75.33$ ppm (t, $J = 9$ Hz).

Cumene (4); Typical Procedure for One-Pot Preparation:

Triflic anhydride (1.93 g, 6.8 mmol) is added at 0 °C to a stirred solution of isopropyl trimethylsilyl ether (**1g**; 0.9 g, 6.8 mmol) in pentane (5 ml). After 30 min, benzene (6 ml) is added to the mixture and

Table. Preparation of Triflates **2** from Trimethylsilyl Ethers **1**

Product	Yield[a] [%]	Molecular Formula[b] or Lit. data (yield)	^{1}H-N.M.R. ($CDCl_3$)[c] δ [ppm]
2a	72[d]	36[e,6]	1.03 (t, J = 7 Hz, 3H); 1.78 (q, J = 7 Hz, 2H); 4.48 (t, J = 7 Hz, 2H)
2b	72	68[13]	0.95 (t, J = 7 Hz, 3H); 1.66 (m, 4H); 4.48 (t, J = 7 Hz, 2H)
2c	78	85[4]	0.90 (m, 3H); 1.42 (m, 4H); 1.82 (m, 2H); 4.45 (t, J = 7 Hz, 2H)
2d	91	$C_9H_{17}F_3O_3S$ (262.3)	0.90 (m, 3H); 1.16–1.78 (m, 12H); 4.38 (d, J = 5 Hz, 2H)
2e	76	$C_9H_9F_3O_3S$ (254.2)	3.02 (t, J = 7 Hz, 2H); 4.58 (t, J = 7 Hz, 2H); 7.15 (s, 5H)
2f	88	–[f,13]	2.12 (q, J = 7 Hz, 2H); 2.72 (t, J = 7 Hz, 2H); 4.45 (t, J = 7 Hz, 2H); 7.15 (s, 5H)
2g	75[d]	90[4]	1.45 (d, J = 7 Hz, 6H); 5.15 (sept, J = 7 Hz, 1H)
2h	0[g]	90[10]	–

[a] Yield of isolated pure product. Because of their unstability, the triflates cannot be distilled or chromatographed; the isolated products are pure as evidenced by ^{1}H-N.M.R.

[b] Satisfactory microanalyses obtained: C ±0.25, H ±0.15, F ±0.32.

[c] For all products, characteristic data (^{1}H-, ^{19}F-N.M.R. and I.R.) for the triflate group are observed: ^{19}F-N.M.R. ($CFCl_3$): δ = 75.5–75.8 ppm; I.R. (CCl_4): ν = 1420, 1210, 1150, 940 cm^{-1} (OSO_2—CF_3).

[d] Yields determined by ^{1}H-N.M.R. with an internal standard because of the high volatility of the products.

[e] The rearranged triflate **2g** was also obtained (yield: 50%) besides triflate **2a**.

[f] The yield was not reported.

[g] Phenol is obtained (100%). Apparently catalysis by fluoride ions seems to be essential[10] for activating aryl trimethylsilyl ethers.

the stirring is continued at room temperature for 16 h. After hydrolysis with water (10 ml), the mixture is extracted with pentane (3 × 20 ml), the organic phase is dried with magnesium sulfate, concentrated to 10 ml, and chromatographed on silica gel using pentane as eluent to give **4** in a pure state as confirmed by G.L.C. and ^{1}H-N.M.R. analysis; yield: 0.4 g (50%).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 1.22 [d, 6H, J = 7 Hz, $CH(C\underline{H}_3)_3$]; 2.87 [sept, 1H, J = 7 Hz, $C\underline{H}(CH_3)_2$]; 7.17 ppm (s, 5H_{arom}).

***n*-Pentyl Trifluoroacetate (5c); Typical Procedure:**

Trifluoroacetic anhydride (0.615 g, 2.93 mmol) is added at 0 °C to a stirred solution of pentyl trimethylsilyl ether (**1c**; 0.469 g, 2.93 mmol) in dichloromethane (5 ml). After 2.5 h, the reaction mixture is hydrolyzed with water (40 ml), the organic layer is extracted with pentane (3 × 20 ml). The combined extracts are washed with water (4 × 10 ml), dried with magnesium sulfate, and concentrated. Chromatography of the residue on a Florisil column using pentane as eluent gives the pure (by G.L.C.) trifluoroacetate **5c**[15]; yield: 0.477 g (88%).

I.R. (CCl_4): ν = 1790 cm^{-1} (C=O).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 0.85 (m, 3H, CH_3); 1.28 (m, 4H, —CH_2CH_2—); 1.65 (m, 2H, $C\underline{H}_2CH_2O$); 4.32 ppm (t, 2H, J = 7 Hz, $C\underline{H}_2O$).

3-Phenylpropyl trifluoroacetate[16] (**5f**) is prepared similarly from trifluoroacetic anhydride (0.632 g, 3 mmol) and trimethylsilyl ether **1f** (0.627 g, 3 mmol); yield: 0.557 g (80%).

I.R. (CCl_4): ν = 1785 cm^{-1} (C=O).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 2.05 (q, 2H, J = 7 Hz, CH_2); 2.7 (t, 2H, J = 7 Hz, $C\underline{H}_2CH_2O$); 4.28 (t, 2H, J = 7 Hz, $C\underline{H}_2O$); 7.16 ppm (s, 5H_{arom}).

Trifluoroacetates **5c** and **5f** are identical (G.L.C. and spectral data) with the corresponding authentic samples[15,16].

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