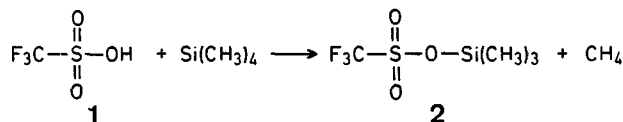


This disadvantage is not encountered when the polymeric form, Nafion-TMS is used, which resists hydrolytic cleavage<sup>2,4,5,6</sup> considerably. However, monomeric trimethylsilyl triflate is advantageous over the polymer<sup>2</sup>; for example, because of its higher electrophilicity it may be used to cleave cyclopropanes at ambient temperature<sup>4</sup>. A cheap *in situ* preparation giving only inert by-products therefore appeared desirable.

Trimethylsilyl triflate (**2**) has so far been accessible by the following procedures none of which meets with all of the above requirements: Treatment of chlorotrimethylsilane with (expensive) silver trifluoromethanesulfonate in boiling benzene<sup>7</sup> or with neat trifluoromethanesulfonic acid (**1**) at 120 °C for several hours and driving off the hydrochloric acid formed<sup>8</sup>. Further, compound **2** has been prepared *in situ* by reaction of **1** with phenyltrimethylsilane<sup>9</sup> or allyltrimethylsilane<sup>10</sup>, both of which are expensive reagents.

The reaction of trifluoromethanesulfonic acid (**1**) with tetramethylsilane should combine all of the desired advantages but this reaction has been reported<sup>7</sup> not to proceed even at reflux temperature with a reaction time of 48 h. This negative result is surprising since sulfuric acid reacts with tetramethylsilane at room temperature (1.5 h) to afford trimethylsilyl sulfate<sup>11</sup>. The even stronger trifluoromethanesulfonic acid (**1**) should therefore also be expected to react with tetramethylsilane. We have now indeed found that mixing of trifluoromethanesulfonic acid (**1**) with (commercial or redistilled) tetramethylsilane under argon at room temperature causes evolution of methane (analyzed by G.L.C. using a 48 m glass capillary column OV1 at 0 °C and by mass spectrometry); after 1 h, formation of trimethylsilyl triflate (**2**) is complete as evidenced by <sup>1</sup>H-N.M.R. monitoring.



Neither trifluoroacetic acid, which is similar in acidity to sulfuric acid, nor the less acidic methanesulfonic acid react with tetramethylsilane, not even at elevated temperatures.

**Trimethylsilyl Trifluoromethanesulfonate (2, Trimethylsilyl Triflate):** Trifluoromethanesulfonic acid (**1**; 1.5 g, 10 mmol) and tetramethylsilane (1.1 g, 12.5 mmol) are mixed under an argon atmosphere at room temperature. After 1 h, evolution of methane ceases and formation of **2** is complete. Distillation of the mixture affords product **2** as a colorless liquid; yield: 2.2 g (99%); b.p. 40 °C/11 torr (Ref.<sup>7</sup>, b.p. 36.5 °C/10 torr); purity: 96% (G.L.C. 50 m glass capillary column, OV 1). C<sub>4</sub>H<sub>9</sub>F<sub>3</sub>O<sub>3</sub>SSi (222.2).

M.S. (70 eV): *m/e* = 222 (M<sup>+</sup>), 207, 147, 77, 73, 69.

<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>/TMS<sub>int</sub>): δ = 0.50 ppm (cf. Ref.<sup>10</sup>).

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## A Convenient *in situ* Preparation of Trimethylsilyl Trifluoromethanesulfonate<sup>1</sup>

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Trimethylsilyl trifluoromethanesulfonate (**2**, TMS triflate) is commercially available and widely used in various synthetic applications<sup>2-6</sup>. The reagent is rapidly hydrolyzed in the air.

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<sup>1</sup> Patent applications submitted.

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