

NEW METHOD FOR THE PREPARATION OF *t*-BUTYLDIMETHYLSILYL TRIFLATE

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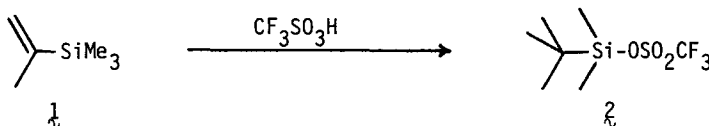
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Abstract: *t*-Butyldimethylsilyl triflate is easily prepared from the reaction of triflic acid with isopropenyltrimethylsilane.

The *t*-butyldimethylsilyl group has become one of the most widely used protecting groups in organic synthesis.¹ It was originally introduced for the protection of enols,² as an alternative to the more hydrolytically sensitive trimethylsilyl group.³ It has since become extremely useful for the protection of alcohols,⁴ and has also been used for the protection of a number of other functional groups such as carboxylic acids,^{4,5} amides,⁶ and phenols.^{1e} The *t*-butyldimethylsilyl group has also been useful in various carbon-functional organosilicon compounds, such as α -silyl aldehydes.⁷

t-Butyldimethylsilyl groups are usually introduced using *t*-BuMe₂SiCl. This compound has been moderately expensive, probably a consequence of the cost of the *t*-BuLi used in its preparation (from Me₂SiCl₂ and *t*-BuLi).⁸ Recently, *t*-butyldimethylsilyl triflate was found to be useful for the silylation of unreactive substrates.⁹ It was prepared from *t*-BuMe₂SiCl by reaction with AgOTf^{9a} or TfOH.^{9b,c} We wish to report a new method for preparing *t*-butyldimethylsilyl triflate from inexpensive, readily available starting materials.

The key reaction is the triflic acid induced rearrangement of isopropenyltrimethylsilane (**1**). In 1954, Sommer and Evans reported the rearrangement of **1** with concentrated sulfuric acid to produce, after hydrolysis, *t*-butyldimethylsilanol.¹⁰ Although this type of reaction has been used to prepare silyl fluorides (by treating the rearrangement products with NH₄HF₂),¹¹ as far as we know, no other acids have been reported for this type of rearrangement. We have investigated the reaction of **1** with triflic acid in pentane, in CCl₄, and without solvent. In each case, *t*-butyldimethylsilyl triflate (**2**) was formed, and the reaction was complete within a few minutes at 0°C. About 10-15% of a cleavage product (Me₃SiOTf) was also formed; this could be separated from the higher boiling *t*-BuMe₂SiOTf (**2**) by distillation. The *t*-BuMe₂SiOTf (**2**) was characterized by NMR, and was analyzed by conversion to the *t*-butyldimethylsilyl ether of cyclohexanol.



We have prepared isopropenyltrimethylsilane (**1**)^{12,13} from both 2-bromopropene and 2-chloropropene, via the organolithium reagent, the Grignard reagent (of 2-bromopropene), and by a Wurtz-Fittig reaction¹⁴ (of 2-chloropropene) with sodium in 4:1 ether:HMPA. 2-Chloropropene

can be easily prepared from the reaction of acetone with PCl_5 .¹⁵ Thus, the reaction described here provides a convenient route for the preparation of $\underline{t}\text{-BuMe}_2\text{SiOTf}$ from inexpensive starting materials.

Experimental. To an ice-cooled mixture of 0.65 ml (7.3 mmol) of triflic acid and 5 ml of pentane under argon was added a solution of 1.0 g (8.77 mmol) of silane $\underline{\lambda}$ in 1 ml of pentane, and the resulting mixture was stirred for 10 min. The reaction mixture was then distilled, initially at bath temperature 30°C (10 mm) to remove volatile materials (pentane, excess $\underline{\lambda}$ (bp 82°C), and Me_3SiOTf (bp 140°C)), then at bath temperature 90°C, giving 1.268 g (66% yield, based on TfOH) of $\underline{t}\text{-BuMe}_2\text{SiOTf}$ ($\underline{\lambda}$) as a colorless liquid, bp 66-68°C (10 mm) (lit.^{9c} bp 60°C (7 mm)). The NMR spectrum was in agreement with that reported.^{9c}

To 1.1 mmol of cyclohexanol and 2.2 mmol of Et_3N in 2 ml of CH_2Cl_2 was added 1.3 mmol of $\underline{t}\text{-BuMe}_2\text{SiOTf}$, and the reaction mixture was stirred for 20 min at room temperature. Aqueous workup (pentane, NaHCO_3), concentration, and evaporative (Kugelrohr) distillation gave 221 mg (94%) of the $\underline{t}\text{-BuMe}_2\text{Si}$ ether of cyclohexanol. VPC analysis (SE-30) showed the compound to be 95% pure, with 2% of the Me_3Si ether of cyclohexanol present.¹⁶

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