Tetrahedron Letters,Vol.26,No.11,pp 1389-1390,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

NEW METHOD FOR THE PREPARATION OF t-BUTYLDIMETHYLSILYL TRIFLATE

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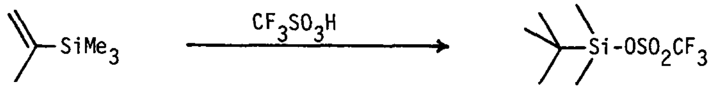
Abstract: t-Butyldimethylsilyl triflate is easily prepared from the reaction of triflic acid with isopropenyltrimethylsilane.

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-$BuMe_2SiCl$. This compound has been moderately expensive, probably a consequence of the cost of the t-BuLi used in its preparation (from Me_2SiCl_2 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-$BuMe_2SiCl$ 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 NH_4HF_2),[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 CCl_4, 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 (Me_3SiOTf) was also formed; this could be separated from the higher boiling t-$BuMe_2SiOTf$ (2) by distillation. The t-$BuMe_2SiOTf$ (2) was characterized by NMR, and was analyzed by conversion to the t-butyldimethylsilyl ether of cyclohexanol.



1 2

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 reaction[14] (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 *t*-BuMe$_2$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 **1** 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 **1** (bp 82°C), and Me$_3$SiOTf (bp 140°C)), then at bath temperature 90°C, giving 1.268 g (66% yield, based on TfOH) of *t*-BuMe$_2$SiOTf (**2**) 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$_3$N in 2 ml of CH$_2$Cl$_2$ was added 1.3 mmol of *t*-BuMe$_2$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 *t*-BuMe$_2$Si ether of cyclohexanol. VPC analysis (SE-30) showed the compound to be 95% pure, with 2% of the Me$_3$Si ether of cyclohexanol present.[16]

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16. We thank the National Science Foundation (grant no. CHE-8304867) for support of this work.

(Received in USA 4 December 1984)