

REAGENTS AND SYNTHETIC METHODS 55. NEW METHODS FOR THE PREPARATION
OF *t*-BUTYLDIMETHYLSILYL TRIFLATE AND TRIMETHYLSILYL TRIFLATE.

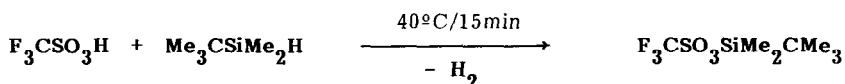
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Abstract: An expeditious synthesis of *t*-butyldimethylsilyl triflate is described from triflic acid and *t*-butyldimethylsilane. Reaction between trichloromethyltrimethylsilane and triflic acid is also reported.

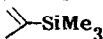
During the past few years, trialkylsilyl triflates have been recognized as useful reagents for the introduction of the silicon group in a variety of organic compounds¹. Although some of these reagents are now commercially available, they are highly moisture sensitive, thus making them difficult to handle. A cheap "in situ" preparation giving only inert by-products therefore appeared desirable. In this paper, we report new preparative methods for the synthesis of *t*-butyldimethylsilyl triflate and trimethylsilyl triflate.

***t*-Butyldimethylsilyl triflate.** This reagent was found to be useful for the silylation of "unreactive" substrates^{2a}, for the preparation of allylic silyl ethers from epoxides^{2b} and for the synthesis of *t*-butyldimethylsilyl enol ethers from "sterically hindered" ketones^{2c}. However, few methods are available for the preparation of *t*-butyldimethylsilyl triflate (TBDMSOTf), thus it has been previously prepared from triflic acid and *t*-butyldimethylsilyl chloride (TBDMSCl)^{3a} or by reaction of the extremely expensive silver triflate with TBDMSCl^{3a}. Recently, Hudrlík et al^{3b} have reported the preparation of TBDMSOTf in moderate yield from triflic acid and isopropenyltrimethylsilane; however, from this method, competitive side products are also formed. To this narrow group of methods for TBDMSOTf preparation, we have developed an alternative synthesis based on the readily available materials, as shown in the Scheme.



The experimental procedure can be considered as follows: *t*-butyldimethylsilane⁴ (1.27g, 11mmol) is dropwise added over ice-cooled triflic acid (0.88ml, 10mmol), while fast evolution of hydrogen is observed. The mixture is warmed at 40°C and stirred for 15min, and the resulting colourless solution is distilled under reduced pressure to afford pure *t*-butyldimethylsilyl triflate (2.37g, 90%; yield based on TfOH). b.p: 66-68°C/10torr (lit. b.p: 60°C/7torr)^{2a}. ¹H-NMR (CCl₄) δ ppm: 0.40 (s, 6H, SiMe₃), 0.98 (s, 9H, CMe₃). The table shows the reaction conditions used for the preparation of TBDMSOTf and are compared with the known methods. It is interesting to note that no by-products are formed, therefore, TBDMS triflate can be quickly generated and used "in situ" from the method described here; thus the resulting crude TBDMSOTf prepared as above was diluted with dichloromethane (5ml). To this solution was added a mixture of acetophenone (1.17ml, 10mmol) and triethylamine (2.1 ml, 15mmol) in the same solvent (5ml). After work-up^{2c} the TBDMS enol ether of acetophenone was isolated in 80% yield, b.p: 72-74°C/0.2torr. ¹H-NMR (CDCl₃) δ ppm: 0.21 (s, 6H, SiCH₃), 1.02 (s, 9H, CCH₃), 4.40, 4.89 (d, d, 1H, 1H, =CH₂), 7.25, 7.57 (m, m, 5H, arom.). A further advantage is that our starting material, *tert*-butyldimethylsilane, is not moisture sensitive. As shown by the results reported here, our procedure could be the method of choice in some laboratories, despite the fact that TBDMS triflate is now commercially available⁵.

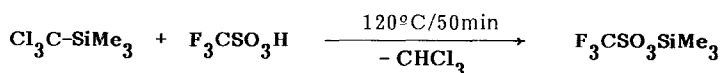
Table. Preparation of TBDMS triflate.

Reagents		Temp(°C)	time	Yield(%)	by-product
F ₃ CSO ₃ H	Me ₃ CMe ₂ Si-Cl	25	12h	84	AgCl
F ₃ CSO ₃ H	Me ₃ CMe ₂ Si-Cl	60	10h	80	_____ a
F ₃ CSO ₃ H	 -SiMe ₃	0	10min	66	Me ₃ SiOTf
F ₃ CSO ₃ H	Me ₃ CMe ₂ Si-H	40	15min	90	_____ b

a) Hydrogen chloride was evolved.

b) Hydrogen was evolved.

Trimethylsilyl triflate. Attempts to apply this procedure to the preparation of the parent trimethylsilyl triflate from triflic acid and trimethylsilane gave poor yields. However, we have developed an alternative pathway for its preparation. Our finding is that reaction of the commercially available trichloromethyltrimethylsilane⁶ with triflic acid leads to the formation of trimethylsilyl triflate in 88% yield.



Thus, a mixture of trichloromethyltrimethylsilane (1.91g, 10mmol) and triflic acid (0.97ml, 11mmol) is refluxed under nitrogen at 120°C (oil bath) for 50min and the resulting dark solution is distilled under reduced pressure to afford colourless trimethylsilyl triflate (1.95g, 88%); b.p: 42-44°C/20torr (lit.b.p: 36°C/12torr)^{7a}. ¹H-NMR (CCl₄) δ ppm: 0.50 (s, CH₃). To our knowledge, this simple and high yield synthesis of TMS triflate has not been reported previously⁷.

REFERENCES AND NOTES:

- 1.- For reviews, see: a) H.H. Hergott et al, *Synthesis*, 1 (1982); b) R. Noyori, S. Murata, M. Suzuki, *Tetrahedron*, **37**, 3899 (1981).
- 2.- a) E.J. Corey, H. Cho, C. Rucker, D.H. Hua, *Tetrahedron Lett*, **22**, 3455 (1981); b) S. Murata, M. Suzuki, R. Noyori, *J. Am. Chem. Soc.*, **101**, 2738 (1979); c) L.N. Mander, S.P. Sethi, *Tetrahedron Lett*, **25**, 5953 (1984).
- 3.- a) M. Riediker, W. Graf, *Helv. Chim. Acta*, **62**, 205 (1979); b) P.F. Hudrlik, A.K. Kulkani, *Tetrahedron Lett*, **26**, 1389 (1985).
- 4.- tert-Butyldimethylsilane was prepared in 90% yield from chlorodimethylsilane and tert-butylolithium, following the Barton's method; see: Th.J. Barton, Ch.R. Tully, *J. Org. Chem.*, **43**, 3649 (1978).
- 5.- Current Fluka Chemical prices: tert-butyltrimethylsilyl chloride, approximately, 48sFr/mol, trifluoromethanesulfonic acid, 220sFr/mol, tert-butyltrimethylsilyl triflate 1300sFr/mol. tert-butylolithium, 18sFr/mol and chlorodimethylsilane 45sFr/mol. Therefore, TBDMS triflate can be prepared by our method at a cost of approximately 300sFr/mol.
- 6.- For preparation of trichloromethyltrimethylsilane, see: H.H. Hergott, G. Simchen, *Synthesis*, 626 (1980). For synthetic applications, see: a) R.F. Cunico, B.B. Chou, *J. Organometal. Chem.*, **154**, C45 (1978); b) J. Dunogues et al., *ibid.* **71**, 377 (1974); c) J.P. Battioni et al., *ibid.* **214**, 303 (1981). d) J.F. Gisch, J.A. Landgrebe, *J. Org. Chem.*, **50**, 2050 (1985); e) M. Fujita, T. Hiyama, *J. Am. Chem. Soc.*, **107**, 4085 (1985).
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