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Di-*t*-butylsilyl Bis(trifluoromethanesulfonate)

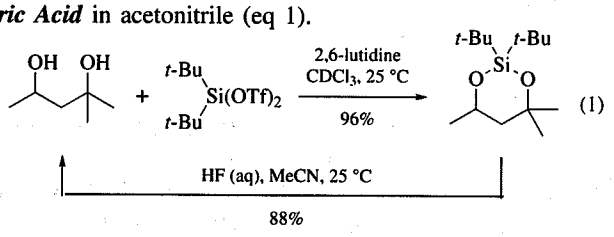
$t\text{-Bu}_2\text{Si}(\text{OSO}_2\text{CF}_3)_2$

[85272-31-7] $C_{10}H_{18}F_6O_6S_2Si$ (MW 440.44)

(reagent for the protection of diols)

Physical Data: bp 73–75 °C/0.35 mmHg; *d* 1.208 g cm^{-3}.
Solubility: sol most common organic solvents.
Form Supplied in: liquid.
Preparative Method: by the treatment of di-*t*-butylchlorosilane with ***Trifluoromethanesulfonic Acid***, followed by distillation (71% yield).[1]
Purification: distillation.
Handling, Storage, and Precautions: moisture sensitive; reacts with hydroxylic solvents; corrosive.

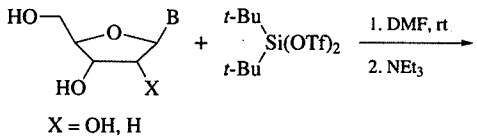
Protection of Alcohols. Di-*t*-butylsilyl bis(trifluoromethanesulfonate) is a reagent for the selective protection of polyhydroxy compounds. This reagent reacts with 1,2-, 1,3-, and 1,4-diols under mild conditions to give the corresponding dialkylsilylene derivatives in high yield (0–50 °C, 79–96%). Deprotection is conveniently achieved by using aqueous ***Hydrofluoric Acid*** in acetonitrile (eq 1).

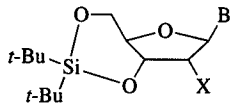


(1)

Unlike ***Di-t-butyldichlorosilane***, this reagent reacts with hindered alcohols. Even pinacol reacts to give the silylene derivative (100 °C, 24 h, 70%). Di-*t*-butylsilylene derivatives of 1,2-diols are more reactive than those of 1,3- and 1,4-diols and undergo rapid hydrolysis (5 min) in THF/H_2O at pH 10, while the 1,3- and 1,4-derivatives are unaffected at pH 4–10 (22 °C) for several hours. This protecting group is stable under the conditions of PDC oxidation of alcohols (CH_2Cl_2, 25 °C, 27 h) and tosylation of alcohols (pyridine, 25 °C, 27 h).

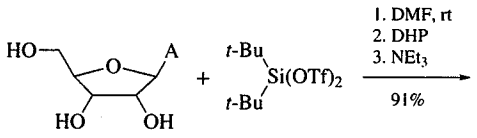
The reagent has seen limited use for the protection of alcohols but has been used to protect nucleosides (eq 2).[2-5] The procedure consists of sequential addition of the ditriflate and ***Triethylamine*** to the nucleoside in DMF. The choice of solvent is critical.

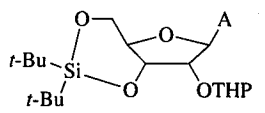




(2)

The ribonucleosides of uracil, adenine, and guanine give the protected derivative in 94–95% yield.[2] Cytidine gives a low yield of the desired product under these conditions. Subsequent studies suggested that O^2 of cytosine participates in the reaction. Addition of ***Trifluoromethanesulfonic Acid*** or ***Silver(I) Trifluoromethanesulfonate*** at 0 °C prior to addition of the silylating agent results in a 99% yield of the desired derivative.[3] The derivatives are acid sensitive, presumably due to the proximity of the 2′-hydroxy group. Acetylation, tetrahydropyranylation, methoxytetrahydropyranylation, and silylation of the 2′-hydroxy group are accomplished without affecting the dialkylsilylene protecting group. The 2′-deoxyribonucleosides, including 2′-deoxycytidine, can also be prepared by the aforementioned procedure (yields 90–99%). These cyclic silylene derivatives of nucleosides can be deprotected conveniently using tributylamine hydrofluoride in THF (5 min, 1 M, rt, 20 equiv).[4] A one-pot procedure has been reported for simultaneously protecting the 2′-, 3′-, and 5′-hydroxys of a ribonucleoside, which utilizes the acid generated upon silylating the 3′- and 5′-hydroxys for catalyzing the formation of a THP acetal at the 2′-position (eq 3).[5]

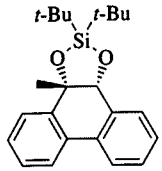




(3)

Derivatization of Alcohols. Di-*t*-butylsilyl bis(trifluoromethanesulfonate) has been used to derivatize hindered diols, to give derivatives such as (**1**), for analysis by gas chromatography–

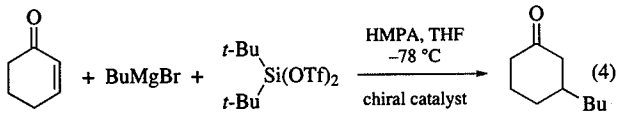
electron impact mass spectrometry.[6] The major fragmentation is that of the Si–C bonds.



m/z 366 (M^+), 309 (M^+ – Bu), 191 (*B*)

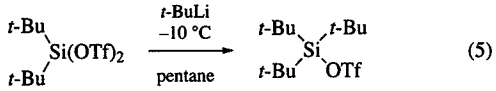
(1)

Reagent in Enantioselective Additions. In a study of enantioselective conjugate addition to cyclohexanone it was found that the presence of HMPA and various silyl reagents markedly increases the enantioselectivity (eq 4).[7] Di-*t*-butylsilyl bis(trifluoromethanesulfonate) gives a 67% yield and 40% ee but ***t*-Butyldiphenylchlorosilane** gives a 97% yield and 78% ee.



(4)

Other Substitution Reactions. An extremely hindered silyl reagent, tri-*t*-butylsilyl trifluoromethanesulfonate, was prepared from di-*t*-butylsilyl bis(trifluoromethanesulfonate) and ***t*-Butyllithium** (eq 5).[8] This reagent might find use in the protection of alcohols.



(5)

In conjunction with the study of alkyl-substituted silyl triflates, (**2**) and (**3**) have been prepared from the corresponding alkynyllithium reagents and di-*t*-butylsilyl bis(trifluoromethanesulfonate).[9]

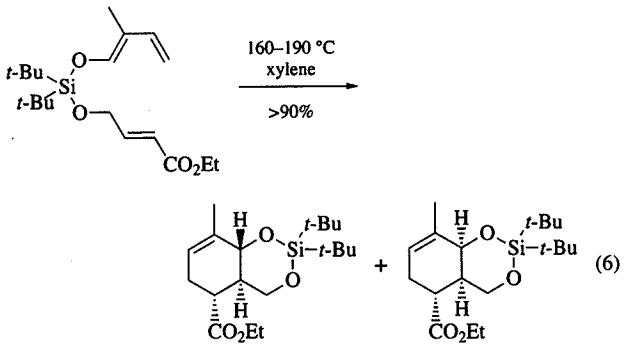
(2) (3)

The preparation of other derivatives of di-*t*-butylsilyl bis(trifluoromethanesulfonate) using germanium[10] and phosphorus[11] nucleophiles has been reported and provides bifunctional silanes such as (**4**) and (**5**).

(4) (5)

X = –C≡CPh, –$SiPh_3$, –$N(TMS)_2$, –PHPh, –O-*i*-Pr, –SPh

A compound closely related to di-*t*-butylsilyl bis(trifluoromethanesulfonate) is di-*t*-butylchlorosilyl trifluoromethanesulfonate, which has been used to tether two structurally different alcohol derivatives in order to effect an intramolecular Diels–Alder reaction (eq 6).[12]



(6)

>99:<1

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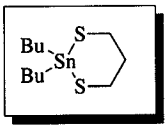
2,2-Dibutyl-2-stanna-1,3-dithiane[1]



[7191-32-4] $C_{11}H_{24}S_2Sn$ (MW 339.20)

(reagent for synthesizing 1,3-dithianes from aldehydes and acetals[2,3])

Alternate Name: DSDT.
Physical Data: mp 63–64 °C; bp 170 °C/0.5 mmHg.
Solubility: insol H_2O; sol most organic solvents.
Analysis of Reagent Purity: ^1H NMR ($CDCl_3$) δ 0.93 (t, 6H, *J* = 7.32 Hz), 1.61 (m, 14H), 2.94 (t, 4H, *J* = 6.10 Hz); ^{13}C NMR ($CDCl_3$) δ 13.40, 24.51, 26.50, 27.82, 30.16.
Preparative Method: to a CH_2Cl_2 solution (400 mL) of Bu_2SnCl_2 (45.8 g, 0.15 mol) and $HS(CH_2)_3SH$ (15.1 mL, 0.15 mol) is added Et_3N (41.8 mL, 0.3 mol) at 0 °C. The solution