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Di-t-butyldichlorosilane, this reagent reacts with hindered alcohols. Even pinacol react to give the silyl derivative (100 °C, 24 h, 70%). Di-t-butyldichlorosilane 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/H2O 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 (CH2Cl2, 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). The procedure consists of sequential addition of the ditriflate and Triethylamine to the nucleoside in DMF. The choice of solvent is critical.

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{HO} & \quad \text{B} \\
\text{Si(OTr)}_2 & \quad \text{t-Bu} \\
\text{X} = \text{OH}, \text{H} \\
\text{1, DMF, rt} & \\
\text{2, NBE}_3 &
\end{align*}
\]

The ribonucleosides of uracil, adenine, and guanine give the protected derivative in 94–95% yield. Cytidine gives a low yield of the desired product under these conditions. Subsequent studies suggested that O^5 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. The derivatives are acid sensitive, presumably due to the proximity of the 2'-hydroxy group. Acetylation, tetrahydrouracil, methoxymethyldihydroxylation, and silylation of the 2'-hydroxy group are accomplished without affecting the dialkysilylene protecting group. The 2'-deoxyribonucleosides, including 2'-deoxyxycytidine, can also be prepared by the aforementioned procedure (yields 90–99%). These cyclic silyl derivatives of nucleosides can be deprotected conveniently using tributylamine hydrofluoride in THF (5 min, 1 M, rt, 20 equiv). 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'-hydroxy for catalyzing the formation of a THP acetal at the 2'-position (eq 3).

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{OH} & \quad \text{A} \\
\text{Si(OTr)}_2 & \quad \text{t-Bu} \\
\text{1, DMF, rt} & \\
\text{2, DHP} & \\
\text{3, NBE}_3 & \\
\text{91%} &
\end{align*}
\]

**Derivatization of Alcohols.** Di-t-butyldichlorosilane bis(trifluoromethanesulfonate) has been used to derivatize hindered diols, to give derivatives such as (1), for analysis by gas chromatography—
electron impact mass spectrometry. The major fragmentation is that of the Si–C bonds.

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). Di-t-butyldisilyl bis(trifluoromethanesulfonate) gives a 67% yield and 40% ee but t-BuButyldiphenylchlorosilane gives a 97% yield and 78% ee.

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

In conjunction with the study of alkyl-substituted silyl triflates, (2) and (3) have been prepared from the corresponding alkylvinylchlorides and di-t-butyldisilyl bis(trifluoromethanesulfonate).

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

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

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

Alternate Name: DSDT.
Physical Data: mp 65–64 °C; bp 170 °C/0.5 mmHg.
Solubility: insol H2O; sol most organic solvents.
Analysis of Reagent Purity: 1H NMR (CDCl3) δ 0.93 (t, 6H, J = 7.32 Hz), 1.61 (m, 14H), 2.94 (t, 4H, J = 6.10 Hz); 13C NMR (CDCl3) δ 13.40, 24.51, 26.50, 27.82, 30.16.
Preparative Method: to a CH2Cl2 solution (400 mL) of Bu3SnCl (45.8 g, 0.15 mol) and HS(CH2)3SH (15.1 mL, 0.15 mol) is added Et3N (41.8 mL, 0.3 mol) at 0 °C. The solution

Avoid Skin Contact with All Reagents

8. Uhlig, W. CB 1992, 125, 47.