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Di-*t*-butyldichlorosilane



[18395-90-9]

C₈H₁₈Cl₂Si

(MW 213.22)

(reagent for the protection of diols; used as a silylene precursor)

Physical Data: mp -15 °C; bp 190 °C/729 mmHg; *d* 1.009 g cm⁻³.

Solubility: sol most common organic solvents.

Form Supplied in: liquid.

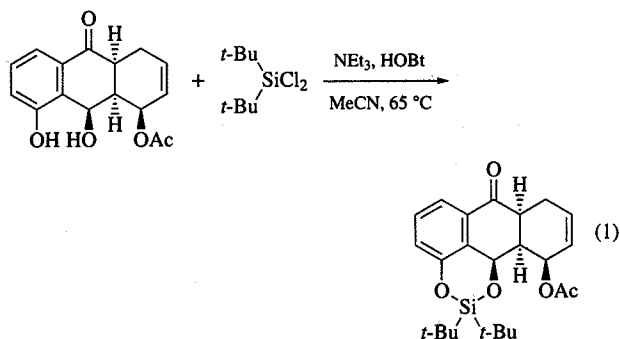
Preparative Methods: can be conveniently prepared by chlorination of di-*t*-butylsilane (CCl₄/PdCl₂ (cat), 85%)^{1,2} but various other methods of preparation have been reported.³⁻⁶

Purification: distillation.

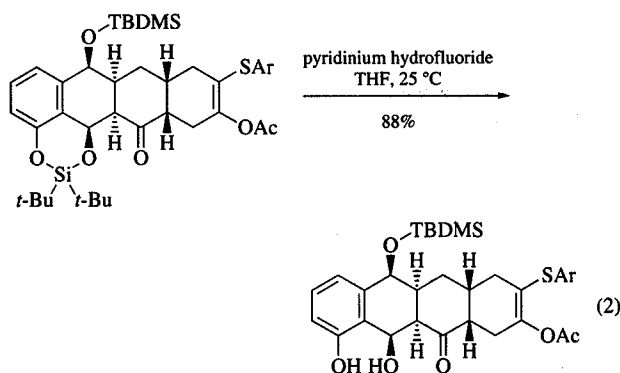
Handling, Storage, and Precautions: moisture sensitive; reacts with hydroxylic solvents, corrosive; lachrymator. Use in a fume hood.

Protection of Alcohols. The presence of the bulky *t*-butyl groups in di-*t*-butyldichlorosilane has been found to increase the Si-C bond lengths slightly and to widen the C-Si-C bond angles by 11.1° relative to *Dichlorodimethylsilane* as determined by electron diffraction and molecular mechanics calculations.⁷

The di-*t*-butylsilylene protecting group for diols was introduced by Trost and Caldwell⁴ and used in a total synthesis of deoxypillaromycinone.⁵ It is introduced by the reaction of di-*t*-butyldichlorosilane with a 1,2- or 1,3-diol in acetonitrile in the presence of *Triethylamine* and *1-Hydroxybenzotriazole* (HOBt) at 45–90 °C (eq 1). For a related, highly reactive reagent see *Di-*t*-butylsilyl Bis(trifluoromethanesulfonate)*.

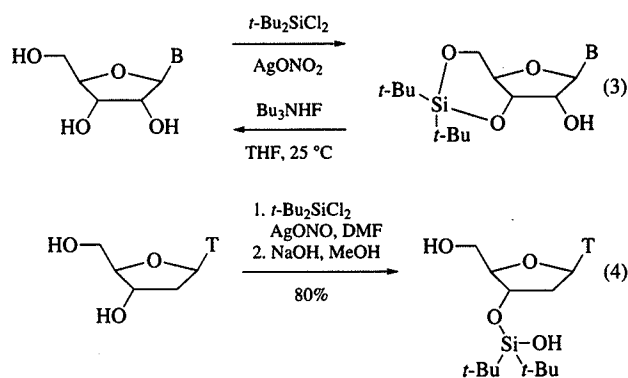


When at least one of the hydroxy groups is phenolic or primary, reactions proceed smoothly at 25–65 °C, but when both hydroxy groups are secondary, more forcing conditions (95 °C, sealed tube) are required. In all cases, yields range from 64% to 85%. No examples have been reported with tertiary alcohols. *Pyridinium Poly(hydrogen Fluoride)* is used for deprotection and under those conditions a *t*-butyldimethylsilyl ether and a β -hydroxy ketone are unaffected (eq 2).

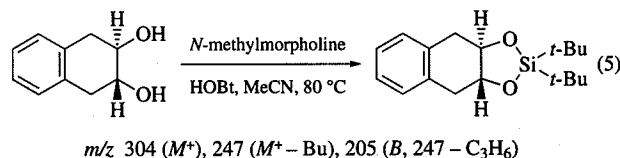


This protecting group has seen limited use but has been applied in ribonucleoside chemistry.^{8–10} The reagent reacts slowly with nucleosides in the presence of imidazole/DMF but formation of the more reactive di-*t*-butylsilyl dinitrate in situ, followed by addition of cytidine, results in a protected 3',5'-silylene derivative in excellent yield (90%) (eq 3). The protecting group can be removed conveniently with tributylamine hydrofluoride.¹¹

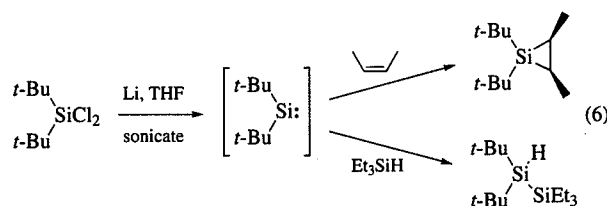
A one-pot procedure has been reported for the selective protection of a secondary alcohol over a primary alcohol in a 1,3-diol in 2'-deoxynucleosides (eq 4).^{12,13}



Derivatization of Diols and Hydroxy Acids. Di-*t*-butyldichlorosilane has been used to derivatize α -hydroxy acids, β -hydroxy acids, alkylsalicylic acids, anthranilic acid, catechols, and 1,2- and 1,3-diols for analysis by gas chromatography–electron impact mass spectrometry (eq 5).^{14,15} These derivatives are useful for separation. The major fragmentation is that of Si-C bonds. The 1,2-diol in the antibiotic sorangicin has also been derivatized with di-*t*-butyldichlorosilane.¹⁶



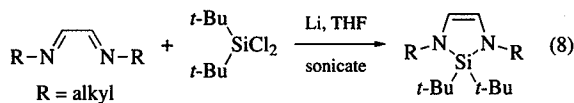
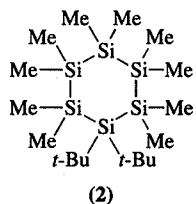
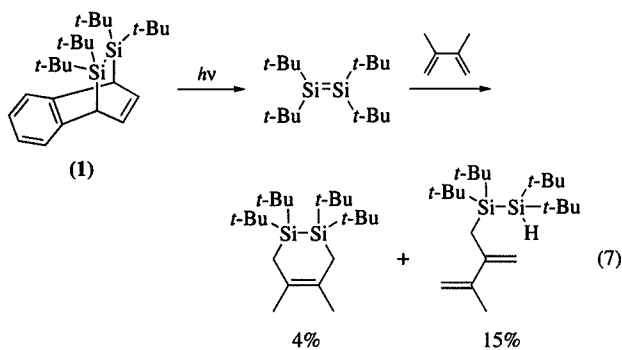
Silylene Precursor. Di-*t*-butyldichlorosilane can be reduced using *Lithium*/THF to give a putative silylene derivative that will react with double bonds to give 1,1-silirane derivatives^{17–19} or react with triethylsilane to give an Si-H insertion product (eq 6).¹⁷



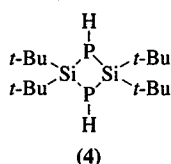
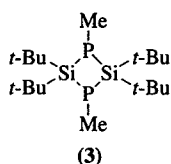
Reaction of di-*t*-butyldichlorosilane with *Lithium Naphthalenide* in DME gives compound (1) which upon irradiation gives, in addition to naphthalene, tetra-*t*-butyldisilene that subsequently reacts with 2,3-dimethylbutadiene to give a Diels-Alder adduct along with a product arising from an ene reaction (eq 7).²⁰

Reduction of di-*t*-butyldichlorosilane with lithium in THF at 0 °C in the presence of an excess of *Dichlorodimethylsilane* gives compound (2).²¹ Reaction of di-*t*-butyldichlorosilane with lithium and 1,4-diaza-1,3-butadienes gives 1,3-diaza-2-sila-4-cyclopentenes (eq 8).²²

Other Substitution Reactions. The chlorine atoms in di-*t*-butyldichlorosilane can be replaced with various nucleophiles.



Di-*t*-butyldifluorosilane has been prepared by using SbF_3 ,^{23,24} ZnF_2 ,²⁵ or $(\text{NH}_4)_2\text{SiF}_6$.^{26,27} Reaction of di-*t*-butyldichlorosilane with **Lithium Aluminum Hydride** gives di-*t*-butylsilane²⁸ and reaction with **Sodium Azide** gives di-*t*-butyldiazidosilane; upon irradiation this gives a putative di-*t*-butylsilylene which undergoes various reactions depending on the conditions.²⁹ Reactions of di-*t*-butyldichlorosilane with LiPHMe ³⁰ and LiPH_2 ³¹ yield (3) and (4), respectively.



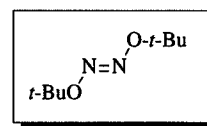
Treatment of di-*t*-butyldichlorosilane with **Trimethylsilyllithium** gives di-(*t*-butyl)bis(trimethylsilyl)silane.³²

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Di-*t*-butyl Hyponitrite¹



[14976-54-6]

$\text{C}_8\text{H}_{18}\text{N}_2\text{O}_2$

(MW 174.24)

(E)

[82554-97-0]

(a convenient, low-temperature source of *t*-butoxyl radicals;¹ induces serial cyclization of polyunsaturated hydroperoxides,² rearrangement of allylic hydroperoxides,³ and reduction of alkyl halides or dialkyl sulfides with Et_3SiH ;⁴ used in radical-trapping experiments;⁵ and as initiator for dimerization⁶ and polymerization⁷)

Alternate Names: DTBN; TBHN; DBH.

Physical Data: white crystals mp 84.5 °C (dec);^{1d} volatile (0.1 mmHg at rt).^{1a}