Di-t-butylidichlorosilane

$$\text{[18395-90-9]}$$

$$\text{C}_6\text{H}_{18}\text{SiCl}_2$$

(MW 213.22)

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

Physical Data: mp $-15\,^\circ\text{C}$; bp 190 $\circ\text{C}$/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 (CCl$_4$/PdCl$_2$ (cat), 85%)$^{12}$ but various other methods of preparation have been reported.$^{3,4}$

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-butyl dichlorosilane has been found to increase the Si–C bond lengths slightly and to widen the CSIC bond angles by 11.1° relative to Dichloromethylsilane 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 deoxypimarol,7,8 In it is generated by the reaction of di-t-butyl dichlorosilane 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.9-10 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′-deoxyribonucleosides (eq 4).12,13

Derivatization of Diols and Hydroxy Acids. Di-t-butyl dichlorosilane has been used to derivatize α-hydroxy acids, β-hydroxy acids, aldehydes, and antranilic 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-butyl dichlorosilane.16

Silylene Precursor. Di-t-butyl dichlorosilane can be reduced using Lithium/THF to give a putative silylene derivative that will react with double bonds to give 1,1-silyl derivatives17 or react with triethylsilane to give an Si–H insertion product (eq 6).17

Reaction of di-t-butyl dichlorosilane 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-butyl dichlorosilane with lithium in THF at 0 °C in the presence of an excess of Dichloromethylsilane gives compound (2).21 Reaction of di-t-butyl dichlorosilane 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-butyl dichlorosilane can be replaced with various nucleophiles.

Avoid Skin Contact With All Reagents.
Di-1-butyl difluorosilane has been prepared by using $\text{SbF}_3$, or $(\text{NH}_2)_2\text{SiF}_6$ Reaction of di-1-butyl dichlorosilane with lithium aluminum hydride gives di-1-butylsilane and reaction with sodium azide gives di-1-butyl diazidosilane; upon irradiation this gives a putative di-1-butyldisilene which undergoes various reactions depending on the conditions. Reactions of di-1-butyl dichlorosilane with LiPHMe and LiPH$_2$ yield (3) and (4), respectively.

Treatment of di-1-butyl dichlorosilane with trimethylsilyllithium gives di-(1-butyl)bis(trimethylsilyl)silane.

23. Weidenbruch, M.; Peter, W. AO(E) 1975, 14, 642.

Snorri T. Sigurdsson & Paul B. Hopkins
University of Washington, Seattle, WA, USA

Di-1-butyl Hyponitrite

\[
\begin{align*}
\text{C}_9\text{H}_{18}\text{N}_2\text{O}_2 & \quad (\text{MW} 174.24) \\
(\text{E}) & \quad [14976-54-6] \\
(\text{E}) & \quad [82554-97-0]
\end{align*}
\]

(a convenient, low-temperature source of t-butoxy radicals; induces serial cyclization of polyunsaturated hydroperoxides, rearrangement of allylic hydroperoxides, and reduction of alkyl halides or dialkyl sulfides with Et$_3$SiH used in radical-trapping experiments, and as initiator for dimerization and polymerization.)

Alternate Names: DTBN; TBHN; DBH.

Physical Data: white crystals mp 84.5 °C (dec); volatile (0.1 mmHg at rt).