Di-tert-butyldisilyl Bis(trifluoromethanesulfonate)

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Introduction

Di-tert-butyldisilyl bis(trifluoromethanesulfonate) is a useful reagent in organic synthesis. It is a colorless to yellow or light brown-yellow liquid with a boiling point of 73–75 °C, it is sensitive towards moisture, corrosive and reacts with hydroxylic solvents. It has been prepared by reaction of di-tert-butyldichlorosilane with trifluoromethanesulfonic acid1 but it is also commercially available. It has been applied in intramolecular cyclizations as a novel promoter for a Boekelheide reaction.2 It acts as protecting group for 1,3-diols to improve yield and stereoselectivity of organic reactions,3 for 1,2-diols in a synthesis of dienophiles4 and 1,4-diols to obtain 3,6-bridged glycosyl donors5 and to receive natural products.6 Triethylsilyl ether, isopropylidene ketal would perform the same role as the t-Bu2Si(OTf)2; however, their acidic removal could be problematic in some cases.7 The bridging di-tert-butyldisilylene can be cleaved to give the corresponding fullerene polyls.8 Moreover, this reagent is a valuable material for the synthesis of prodrugs of chemotherapeutics.9

Table 1 Use of Di-tert-butyldisilyl Bis(trifluoromethanesulfonate)

(A) Massaro and co-workers have treated (aminoalkyl)quinoline N-oxide 1 with t-BuSi(OTf)2 and triethylamine in dichloromethane to obtain 2-(N-benzylpyrrolidin-2-yl)quinoline 2 by intramolecular Boekelheide reaction.2 The cyclized product 2 was synthesized in 51% yield, which was increased to 75% by using microwave irradiation.

(B) Di-tert-butyldisilyl bis(trifluoromethanesulfonate) is reported to be a useful reagent for the preparation of C3−5-O-silylated 2-deoxythioglycoside 4. This product was formed from the corresponding thioglycoside 3 in the presence of 2,6-lutidine in good yield (83%). The C3−5-O-silylated group of compound 4 influences the stereoselectivity during its glycosylation.1

(C) The electron-rich dienophile 7 was obtained starting from the commercially available peracetyl fucal 5.4 Compound 5 was first deprotected and then the hydroxyl groups at C-3 and C-4 of 6 were protected by reaction with di-tert-butyldisilyl bis(trifluoromethanesulfonate) under mild conditions. Fucal derivative 7 was used in a highly selective Diels–Alder reaction.
(D) The reaction of 2,4-di-O-benzyl-1-thio derivatives of glucose, mannose and galactose 8–10 with di-tert-butylsilyl bis(trifluoromethanesulfonate) in 2,6-lutidine led to 3,6-bridged glycosyl donors 11–16 in moderate yields. A number of other bridging reagents were examined but no products were observed.

(E) The reaction of substituted dibenzofuran with di-tert-butylsilyl bis(trifluoromethanesulfonate) in the presence of a base such as pyridine has given the derivative of dibenzofuran 18. The reaction was applied to obtain aglycone fulicinerine.

(F) Treating compounds 19a–b (2 equiv) with t-Bu₂Si(OTf)₂ (1 equiv), Guerra and co-workers have afforded the corresponding bis-malonates 20a–b, which they then used for the regioselective bifunctionalization of C₁₀.

(G) Asymmetric bifunctional silyl ether (ABS) prodrugs of chemotherapeutics (camptothecin, dasatinib, and gemcitabine) were obtained in one step by reacting a dichlorodialkyl silane (t-Pr, Et,) or t-Bu₂Si(OTf)₂ with the pendant alcohol on the chemotherapeutic. This kind of combination of a silyl ether, a chemotherapeutic and a polymerizable monomer ensures protection for the drugs and decreases the rate of degradation.

References

(2) (a) Boekelheide, V.; Linn, W. J. Am. Chem. Soc. 1954, 76, 1286.