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Di-Tert Butyl Chlorosilane

Grainne C. Hargaden
Dublin Institute of Technology, grainne.hargaden@dit.ie

Timothy P. O'Sullivan
University College Cork, tim.osullivan@ucc.ie

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Di-*tert*-butylchlorosilane

$(t\text{-Bu})_2SiClH$

[56310-18-0] $C_8H_{19}ClSi$ MW 178.775

Physical Data: bp 82-85 ºC/45 mmHg; flash point 39 ºC – closed cup; *d*. 0.880 g/cm3

Form: clear, colourless liquid

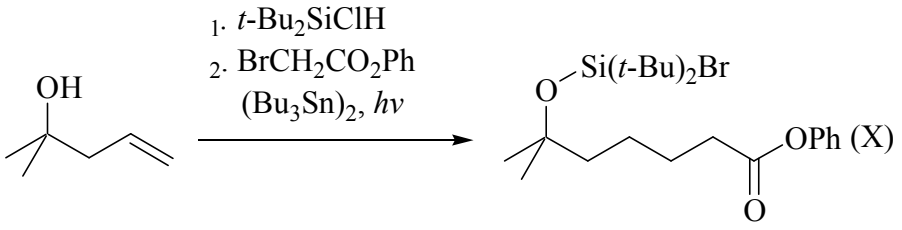
Preparative Methods: Can be prepared by the chlorination of di-tert butylchlorosilane, or by treatment of silicon tetrachloride with *t*-BuLi. {Dexheimer, 1975 #78}{Doyle, 1975 #77}

Purification: Distillation

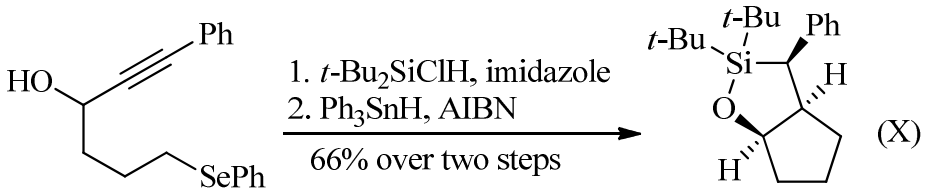
Handling, Storage and Precautions: Moisture sensitive; avoid strong oxidizing agents and strong bases; flammable; causes burns; avoid inhalation of vapour or mist; use in a fume hood.

Intramolecular reducing agent

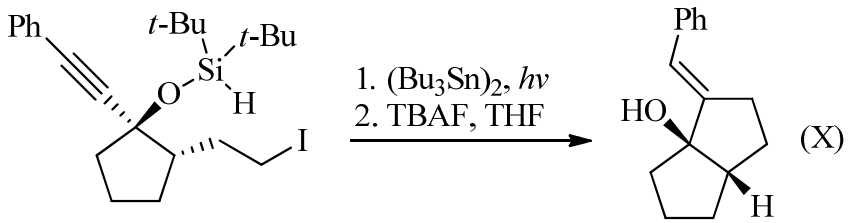
Considerable study of alkoxysilanes as intramolecular hydrogen transfer agents has been undertaken (eq X).Curran, 1995 #80}{Curran, 1995 #45} The di-*tert*-butyloxysilanes, prepared from di-*tert*-butylchlorosilane and the requisite alcohol, are especially effective and are generally more stable to column chromatography.



These alkoxysilanes are particularly useful for making five-membered rings *via* a 5-*endo*-trigonal radical cyclisation from a selenide precursor (eq X).{Clive, 1995 #48}{Clive, 1996 #42} It was observed that the (di-*tert*-butyl)silyl group may be difficult to cleave in the absence of an adjacent oxygen function.

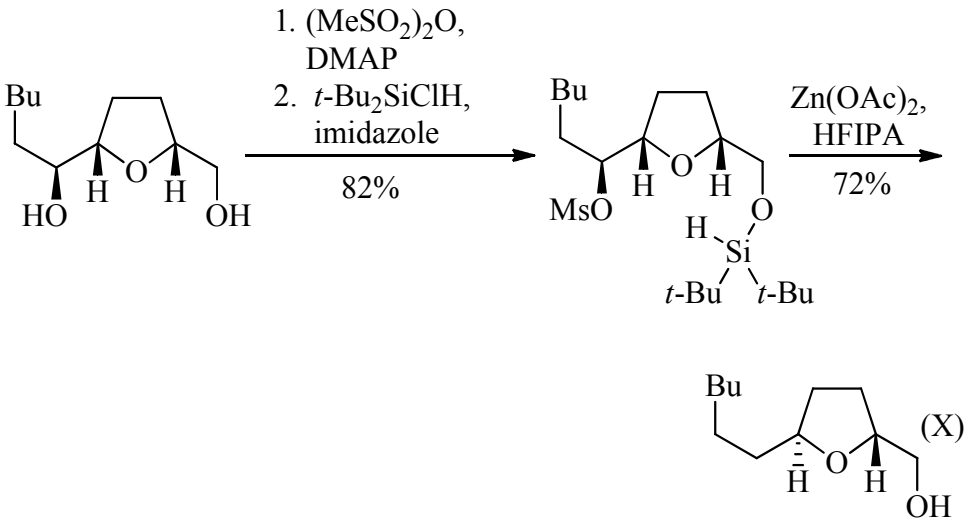


This approach has been further developed to encompass polycyclic compounds.{Clive, 2001 #28} The reaction proceed by a sequential 5-*exo*-diogonal cyclization, followed by 1,5-hydrogen tranfer and then a final 5-*endo*-trigonal cyclization. This methodology has been applied to the synthesis of optically pure products when a single enantiomer of the chiral alcohol is used as the intial substrate.{Clive, 2001 #27} Additionally, alkyl iodides can be substituted in place of the selenide prescursors.{Martinez-Grau, 1997 #38}{Martinez-Grau, 1995 #81}



The (di-*tert*-butyl)silyl group has also proved effective for the conversion of *cis*-2,5-disubstituted THF derivatives to the corresponding of *trans*-2,5-disubstituted rings.{Donohoe, 2008 #9} Activation of the hydroxyl group followed by a 1,2-hydride shift

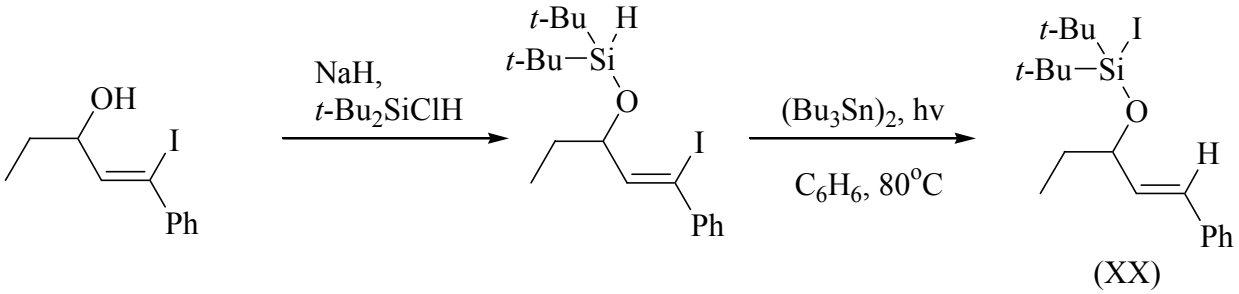
generates the oxonium ion at the C-2 position. The di-*tert*-butyloxysilane then delivers the hydride stereospecifically to form the *trans*-disubstituted product. This motif is found in many natural-product targets and a similar approach been successfully applied to the synthesis of (+)-Sylvaticin.{Donohoe, 2009 #5}



Silicon-Hydride

Di-*tert*-buylchlorosilane has been used in a number of synthetic sequences which involve a silicon-hydride transfer as the key step.

Treatment of a γ–iodoallylic alcohol with NaH and t-Bu_2SiHCl afforded the corresponding silylated alcohol which was then exposed to UV irradiation in the presence of 10% hexabutylditin in a so-called UniMolecular Chain Transfer (UMCT) reaction of silicon hydrides to afford the silicon iodide (eq xx). {Martinez-Grau, 1997 #38}



Di-*tert*-buylchlorosilane has also found application in the Rhodium-catalyzed Si-H insertion of carbenoids, formed by the decomposition of α-diazoesters (eq xx). The chlorosilanes generated can be readily converted to alkoxysilanes by treatment with an alcohol and a base. In a study of a range of chlorosilanes by Landais, it was found that the bulky t-Bu_2SiClH was found to be the most reactive in this process.

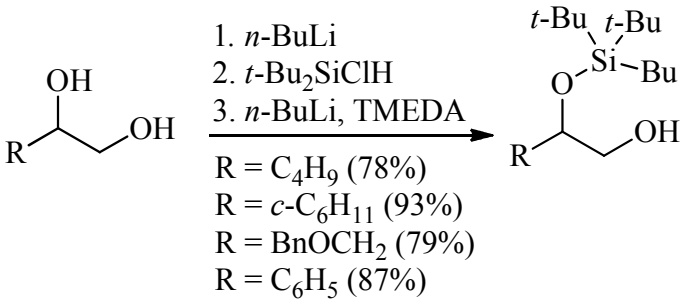
{Andrey, 1993 #54}

{Andrey, 1995 #46}

{Landais, 1997 #40}

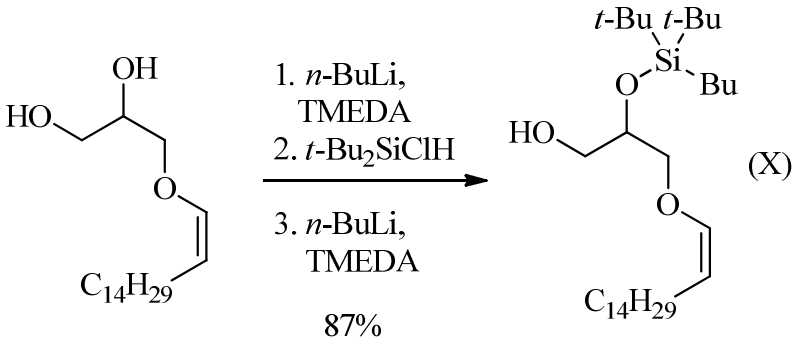
Selective protecting group

Silyl groups have been widely employed as protecting groups for alcohols. Where a choice exists, typical silylation conditions lead to selective protection of the less-hindered hydroxy group. In contrast, di-*tert*-butylchlorosilane can be used for the one-pot silylation of the internal hydroxy group of a 1,2-alkanediol.{Tanino, 1998 #34} The observed selectivity arises from the kinetically controlled ring cleavage of the cyclic silyl ether intermediate where lithium complexes preferentially at the less hindered oxygen. Selectivity was noted to increase when *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was present in the reaction mixture.



(X)

Silyl ether protecting groups are of interest in the synthesis of compounds containing vinyl ether groups, such as in the plasmalogens, where other protecting groups strategies invariably lead to decomposition.{Van, 2007 #12}

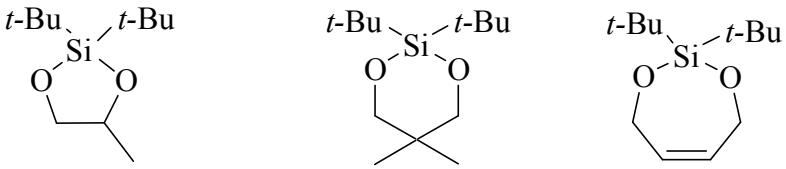


(X)

Protection of diols

Di-*tert*-buylchlorosilane has been used in the preparation of di-*tert*-butylsilyl ditriflate, a highly effective reagent for the protection of a wide range of 1,2-, 1,3- and 1,4-diols under mild conditions (X) {Corey, 1982 #69}

$$t\text{-}Bu_2SiClH + 2\ CF_3SO_3H \longrightarrow t\text{-}Bu_2Si(OSO_2CF_3)_2 + H_2 + HCl$$

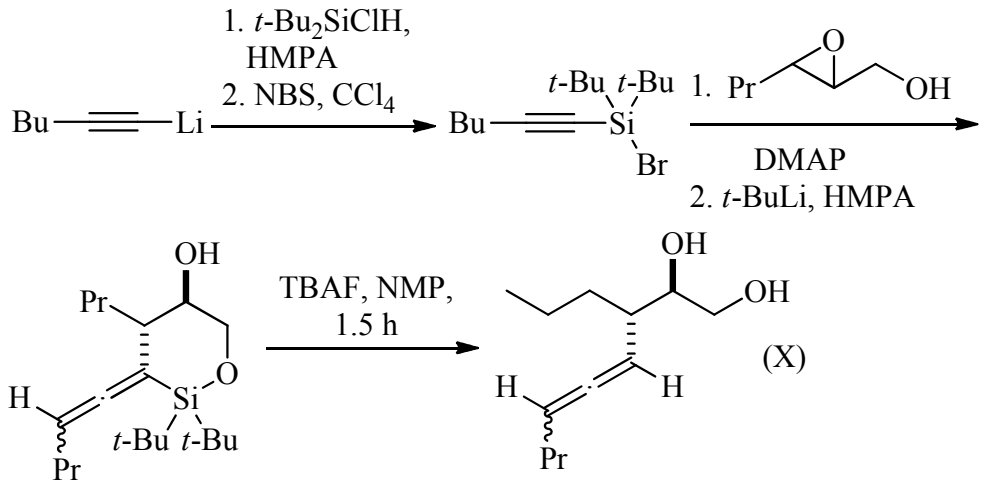


84% 95% 79%

Preparation of alkynylsilanes

Alkynylsilanes are versatile synthetic intermediates which display interesting reactivity.{Molander, 2002 #23}{Mukherjee, 2009 #3} Such groups allow for the introduction of allene substitutents at the C3 position of 2,3-epoxyalcohols.{Tanino, 2000 #30} The regioselectivity is depenedent on the configuration of the epoxide moiety with *cis*-epoxides proceeding by 5-*exo* type cylization while *trans*-epoxides undergo a 6-*endo*

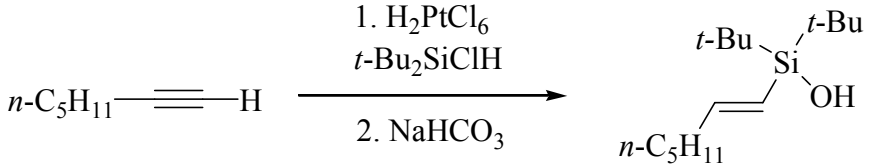
cyclization. The allenylsilane intermediates are readily converted to the corresponding allenes with TBAF in 1-methyl-2-pyrrolidione (NMP).



(X)

Hydrosilylation of alkynes

Di-*tert*-butylchlorosilane has been utilised in the preparation of (*E*)-di-*tert*-butyl-(1-heptenyl)silanol by hydrosilylation of 1-heptyne and hydrolysis of the intermediate chlorosilanes (eq xx). {Denmark, 2006 #14}

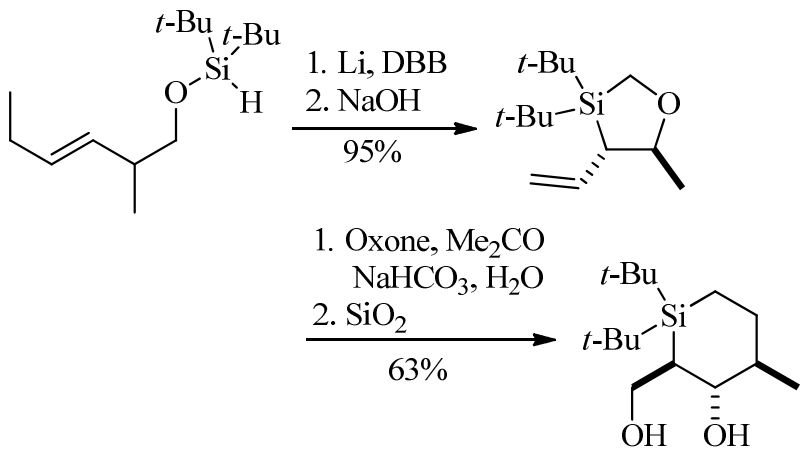


60% (X)

Internal controlling groups

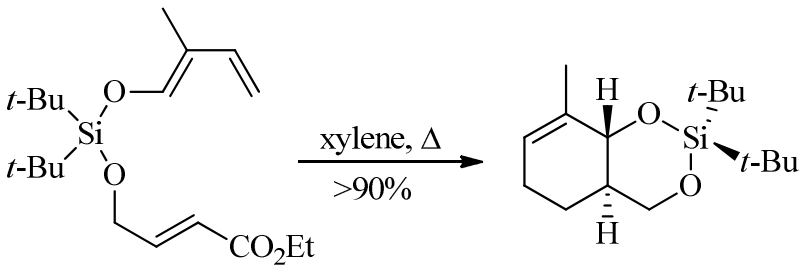
Di-*tert*-butylsilyl ethers have been used as a means of controlling the regioselecivity and stereoselectivity in certain reaction. The ability of silyl groups to stabilise carbocations at the β-position has been exploited in the diastereoselective synthesis of cyclic polyols.{Tanino, 1997 #36} The di-*tert*-butylsilyl ether group undergoes regio- and stereoselective migration in the presence of of lithium and 4,4'-di-*t*-butylbiphenyl (DBB) followed by cyclisation under

basic condidtions to form the allylsilane. Epoxidation of the double bond occurs primarily on the face opposite to the bulky *t*-butyl group. Ring-opening induced by SiO_2 leads to a β-silyl cationic intermediate and stereoselective introduction of the hydroxy group *via* neighbouring-group participation.



(X)

By linking reactive dienes and dienopiles with silaketal tether, the course of the intramolecular Diels-Alder reaction can be controlled with a high degree of stereoselectivity and with regiochemistry opposite to that predicted by bond polarization models.{Gillard, 1991 #61} The cyclisation proceeds in a 'head-to-tail' manner and the methyl group on the diene strongly favours an endo cyclisation due to steric factors imposed in the transition state. The di-*tert*-butylsilyl group was found more thermally stable than related alkylsilyls.

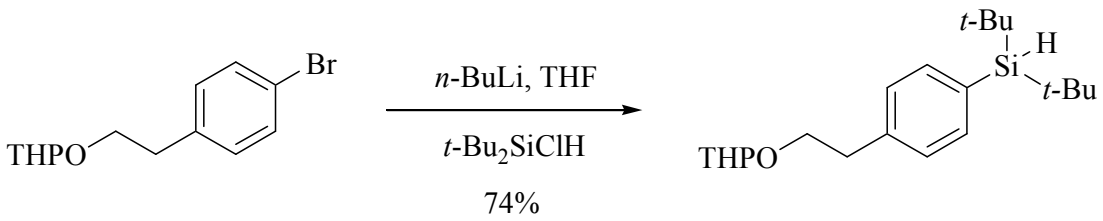


(X)

Applications in PET imaging

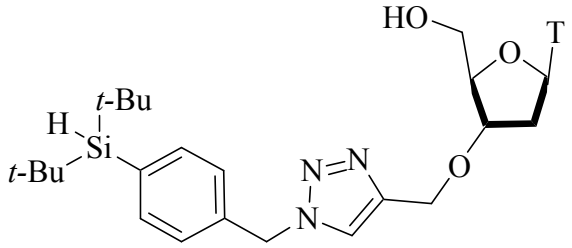
Di-*tert*-buylchlorosilane has been utilised in the synthesis of silicon-based building blocks for ^{18}F-radiolabeling of peptides for application in PET imaging. {Mu, 2008 #8}

Nucleophilic substitution of di-*tert*-buylchlorosilane with {4-[2-(tetrahydro-2H-pyran-2-yloxy)ethyl]phenyl}lithium proceeded in 74% yield, the product of which was further modified to afford the ^{18}F-radiolabeled compound. (eq. X)



(XX)

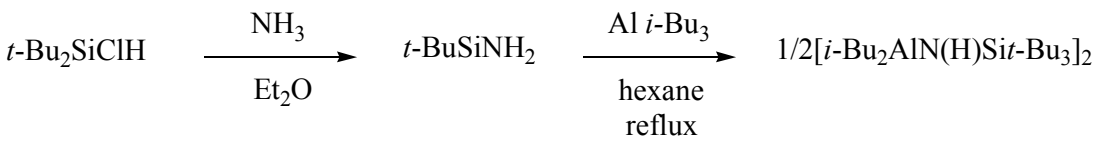
The lithiated derivative of di-*tert*-butylchlorosilane has been utilized in the synthesis of 3´-silylated thymidine derivatives for application in PET imaging. (eq. X) {James, 2010 #2}



(xx)

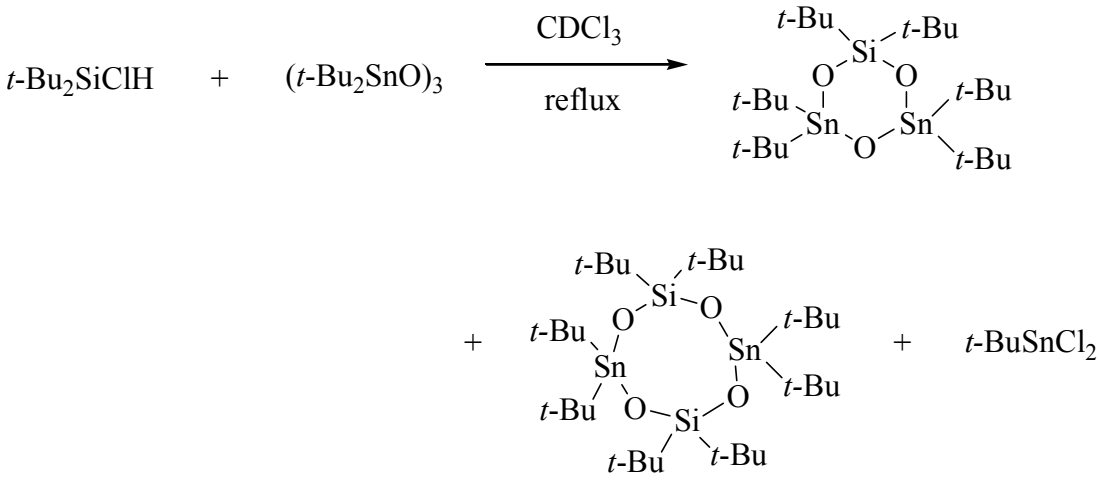
Formation of organometallic complexes

Di-*tert*-buylchlorosilane has been used in the preparation of a range of organometallic complexes, many through an oxidative addition process to Iridium, Manganese and Molybdenum. {Handwerker, 1992 #58} {Koloski, 1994 #53} {Zarate, 1995 #47} {Driess, 1996 #44}



(XX)

They have also been utilised in the synthesis of aluminium amides (eq xx) and metallasiloxanes containing Si-O-Sn linkages (eq xx). {Choquette, 1992 #60} {Beckmann, 1998 #33}



(XX)

References

Contributors