

Silylation and Silanes in Organic Synthesis

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Organosilicon compounds have many applications in organic chemistry, most notably as derivatizing and protecting reagents, intermediates in organic synthesis and reducing agents. Silicon is considerably less electronegative than either carbon or hydrogen with consequent implications for the polarity of bonds between silicon and other elements. Also of significance are the high bond energies of the Si-O and Si-F single bonds (typical bond energies 108 kcal mol⁻¹; 452 kJ mol⁻¹, and 139 kcal mol⁻¹; 582 kJ mol⁻¹ respectively),¹ providing a driving force in many of the reactions of silanes with oxygen and fluoride nucleophiles, and the “β-effect”: stabilization of a positive charge on a carbon atom β- to silicon.²

Silylating agents

The formation of a silyl ether from a hydroxyl function can be utilized either to provide a volatile derivative for GC and GC-MS, or as a means of protection in synthesis. Silylation at other elements, particularly nitrogen or sulfur, is also a useful protection method. Silylation at carbon is mainly used to influence chemical reactivity in synthesis.

Many different organosilyl protecting groups are known, providing a wide spectrum of chemical stability and steric demand. Those described here have some of the most useful analytical and synthetic applications. A number of different reagents may be available for the introduction of a particular silyl group, allowing silylation under a variety of conditions. Methods of cleavage include acid or base hydrolysis, or, where hydrolytic conditions would be undesirable or ineffective, selective cleavage of most silyl groups can be effected with fluoride ion under mild conditions. Further details of methods of silylation and cleavage can be found in the relevant text entries in the main section of the Catalogue, and also in a number of reviews and monographs.³⁻¹³

Trimethylsilyl [TMS]

The widest choice of reagents is available for this, the most commonly encountered silyl protecting group. Generally, TMS ethers are readily hydrolyzed, with N-TMS more labile still, limiting the use of either in synthesis mainly to anhydrous, non-protic systems. The TMS-carbon bond is much more hydrolytically stable, allowing the use of C-TMS compounds in a variety of synthetic transformations.

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The formation of the TMS ether from an alcohol and TMS chloride typically requires a base such as triethylamine or pyridine. For greater reactivity, TMS bromide or iodide can be used. TMS triflate is a particularly valuable, powerful reagent for the silylation of unreactive species, including enols. TMS amines act as their own base; an imidazole or triazole ring in the molecule behaves as an activating group. The convenient, relatively low-cost hexamethyldisilazane (HMDS) produces only gaseous ammonia as by-product, although it often requires a catalyst. In contrast, N-TMS and N,O-bis(TMS) amides are normally effective under neutral conditions without added base or catalyst. Other interesting silylation methods include the use of allyltrimethylsilane with an acidic catalyst, giving gaseous propene as the only by-product; ethyl (trimethylsilyl)acetate in the presence of fluoride ion (by-product ethyl acetate); and hexamethyldisilane in the presence of fluoride or various other catalysts.

A14662 Allyltrimethylsilane

L00183 N,O-Bis(trimethylsilyl)acetamide [BSA]

B23608 Bis(trimethylsilyl) sulfate

A12033 N,O-Bis(trimethylsilyl)trifluoroacetamide [BSTFA]

L01301 N,N'-Bis(trimethylsilyl)urea [BSU]

A15334 Bromotrimethylsilane [TMSBr]

A13651 Chlorotrimethylsilane [TMSCI]

A17707 Ethyl (trimethylsilyl)acetate [ETSA]

L04240 Heptamethyldisilazane

A13155 Hexamethyldisilane

A15139 1,1,1,3,3,3-Hexamethyldisilazane [HMDS]

42039 1,1,1,3,3,3-Hexamethyldisilazane,
Electronic grade, 99+%

A12902 Iodotrimethylsilane [TMSI]

L04101 N-Methyl-N-trimethylsilylacetamide [MSA]

L17352 Methyl N-trimethylsilylcarbamate

A13141 N-Methyl-N-(trimethylsilyl)-
trifluoroacetamide [MSTFA]

B23102 Nonamethyltrisilazane

A13884 N-Trimethylsilylacetamide

A18149 N-(Trimethylsilyl)diethylamine [TMSDEA]

A16550 N-(Trimethylsilyl)dimethylamine [TMSDMA]

A12512 N-Trimethylsilylimidazole [TMSIM]

B21105 1-Trimethylsilyl-1,2,4-triazole

A12535 Trimethylsilyl trifluoromethanesulfonate
[TMS-OTf]

Dimethylsilyl [DMS]

This group finds limited use in GC-MS where greater volatility compared with TMS is required. Its use in synthesis is limited by its extreme ease of hydrolysis. For use in the regioselective conversion of allylic and homoallylic alcohols to 1,3-diols, see reference under Chlorodimethylsilane.

A13113 Chlorodimethylsilane

L03503 Dimethylsilyldiethylamine

A14304 Tetramethyldisilazane

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tert-Butyldimethylsilyl [TBDMS, TBS]

The much greater stability to hydrolysis of this group in comparison with TMS, combined with its facile selective cleavage, has led to its adoption as one of the most popular OH blocking groups, especially in synthetic applications. Silylation is typically carried out with the silyl chloride and a base/catalyst such as imidazole, DMAP or DBU. The group will survive many types of aqueous work-up and chromatography, but is readily cleaved under mild conditions by fluoride ion, for example tetra-n-butylammonium fluoride (TBAF), or by various acidic catalysts.

A13064 tert-Butyldimethylchlorosilane [TBDMSCl]

B21286 tert-Butyldimethylchlorosilane, 50%
w/w in toluene

41462 tert-Butyldimethylsilylimidazole

B23760 N-(tert-Butyldimethylsilyl)-N-methyltrifluoroacetamide [TBSTFA, MTBSTFA]

A12174 tert-Butyldimethylsilyltrifluoromethane sulfonate [TBDMS-OTf]

Thexyldimethylsilyl [Dimethyl(2,3-dimethylbutyl)silyl, TDS]

The greater steric hindrance compared with TBDMS confers increased (at least 2-3x) stability to acid or base hydrolysis. Cleavage with fluoride is also about 2-3x slower than for TBDMS. TDS is also a valuable protecting group for nitrogen functions, providing readily purifiable derivatives which survive a variety of chemical transformations, but are readily cleaved by fluoride.

A19140 Thexyldimethylchlorosilane

tert-Butyldiphenylsilyl [TBDPS]

This group is sometimes preferred to TBDMS, because of its greater steric bulk, allowing selective protection of primary alcohols in the presence of secondary, and enhanced stability (>100x) to acid hydrolysis. Another useful property is the crystalline nature of most TBDPS ethers which facilitates purification. Cleavage occurs with fluoride ion, typically TBAF in THF.

A12721 tert-Butyldiphenylchlorosilane

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Triethylsilyl [TES]

The TES group is considered to be intermediate in hydrolytic stability and steric bulk between TMS and TBDMS. TES ethers can be formed by analogous methods to TMS, or using triethylsilane catalyzed by TBAF-THF under very mild conditions. Cleavage can be accomplished with TBAF-THF, or aqueous acetic acid which allows selective removal in the presence of more stable silyl groups.

A13064 tert-Butyldimethylchlorosilane [TBDMSCl]

B21286 tert-Butyldimethylchlorosilane, 50%
w/w in toluene

41462 tert-Butyldimethylsilylimidazole

B23760 N-(tert-Butyldimethylsilyl)-N-methyltrifluoroacetamide [TBSTFA, MTBSTFA]

A12174 tert-Butyldimethylsilyltrifluoromethane sulfonate [TBDMS-OTf]

Triisopropylsilyl [TIPS]

The steric bulk of TIPS makes it useful as a regio- and stereo-directing group. Formation of TIPS ethers is usually carried out with the silyl chloride in the presence of a nucleophilic catalyst such as imidazole or DMAP. An alternative method uses triisopropylsilane and TBAF-THF. TIPS ethers are more resistant to acidic hydrolysis than TBDMS but less so than TBDPS, whereas they are more resistant than either to basic hydrolysis. Cleavage with fluoride ion is usually effective.

A17376 Chlorotriisopropylsilane [TIPSCl]

L09585 Triisopropylsilane

B21127 Triisopropylsilyl trifluoromethanesulfonate [TIPS-OTf]

tert-Butoxydiphenylsilyl

Ethers of this protecting group are about 10x more stable to hydrolysis than TBDMS, but are cleaved with TBAF about 25x more readily. Selective cleavage in the presence of TBDMS and TBDPS groups can also be achieved with sodium sulfide.

L14047 tert-Butoxychlorodiphenylsilane

Dimethylphenylsilyl [DMPS] and 3,5-Bis(trifluoromethyl)phenyldimethylsilyl

The dimethylphenylsilyl group finds some limited use as a derivatizing and protecting group, as it is somewhat more resistant to hydrolysis than TMS. C-Silylated derivatives have interesting chemistry in which DMPS can behave as a masked hydroxyl group. See references in Chlorodimethylphenylsilane text entry for further details.

L13709 3,5-Bis(trifluoromethyl)phenyldimethylchlorosilane

A15638 Chlorodimethylphenylsilane [DMPSCl]

L04558 Dimethylphenylsilane

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Diphenylmethylsilyl [DPMS]

Ethers of this bulky group have hydrolytic stability between the TMS and TBDMS groups. They are stable to chromatography on silica, but can be cleaved with fluoride ion or with aqueous acid or base.

L04162 Diphenylmethylchlorosilane [DMPSCI]

L04211 Diphenylmethylsilane

(Chloromethyl)dimethylsilyl [CMDMS]

This group has been used for the derivatization of sterols for GC-MS.

A14899 (Chloromethyl)dimethylchlorosilane

Flophemesyl [Pentafluorophenyldimethylsilyl]

This group is used to derivatize sterols permitting detection at very low levels by GC or GC-MS.

L00550 Flophemesyl chloride

Allyldimethylsilyl [ADMS]

This group is useful in the derivatization of sterols for GC-MS analysis, since the ethers have similar properties to TBDMS but, since they are less hindered, are more easily formed.

B22237 Allylchlorodimethylsilane [ADMSCI]

Triphenylsilyl [TPS]

TPS ethers have high steric demand. Their stability to basic hydrolysis is similar to TMS ethers but they are much more stable to acidic hydrolysis.

A13678 Triphenylchlorosilane

A11605 Triphenylsilane

Bifunctional silylating agents

Cyclic derivatives of 1,2- or 1,3-diols, hydroxy acids, amines, diamines, etc., either for GC or synthetic applications, are formed with bifunctional silylating agents, under similar conditions to those used for monosilylation. Because of the driving force of ring formation, the less reactive dialkoxy- and diacetoxysilanes are also useful silylating agents in this type of system.

Dimethylsilylene

The use of this group, which is of great importance in silicone chemistry, is limited in analytical or synthetic chemistry by the ease of hydrolysis of its derivatives

B21119 Bis(dimethylamino)dimethylsilane

L14725 Diethoxydimethylsilane

L12133 Dichlorodimethylsilane

A12025 Dimethoxydimethylsilane

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Diethylsilylene [DES]

This group has been found to be useful in derivatization of diols for GC-MS analysis.

L03239 Dichlorodiethylsilane

Di-tert-butylsilylene [DTBS]

DTBS derivatives show enhanced stability to hydrolysis, including chromatography, and are thus of value in analytical and synthetic applications. They are readily cleaved with fluoride.

L03162 Di-tert-butylchlorosilane

Diphenylsilylene

Derivatives of this group find considerable use in synthesis. Disilylation with dichlorodiphenylsilane is improved by the addition of DMAP. Hydrolytic cleavage occurs very readily.

B21119 Bis(dimethylamino)dimethylsilane

L12133 Dichlorodimethylsilane

L14725 Diethoxydimethylsilane

A12025 Dimethoxydimethylsilane

Methylphenylsilylene

Like dimethylsilylene and diphenylsilylene, derivatives of this group are very easily hydrolyzed. Nevertheless, they have a number of applications in synthetic work.

B23999 Dichloromethylphenylsilane

B23684 Diethoxymethylphenylsilane

1,3-(1,1,3,3-Tetraisopropylidisiloxanylidene) [TIPDS]

Protection of diols as TIPDS derivatives is an important technique in carbohydrate and nucleoside chemistry. The high steric demand of the group enables discrimination between primary and secondary hydroxyl substituents. Cleavage is by TBAF-THF or various hydrolytic methods.

L11171 1,3-Dichloro-1,1,3,3-tetraisopropylidisiloxane

1,4-(1,1,4,4-Tetramethyldisilylethylidene) [Stabase]

The importance of this group lies in its ability to form cyclic derivatives of primary amines which are stable in the presence of many reactive species such as: organolithium or Grignard reagents and other strong bases, various oxidants, and fluoride ion. Cleavage can be accomplished with strong aqueous acid or methanolic hydroxide or methoxide (Scheme 1).

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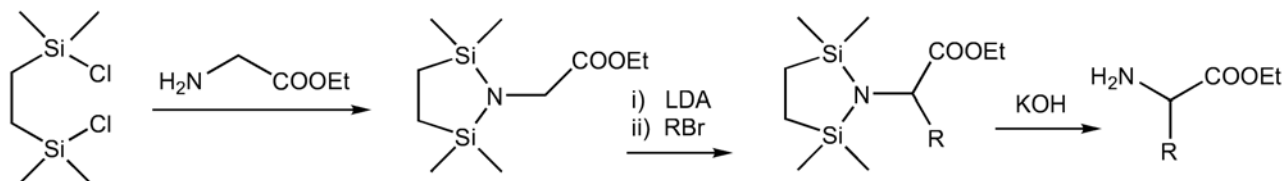
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Scheme 1

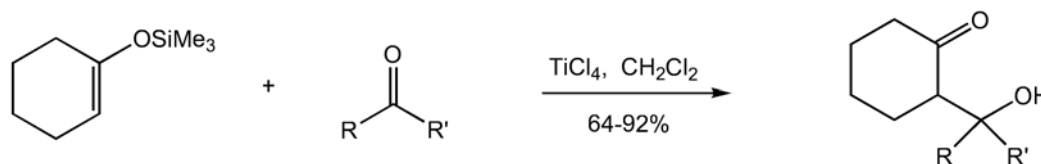


L02570 1,2-Bis(chlorodimethylsilyl)ethane

Silyl enol ethers (vinyl siloxanes)

These are protected forms of carbonyl compounds which undergo many useful reactions such as the crossed aldol condensation (Scheme 2).

Scheme 2



Discussion of the chemistry of these compounds can be found in the review literature¹⁴⁻¹⁶ and also under the Catalogue entries for individual products.

Silyl enol ethers

L06931 1-Methoxy-2-methyl-1-(trimethylsilyloxy)propene

L06100 1-Methoxy-3-(trimethylsilyloxy)-1,3-butadiene, 94%

L14672 1-Methoxy-3-(trimethylsilyloxy)-1,3-butadiene, 98+%

L05308 1-Phenyl-1-trimethylsilyloxyethylene

A16099 1-Trimethylsilyloxycyclohexene

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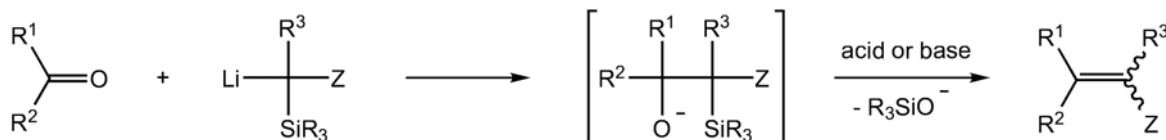
Reactions of C-silyl compounds

Many of the most useful synthetic reactions of organosilanes depend on the influence of the silicon atom on the chemistry of the organic portion of the molecule. In particular, there are significant electronic effects associated with carbon atoms α - or β - to silicon which enhance their reactivity towards metalation and electrophilic substitution, respectively. These areas of chemistry are discussed in greater detail in the standard texts² and in review articles by Fleming and others.¹⁶⁻²¹

Silicon compounds with α -substituents

Silanes which are suitably activated at the α -position can form silicon stabilized carbanions. Reaction of an α -silyl carbanion, most often a lithiated derivative, with a carbonyl compound leads to a β -hydroxy silane which can undergo elimination to give an alkene (Scheme 3).

Scheme 3



This silicon analog of the Wittig reaction is known as the Peterson olefination reaction.²² It is often possible to isolate the intermediate β -hydroxy silane which can be converted stereoselectively to the alkene by treatment either with acid (anti-elimination) or strong base (syn-elimination). The bond energy of the new Si-O bond provides the driving force for the elimination. The mechanism of the Peterson reaction has been discussed in more detail by Bassendale *et al.*,²³ and, presenting evidence that the reaction may not always involve a β -hydroxy silane intermediate, by Hudrlik *et al.*²⁴ The reaction takes place for a wide range of substituents, Z. (For Z = halogen, epoxide formation takes place preferentially.) The presence of TBDPS group instead of TMS has been reported to promote (Z)-stereoselectivity.²⁵ The Peterson reaction has been extensively reviewed by Ager,^{26,35} and also by Flygare²⁷ and Armstrong.²⁸ Several examples appear in text entries for these products in the main section of the Catalogue.

α -Substituted silicon compounds

A13191 Benzyltrimethylsilane

A15662 Bis(trimethylsilyl)methane

L10296 Bis(trimethylsilylmethyl) sulfide

B21879 (Bromomethyl)trimethylsilane

A14303 (Chloromethyl)trimethylsilane

A17707 Ethyl (trimethylsilyl)acetate

L03903 (Trimethylsilyl)acetic acid

L00979 2-Trimethylsilyl-1,3-dithiane

L04251 1-Trimethylsilylmethanol

L00788 (Trimethylsilylmethyl)triphenylphosphonium iodide

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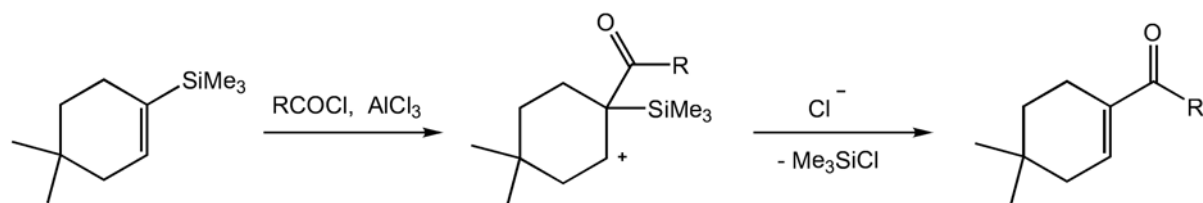
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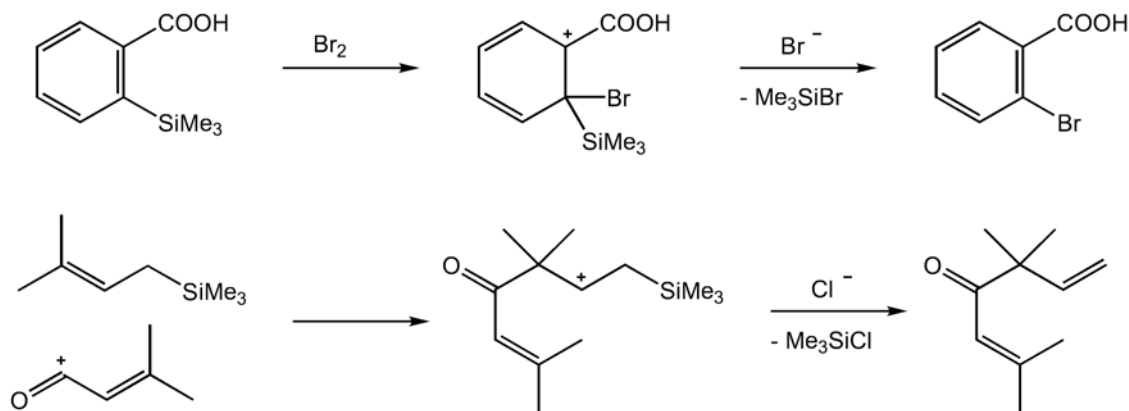
Vinyl, aryl, allyl and alkynyl silanes

The ability of silicon to stabilize a positive charge on a β -carbon atom (the β -effect) is one of the characteristic features of organosilicon chemistry, permitting the use of silyl groups to control the position of electrophilic attack in vinyl, aryl, allyl or alkynyl silanes (Schemes 4-6). In simplistic terms, silicon can be considered to be a "super-proton", directing electrophilic attack to the position previously occupied by the silyl substituent. Further information on the chemistry of these compounds can be found in various reviews,²⁹⁻³² and in several of the Catalogue entries.

Scheme 4



Schemes 5-6



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Silylation and Silanes in Organic Synthesis

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Vinyl silanes

L06072 Trivinylmethylsilane

L04056 Vinyl(chloromethyl)dimethylsilane

L12461 Vinyltriethylsilane

L02498 Vinyltrimethylsilane, 97%

L16989 Vinyltrimethylsilane, 99%

Aryl silanes

A12126 1,4-Bis(dimethylsilyl)benzene

L02876 Phenyltrimethylsilane

L04857 Tetraphenylsilane

L11625 2-(Trimethylsilyl)benzothiazole

B21903 2-(Trimethylsilyl)thiazole

Allyl silanes

A14662 Allyltrimethylsilane

41953 Allyl(chloromethyl)dimethylsilane,

43183 Tetraallylsilane

Alkynyl silanes

A11960 Bis(trimethylsilyl)acetylene

L09246 1,4-Bis(trimethylsilyl)-1,3-butadiyne

L10640 1,3-Bis[(trimethylsilyl)ethynyl]benzene

L09709 1,4-Bis[(trimethylsilyl)ethynyl]benzene

L20217 (Triethylsilyl)acetylene

A12856 (Trimethylsilyl)acetylene

L11251 2-(Trimethylsilylethynyl)pyridine

B24875 1-(Trimethylsilyl)propyne

L14815 4-Trimethylsilyl-3-butyn-1-ol

L09649 3-(Trimethylsilyl)propargyl alcohol

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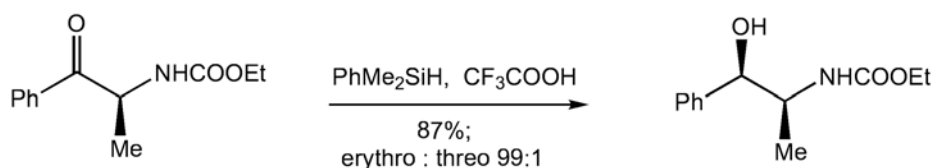
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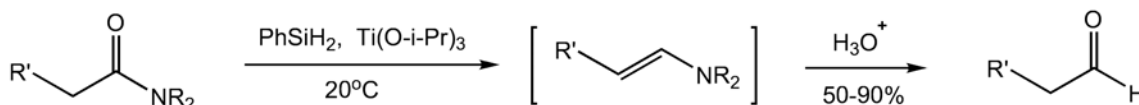
Silanes as reducing agents

Compounds with one or more hydrogens attached to silicon can take part in a variety of reduction reactions (Schemes 7-8). Examples of these, together with literature references, can be found under the relevant product entries in the main section of the Catalogue and in the review literature.^{33,34}

Scheme 7



Scheme 8



A10153 Diethoxymethylsilane
L16468 Diethylsilane
L16197 Dimethoxymethylsilane
L04558 Dimethylphenylsilane
A10884 Diphenylsilane
L14561 Poly(methylhydrosiloxane)
B22063 Triethoxysilane

B23697 1,1,3,3-Tetramethyldisiloxane
A10320 Triethylsilane
L09585 Triisopropylsilane
A11605 Triphenylsilane
L04585 Tri-n-propylsilane
B22457 Tris(trimethylsilyl)silane

Miscellaneous silylated reagents

The following reagents are listed separately because of the importance of the non-silyl functionality, the reactivity of which is modified by the attachment of a trialkylsilyl group. Further details are given in the text entries for these items in the main Catalogue.

A11670 Bis(trimethylsilyl)carbodiimide
L06319 (Phenylthio)trimethylsilane
L13152 1-(Triisopropylsilyl)pyrrole
B20347 (Trifluoromethyl)trimethylsilane

L00173 Trimethylsilyl azide
A19598 Trimethylsilyl cyanide
A12633 Trimethylsilyl isocyanate
L03277 Trimethylsilyl isothiocyanate

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