

Silicon-Based Reducing Agents

Gelest



Reductive Transformations for Organic Synthesis



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Silicon-Based Reducing Agents

Gelest

Edited by Gerald L. Larson, Ph.D.
Vice President, Research Products

Materials for the reduction of:

Aldehydes
Ketones
Acetals
Ketals
Esters
Lactones
Thioesters
Enamines
Imines
Acids
Amides
Halides
Olefins
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Supplement to the Gelest Catalog, "Silicon, Germanium & Tin Compounds,
Metal Alkoxides and Metal Diketonates" which is available on request.

SILICON-BASED REDUCING AGENTS

Introduction

The widely-used organometallic-based reducing agents can be broadly classified as either ionic, such as lithium aluminum hydride and sodium borohydride, or free-radical such as tri-n-butyltin hydride. The mechanistic differences between these two classes of reducing agents very often complement one another in their ability to reduce organic substrates. Organosilanes have been found to possess the ability to serve as both ionic and free-radical reducing agents. These reagents and their reaction by-products are safer and more easily handled and disposed of than other reagents. Their reductive abilities are accomplished by changes in the nature of the groups attached to silicon, which can modify the character of the Si-H bond in the silane. For example, the combination of triethylsilane and an acid has proven to be excellent for the reduction of substrates that can generate a "stable" carbenium ion intermediate. Examples of substrates that fall into this class are olefins, alcohols, esters, lactones, aldehydes, ketones, acetals, ketals, and other like materials. On the other hand, triphenylsilane and especially tris(trimethylsilyl)silane have proven to be free-radical reducing agents that can substitute for tri-n-butyltin hydride. The reductions with silanes can take place with acid catalysis in which the silane provides the hydride to a carbenium ion intermediate. This is often the situation in the reduction of carbonyls, ketals, acetals and similar species. The silane reductions can also be carried out with fluoride ion-catalysis which acts on the silicon moiety to generate a silane with more hydridic character.

Some of the key reductions possible with silanes are summarized in **Table 1**.

TABLE 1 SILANE REDUCTION OF ORGANIC FUNCTIONAL GROUPS

TRANSFORMATION	Cl ₃ Si-H	Et ₃ Si-H	Ph ₃ SiH	Ph ₂ SiH ₂	PhSiH ₃	(Me ₃ Si) ₃ Si-H	PMHS
R ₂ C=CR ₂ → R ₂ CH-CHR ₂		++		+ + ^a	+ ^a		
R-OH → R-H		+	++	+			
R-X → R-H		+	+			++	
RCHO → RCH ₂ OH		++			+		
R ₂ C=O → R ₂ CHOH		++	+	+			+
RCO ₂ R' → RCH ₂ OH		++		++			+
RCOCl → RCH ₂ OH'		++					
RCHO → RCH ₂ OR							
RR'C(OR'') ₂ → RR'CHOR''		++	++ ^b				
RR'C=NHR'' → RR'CHNHR''		+		++			+
RCN → RCH ₂ NH ₂		++					
RCH ₂ NR ₂ ' → RCH ₂ OH		+		+			
R ₃ P=O → R ₃ P:	+		+	++			+
ArNO ₂ → ArNH ₂							+

a. Reduces C=C of enones to saturated ketones.

b. Especially good for reduction of cyclic ketals and acetals.

General Considerations

Hydrosilanes are readily produced on an industrial scale through the use of Grignard chemistry starting with trichlorosilane, methylchlorosilane, and dimethylchlorosilane, among others, as key raw materials. Alternatively, the Si-X (X = primarily Cl or OR) bond can be reduced to Si-H.

The organosilanes are basically hydrocarbon-like in that they are stable to water, are, in general, flammable and are lipophilic. In contrast to hydrocarbons the low molecular weight silanes such as monosilane, methylsilane, and dichlorosilane are pyrophoric. The silanes will react with base or, more slowly, with acid to give the corresponding siloxane with the evolution of hydrogen gas. They show a strong, characteristic, carbonyl-like absorption in the infrared at about 2200 cm⁻¹.

The metallic nature of silicon and its low electronegativity relative to hydrogen - 1.8 versus 2.1 on the Pauling scale - lead to polarization of the Si-H bond such that the hydrogen is hydridic in nature. This provides an ionic, hydridic reducing agent that is milder than the usual aluminum-, boron-, and other metal-based hydrides. Thus, triethylsilane, among others, has been used to provide the hydride in Lewis Acid-catalyzed reductions of various carbenium ion precursors. In addition the Si-H bond can be employed in various radical reductions wherein the silane provides the hydrogen radical.

Table 2 shows the Si-H bond strengths for various silanes. From this data the rather wide variation in the bond strengths from tris(trimethylsilyl)silane on the low-energy end to trifluorosilane on the high-energy end can be noted. This is yet another example of the extraordinary effect that groups attached to silicon can have on the chemistry of the silane and that these effects can go beyond the simple steric effects that have been so successfully applied with the silicon-based blocking agents.^{2,4}

TABLE 2 BOND STRENGTHS OF VARIOUS HYDRIDOSILANES

Compound	Product Code	Bond Strength		Reference
		kJ mol ⁻¹	kcal mol ⁻¹	
F ₃ Si-H	SIT8373.0	419	100	5
Et ₃ Si-H	SIT8330.0	398	95	6
Me ₃ Si-H	SIT8570.0	398	95	7
H ₃ Si-H	SIS6950.0	384	92	6
Cl ₃ Si-H	SIT8155.0	382	91	5
PhMeHSi-H	SIP6742.0	382	91	6
Me ₃ SiSiMe ₂ -H	not offered	378	90	6
PhH ₂ Si-H	SIP6750.0	377	90	6
(MeS) ₃ Si-H	not offered	366	87	6
H ₃ SiSiH ₂ -H	SID4594.0	361	86	5
(Me ₃ Si) ₃ Si-H	SIT8724.0	351	84	6

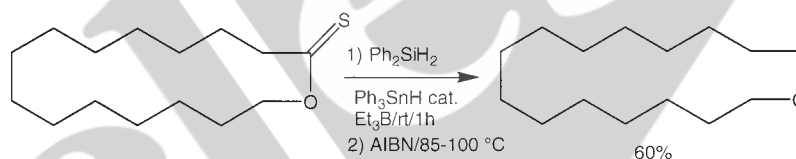
Although triethylsilane has been the most popular of the silicon-based reducing agents, in principal any Si-H-containing system can provide the hydride for many or most of these reductions. Considerations would include availability, economics, and silicon-containing by-products. The silicon-containing by-products are usually the silanol or disiloxane in the case of the trisubstituted silanes, or silicones in the case of the di- or monosubstituted silane reducing agents. Such considerations can result in greater ease of handling and purification of the final product.

Silicon-based reductions have been reviewed, though never in a comprehensive manner.^{6,8-13}

Silicon-Based Radical Reductions

Griller and Chatgililoglu⁶ realized that the low bond energy of the Si-H bond in tris(trimethylsilyl)silane compared well with that of the Sn-H bond in tri-n-butyltin hydride (322 kJ mol⁻¹; 77 kcal mol⁻¹), and that this reagent should, therefore, be a viable alternative for radical reductions and one that would avoid the potential problems of working with toxic tin materials and trace tin-containing impurities in the final product. This proved to be the case and a number of radical reductions with tris(trimethylsilyl)silane have been reported and reviewed.^{14,15} Included among these are the reductions of organic halides,¹⁶⁻¹⁸ esters,¹⁹ xanthates,²⁰ selenides,²⁰ sulfides,²⁰ thioethers,²⁰ and isonitriles²⁰.

As an example, the diphenylsilane reduction of thioesters to ethers has been recently reported.²¹



Ionic Reductions with Silanes – General Considerations

As pointed out above, the silanes provide a mild form of the hydride group and as such can be useful in various hydridic reductions. The general and, admittedly simplified, view of such reductions can be visualized as shown below where a carbenium ion is reduced by a silane. In this scenario the carbenium ion receives the hydride from the silane and the silane takes on the leaving group from the carbon center.



It has been shown that in the gas phase the reaction shown below is exothermic by approximately 8 kcal/mol indicating that the trimethylsilicenium ion is, at least in the gas phase, more stable than the tert-butyl carbenium ion.²² Although the existence of free silicenium ions in solution do not exist under normal, “unbiased” conditions it can be assumed that the silicon center is free to take on considerable positive charge in its reactions. Reductions based on this premise include olefins, ketones, aldehydes, esters, organic halides, acid chlorides, acetals, ketals, alcohols as well as metal salts.



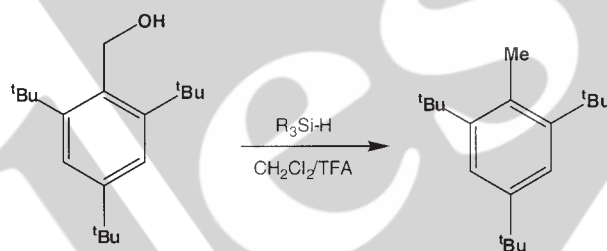
Silane Reduction of Alcohols to Alkanes

The general equation for the silane reduction of alcohols to alkanes is illustrated below. The reaction proceeds best when the alcohol can lead to a stabilized carbenium ion. Thus, secondary and tertiary aliphatic alcohols and benzylic alcohols are readily reduced. Trialkyl substituted silanes are more reactive than dialkylsilanes and di- or triarylsilanes. Typical and highly-effective conditions for these reductions is treatment of the alcohol with the silane and trifluoroacetic acid in dichloromethane. Triethylsilane is often the silane of choice due to its ease of handling and high reactivity.^{22,23}

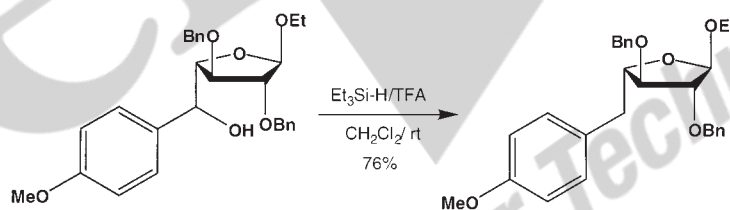


The reduction of secondary alcohols with a silane and a protic acid does not occur. These reductions require the use of a strong Lewis acid such as boron trifluoride or aluminum chloride.^{24,25}

Primary aliphatic alcohols are not reduced with silanes.²⁶ Benzylic alcohols, on the other hand, are reduced under rather mild conditions to the corresponding toluene derivative.²⁷

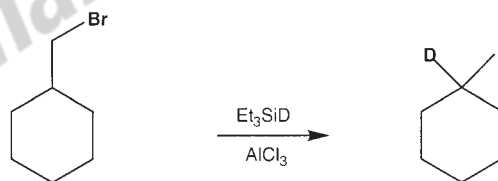


The reduction of a benzylic alcohol in the presence of benzyl ethers, a tetrahydrofuran and an acetal has been reported.²⁸

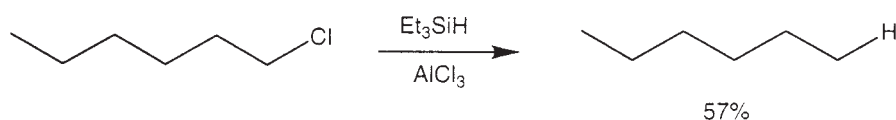


Silane Reduction of Alkyl Halides

As with the reduction of alcohols to alkanes the acid-catalyzed reduction of alkyl halides to alkanes requires the formation of a relatively stable carbenium ion intermediate that can accept the hydride from the silane. Thus, tertiary, secondary, allylic and benzylic halides lend themselves to this type of reduction. Under certain conditions primary halides can be reduced,²⁹ but carbenium ion rearrangements are a problem³⁰.



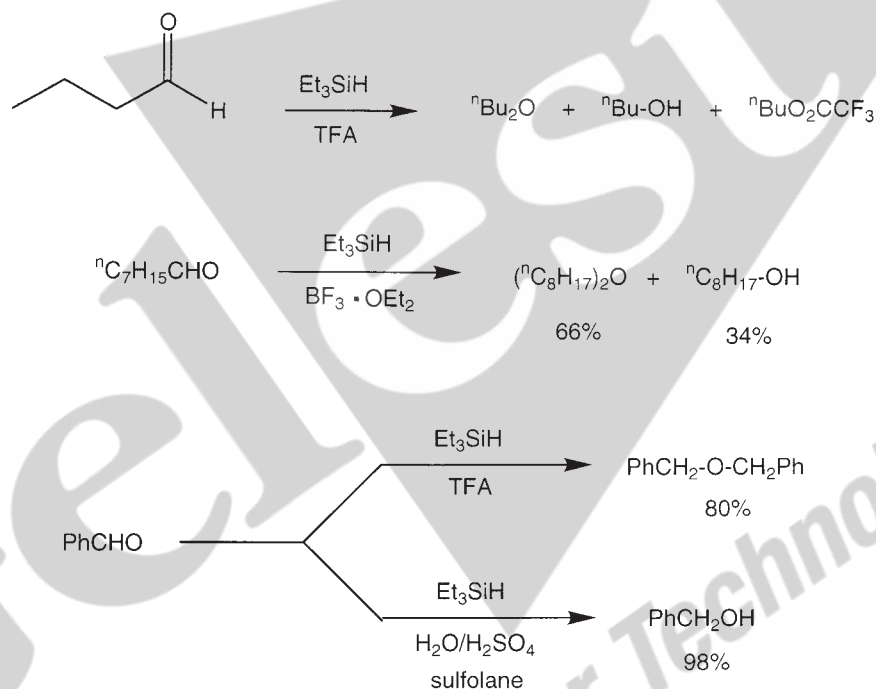
Trialkylsilanes, being better hydride donors, provide less rearranged product in these reductions than their dialkyl or monoalkyl counterparts.³⁰



The reductions of organic halides with pentacoordinate hydridosilanes has been reported.³¹

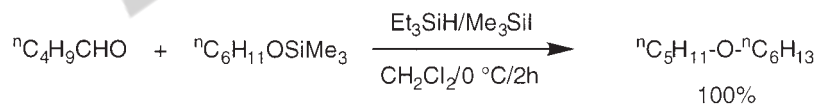
Silane Reduction of Aldehydes

The acid-catalyzed reduction of aldehydes with silanes works best in the presence of water.³² In addition esters can be formed when an organic acid is the catalyst employed.³³



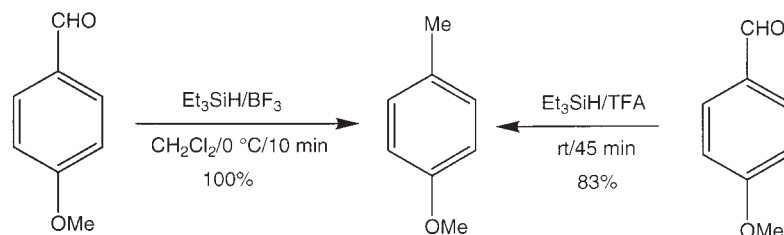
An excellent alternative for the reduction of aldehydes to alcohols is through the use of triethylsilane with uncomplexed boron trifluoride in dichloromethane.³⁴ This method gives the corresponding alcohol in high yield and very short reaction times.

An extremely high-yield reductive conversion of aldehydes to unsymmetrical ethers involves the reaction of the aldehyde with a trimethylsilyl ether in the presence of a silane and a strong Lewis acid, with trimethylsilyl triflate being especially efficient.³⁵ Such silicon-based reductive-condensation chemistry should be applicable to combinatorial chemistry where product isolation is always a crucial issue.

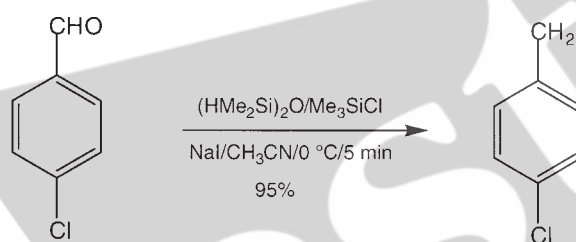


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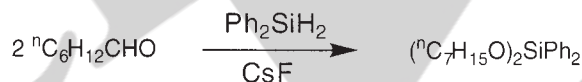
Aromatic aldehydes can be fully reduced to the corresponding toluene derivative.^{34,36}



The conversion of aromatic aldehydes to benzylic halides has also been shown.³⁷⁻³⁹ The best reducing agent for this seems to be tetramethyldisiloxane.

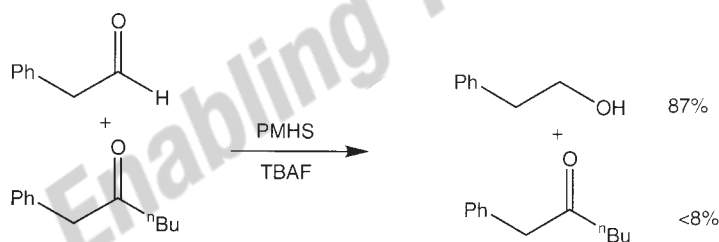


Under catalysis by fluoride ion aldehydes are reduced to the corresponding silyl ether of the alcohol. Hydrolysis of the silyl ethers provides the unprotected alcohols. Cesium fluoride has been shown to be an excellent promoter for these conversions,^{40,41} as have tetra-*n*-butyl ammonium fluoride (TBAF) and tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF)⁴². This can also be used as a route to trimethylsilyl-protected alcohols from aldehydes.



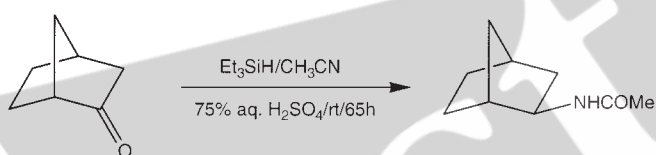
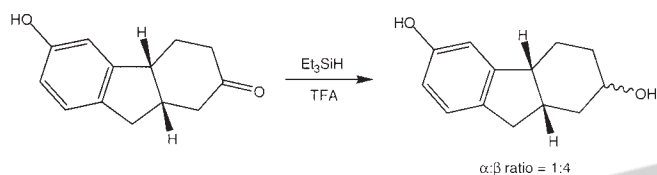
The reduction of aldehydes to alcohols has also been carried out with polymethylhydro-siloxane as the hydride source. In this case the work-up includes reaction with methanol to release the free alcohol.⁴³

The selective reduction of aldehydes over ketones can be realized with polymethylhydro-siloxane as the reducing agent with fluoride ion-catalysis.⁴⁴

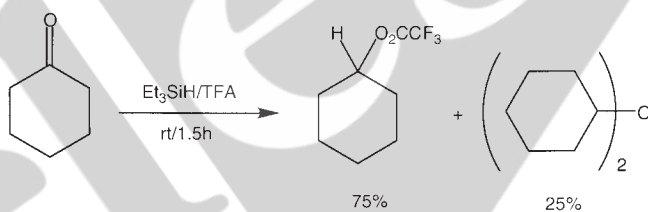


Silane Reduction of Ketones

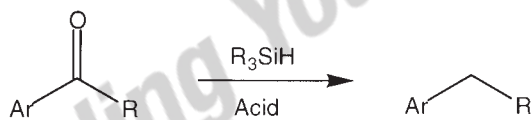
Silanes have been used for the reduction of ketones to alcohols with excellent results.⁴⁵ The reduction of ketones or aldehydes in the presence of acetonitrile and an acid provides an alkyl acetamide.³³ The reduction of aldehydes to alkyl acetamides is also possible.³³



In a similar manner the reduction of ketones and aldehydes to esters has been reported.³³ This reaction is always accompanied with the formation of the symmetrical ether.



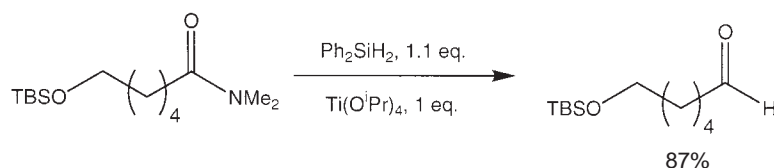
The reduction of aryl ketones (acetophenone derivatives) to the methylene is readily accomplished.⁴⁶ Triethylsilane with titanium tetrachloride works best for this transformation, though other systems also work well.



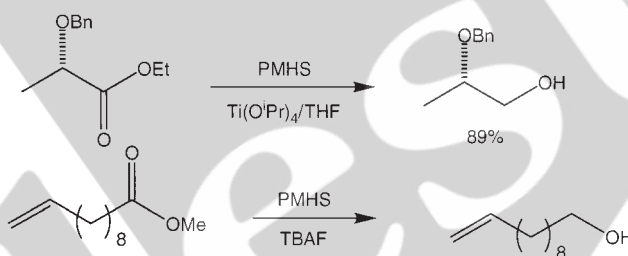
The selective reduction of aryl ketones to alcohols over dialkyl ketones can be carried out with phenyldimethylsilane in the presence of cuprous chloride or cuprous acetate.⁴⁷

Silane Reduction of other Carbonyl Systems

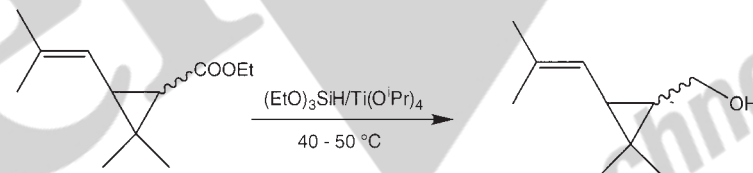
The one-pot reduction of amides to aldehydes with diphenylsilane has been reported.⁴⁸ This provides a potentially highly-useful, non-oxidative entry into aldehydes.



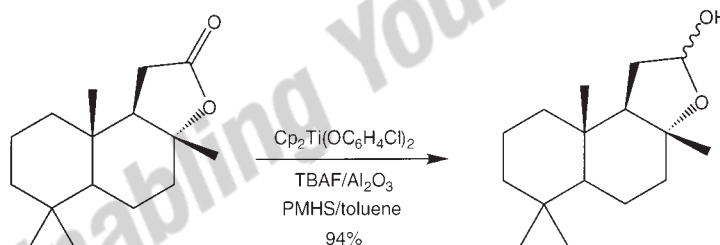
The reduction of acids and esters to alcohols with polymethylhydrogensiloxane occurs in good yields in the presence of titanium tetraisopropoxide⁴⁹ or tetrabutylammonium fluoride⁵⁰. The reduction of esters has also been carried out with diphenylsilane and rhodium catalysis.⁵¹



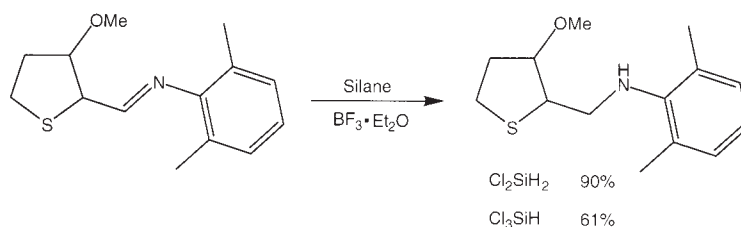
The triethoxysilane reduction of esters to alcohols in high yields is possible.⁵² This transformation also takes place with PMHS as the reductant.^{53,54}



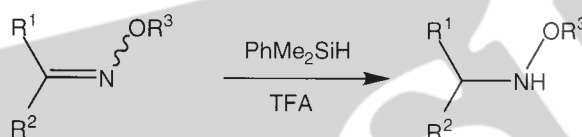
The conversion of lactones to lactols was accomplished with a titanium-catalyzed reduction with PMHS.⁵⁵



The reduction of imines to amines with trichlorosilane and dichlorosilane was reported. Dichlorosilane gave the best results.⁵⁶

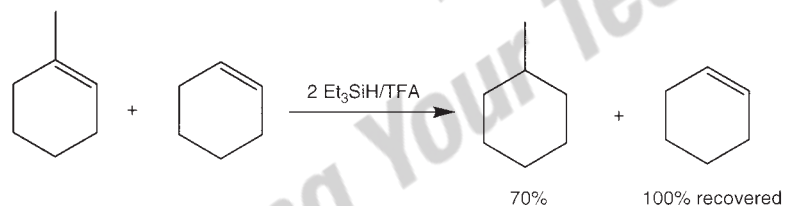


The reduction of oximes to alkoxyamines is accomplished with phenyldimethylsilane and trifluoroacetic acid.⁵⁷

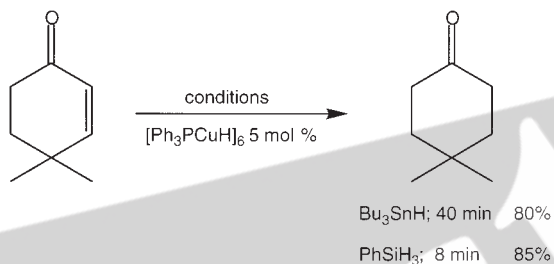
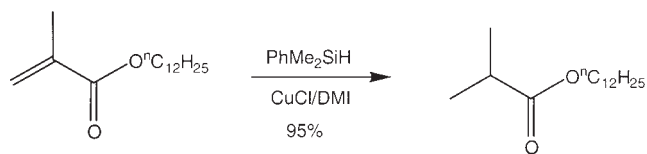


Silane Reduction of Olefins

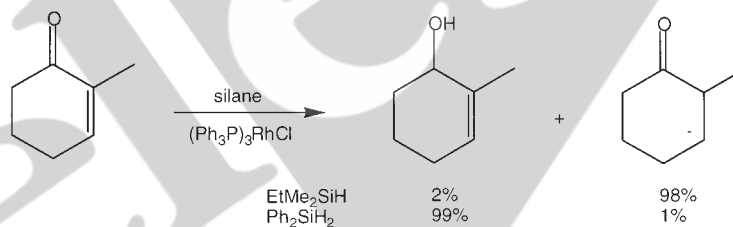
Not surprisingly the ionic reduction of suitable olefins, i.e. those which can generate a relatively stable carbenium ion, can be reduced by silanes in the presence of an acid catalyst. The ability to generate the carbenium ion is essential to the success of the reaction. For example, 1-methylcyclohexene is readily reduced to methylcyclohexane whereas cyclohexene itself is not reduced under the same and even more forcing conditions.⁵⁸ The most common conditions for these reductions is with an excess of trifluoroacetic acid, a strong acid with a conjugate base of low nucleophilicity, and triethylsilane.⁵⁹⁻⁶³ Likewise, terminal olefins that are not styrenic in nature, and 1,2-disubstituted olefins are not reduced with silanes again due to the inability to form a suitable carbenium ion intermediate. On the other hand, the reduction of enol ethers, and similar olefins which can form good carbenium ions, is possible.^{62,64}



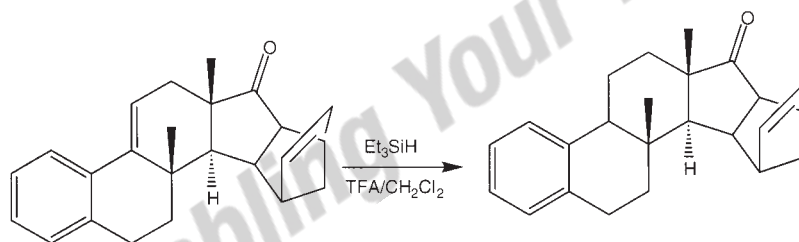
The reduction of α,β -unsaturated carbonyls to their saturated counterparts is conveniently carried out with silanes in the presence of a rhodium or copper catalyst.^{65,66}

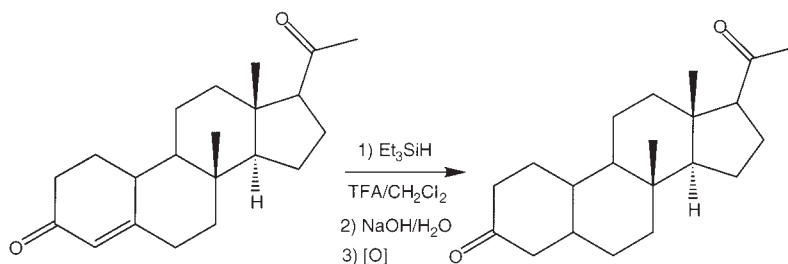


Ojima and Kogure⁶⁷ have shown that the reduction of α,β -unsaturated ketones or aldehydes with triethylsilane or ethyldimethylsilane gives 1,4-addition resulting in reduction of the double bond whereas diphenylsilane gives 1,2-addition and straight reduction of the carbonyl.

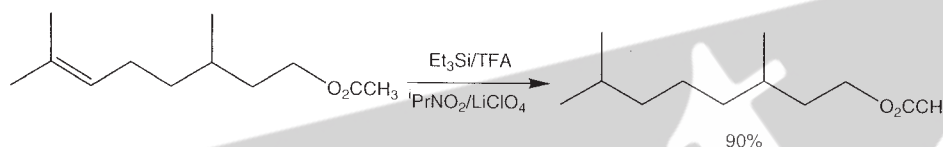


An example of the reduction of a styrenic double bond in the presence of another double bond and a ketone is shown below.⁶⁸ The double bond of an α,β -unsaturated ketone was reduced with the triethylsilane/acid combination, though regeneration of the ketones was necessary.⁶⁹





The reduction of a trisubstituted olefin in the presence of an ester was shown.⁷⁰



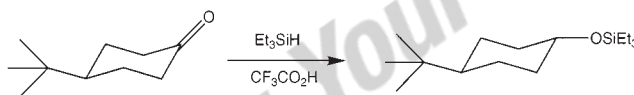
The silane reduction of acetylenes to alkanes is not a practical approach to this transformation.⁷¹

Stereoselective Silane-Based Reductions

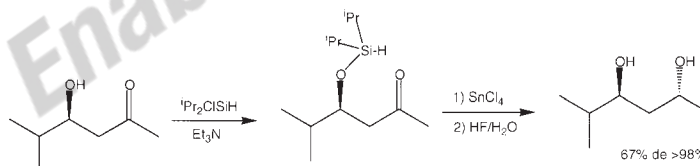
Doyle and West⁷² demonstrated the acid-catalyzed reduction of alkyl-substituted cyclohexanones with di-tert-butylsilane, di-tert-butylmethylsilane and tri-tert-butylsilane to proceed with predominant formation of the less stable isomer as the trifluoroacetate. For example, 4-tert-butylcyclohexanone gives 67% of the cis-4-tert-butylcyclohexyl trifluoroacetate.



The reduction of 4-tert-butylcyclohexanone with triethylsilane or dimethylphenylsilane preferentially gives the trans product. Very high trans to cis stereoselectivity of this transformation with triethoxysilane and TBAF was reported as was the reduction of 3-phenyl-2-butanone to anti 3-phenyl-2-butanol.⁷³

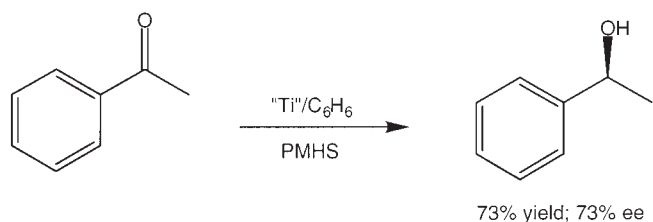


The stereoselective silane reduction of β -hydroxy ketones with diisopropylchlorosilane has been demonstrated.⁷⁴⁻⁷⁶

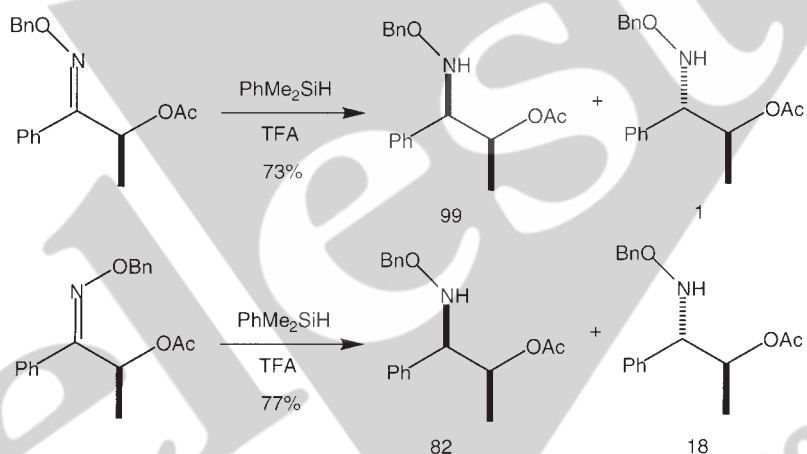


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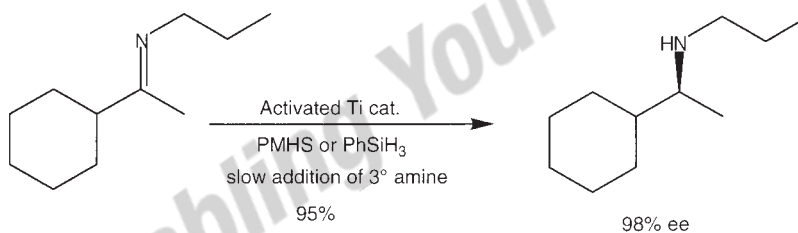
A very efficient asymmetric reduction of arylalkyl ketones has been shown. The reaction, which does not work well for prochiral dialkyl ketones, is carried out with PMHS in the presence of a chiral titanium catalyst.⁷⁷



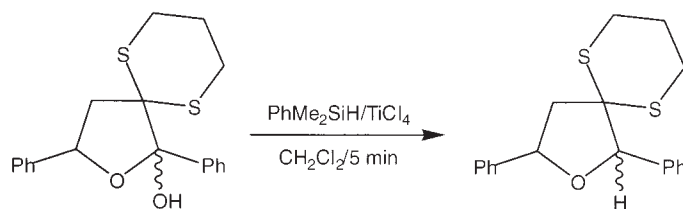
The highly diastereoselective reduction of oximes has been reported.⁵⁷ The diastereoselectivity was much higher than that reported for the corresponding reduction with lithium aluminum hydride in diethyl ether.



Buchwald and coworkers⁷⁸ have reported the reduction of imines in very high enantiomeric excess through the use of a titanium catalyst activated with phenylsilane and the reduction with polymethylhydrosiloxane or phenylsilane.

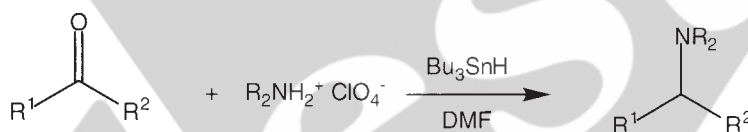


The Lewis acid-catalyzed triphenylsilane reduction of hemiketals was shown to occur with high stereoselectivity.⁷⁹

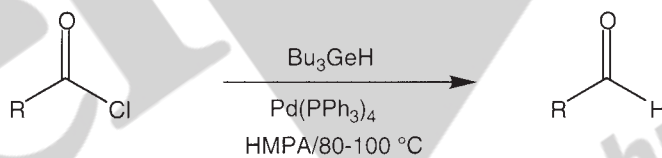


Reductions with other Group 14 Hydrides.

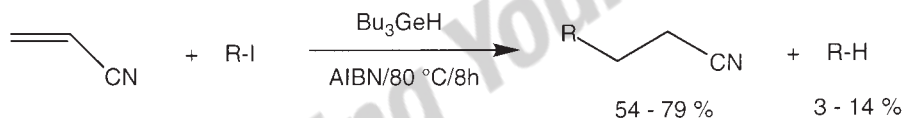
The tri-*n*-butyltin hydride reductions are well-known and have been reviewed.⁸⁰ A recent report shows that tri-*n*-butyltin hydride can provide the hydrogen for the reductive amination of ketones and aldehydes, thus providing an alternative to sodium cyanoborohydride for this transformation.⁸¹ This same transformation was reported using polymethylhydro-siloxane as the reducing agent.⁸²



Triphenylgermane has been shown to reduce acid chlorides to aldehydes with palladium(0) catalysis.⁸³

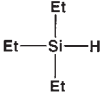
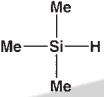
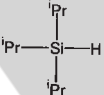
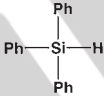
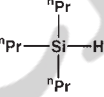
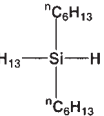
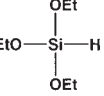
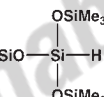


Tri-*n*-butylgermane has been employed in the reductive alkylation of active olefins, in particular acrylonitrile.⁸⁴



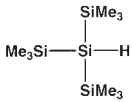
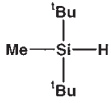
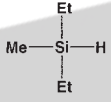
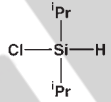
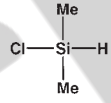
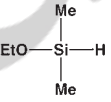
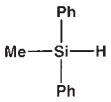
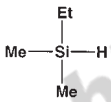
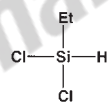
TRISUBSTITUTED SILANE REDUCING AGENTS

TABLE 3

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SIT8330.0 TRIETHYLSILANE [617-86-7] TSCA		Used to reduce metal salts. ⁸⁵ Enhances deprotection of t-butoxycarbonyl-protected amines and tert-butyl esters. ⁸⁶ Used in the reductive amidation of oxazolidinones with amino acids to provide dipeptides. ⁸⁷ Converts aldehydes to symmetrical and unsymmetrical ethers. ⁸⁸ Used in the 'in-situ' preparation of diborane and haloboranes. ⁸⁹	25g/\$28.00 250g/\$196.00 2.5kg/\$750.00
SIT8570.0 TRIMETHYLSILANE [993-07-7] TSCA		Potential reducing agent that will produce low boiling hexamethyldisiloxane by-product.	100g/\$195.00 1kg/\$1540.00 in cylinder
SIT8385.0 TRIIISOPROPYLSILANE [6485-79-6]		Very sterically-hindered silane. Used as a cation scavenger in the deprotection of peptides. ⁹⁰	25g/\$26.00 100g/\$84.00 1.5kg/\$1005.00
SIT8665.0 TRIPHENYLSILANE [789-25-3] TSCA		More effective radical-based reagent for reduction of organic halides than the trialkylsilanes. ⁸⁸ Compares well with tri-n-butyltin hydride in reduction of enones to ketones. ⁸³ Shows good selectivity in the reduction of cyclic hemiacetals. ⁷⁷ Converts O-acetyl furanoses and pyranoses to deoxy sugars. ⁹¹	25g/\$26.00 100g/\$84.00 2kg/\$1000.00
SIT8709.0 TRI-n-PROPYLSILANE [998-29-8] TSCA		Reactivity similar to that of triethylsilane.	10g/\$19.00 50g/\$76.00
SIT8376.0 TRI-n-HEXYLSILANE [2929-52-4] TSCA		Reactivity similar to that of triethylsilane, but has higher boiling point and produces a higher boiling by-product.	25g/\$32.00 100g/\$104.00
SIT8185.0 TRIETHOXY-SILANE [998-30-1] TSCA		Reduces esters in the presence of zinc hydride catalyst. ⁵² Reduces aldehydes and ketones to alcohols via the silyl ethers in presence of fluoride ion. ⁹² Gives 1,2 reduction of enones to allyl alcohols. ⁹³	25g/\$28.00 100g/\$91.00 2.5kg/\$685.00
SIT8721.0 TRIS(TRIMETHYLSILOXY) SILANE [1873-89-8]		Gives highly stereoselective reduction of substituted cyclohexanones. ⁵¹	25g/\$19.00 100g/\$62.00 2kg/\$700.00

TRISUBSTITUTED SILANE REDUCING AGENTS

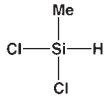
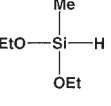
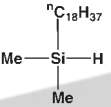
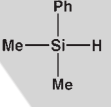
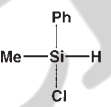
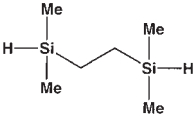
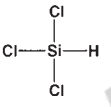
TABLE 3 (cont.)

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SIT8724.0 TRIS(TRIMETHYLSILYL)SILANE [1873-77-4]		Undergoes exothermic decomposition at >100 °C. Radical-based reducing agent for organic halides selenides, xanthates and isocyanides and ketones in high yields. ²⁰ Can provide complementary stereoselectivity to tri-n-butyltin hydride in the reduction of gem dihalides. ⁹⁴ Mild reducing agent in nucleoside chemistry. ⁹⁵	2.5g/\$32.00 50g/\$320.00
SID3258.0 DI-tert-BUTYLMETHYLSILANE [56310-20-4]		Used in reductive trifluoroacetylation of ketones. Reacts faster than di-tert-butylsilane. ⁷²	10g/\$37.00 50g/\$148.00
SID3410.0 DIETHYLMETHYLSILANE [760-32-7] TSCA		Similar to triethylsilane with lower boiling point.	25g/\$32.00 100g/\$104.0 1.5kg/\$900.00
SID3535.0 DIISOPROPYLCHLOROSILANE [2227-29-4] TSCA		Used in a silylation-reduction-allylation sequence of β-hydroxy esters to homoallylic-substituted 1,3-diols. ⁹⁶ Used in the silylation-hydrosilylation-oxidation of allyl alcohols to 1,3-diols. ⁹⁷ Reaction carried out in diastereoselective manner. Reduces β-hydroxy ketones to anti-1,3 diols. ⁹⁸	5g/\$24.00 25g/\$96.00 2kg/\$2800.00
SID4070.0 DIMETHYLCHLOROSILANE [1066-35-9] TSCA		Will form high-boiling polymeric by-products with aqueous work-up.	25g/\$10.00 500g/\$76.00 2kg/\$187.00
SID4125.0 DIMETHYLETHOXY-SILANE [14857-34-2] TSCA		Will form high-boiling polymeric by-products with aqueous work-up.	25g/\$28.00 100g/\$91.00 2.5kg/\$980.00
SID4555.0 DIPHENYLMETHYLSILANE [776-76-1] TSCA		Used to reduce α-alkoxy ketones to diols and α-amino ketones to aminoethanols with high stereoselectivity. ⁹⁹	25g/\$22.00 100g/\$72.00 500g/\$225.00
SIE4894.0 ETHYLDIMETHYLSILANE [758-21-4] TSCA		Similar to triethylsilane with lower boiling point.	10g/\$46.00 50g/\$184.00
SIE4890.0 ETHYLDICHLOROSILANE [1789-58-8] TSCA		Will form high-boiling polymeric by-products with aqueous work-up.	25g/\$60.00 100g/\$195.00 2kg/\$1920.00

PLEASE INQUIRE ABOUT BULK QUANTITIES

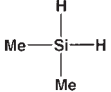
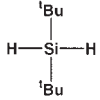
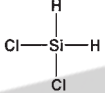
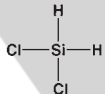
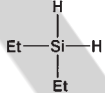
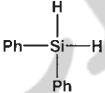
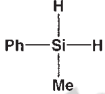
TRISUBSTITUTED SILANE REDUCING AGENTS

TABLE 3 (cont.)

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SIM6504.0 METHYLDICHLOROSILANE [75-54-7] TSCA		Provides better diastereoselective reductive aldol reaction between an aldehyde and an acrylate ester than other silanes. ¹⁰⁰ Forms high-boiling polymeric by-products upon aqueous work-up.	25g/\$12.00 1kg/\$50.00
SIM6506.0 METHYLDIETHOXSILANE [2031-62-1] TSCA		Will form high-boiling polymeric by-products with aqueous work-up.	25g/\$30.00 100g/\$130.00
SIO6619.0 OCTADECYLDIMETHYLSILANE [32395-58-7]		Similar to triethylsilane with much higher boiling point.	5g/\$39.00 25g/\$156.00
SIP6729.0 PHENYLDIMETHYLSILANE [766-77-8] TSCA		Used to reduce α -amino ketones to aminoethanols with high stereoselectivity. ⁹⁹ Used in the fluoride ion-catalyzed reduction of aldehydes and ketones, and α -substituted alkanones to threo products. ⁴² Erythro reduction of α -substituted alkanones to diols and aminoethanols. ¹⁰¹ Together with CuCl reduces aryl ketones, but not dialkyl ketones. ¹⁰² Used in the silylformylation of acetylenes. ¹⁰³ Excellent reducing agent for the reduction of enones to saturated ketones. ¹⁰⁴ Shows better selectivity than LAH in the reduction of oximes to alkoxyamines. ⁵⁷	25g/\$27.00 100g/\$88.00 2kg/\$1080.00
SIP6737.0 PHENYLMETHYLCHLORO-SILANE [1631-82-9] TSCA		Will form high-boiling polymeric by-products with aqueous work-up.	10g/\$44.00 50g/\$176.00 250g/\$450.00
SIT7544.0 1,1,4,4-TETRAMETHYL-DISILETHYLENE [20152-11-8]		Contains two available hydrides for reduction. Has potential for stereoselective reduction of dicarbonyls.	5g/\$42.00 25g/\$168.00
SIT8155.0 TRICHLOROSILANE [10025-78-2] TSCA		Will form high-boiling polymeric by-products with aqueous work-up. Reduces aromatic carbonyl systems to give benzyltrichlorosilanes, which can be desilylated to toluenes. ¹⁰⁵⁻¹⁰⁷ Reduces phosphine oxides to phosphines. ¹⁰⁸	25g/\$12.00 500g/\$42.00 Cylinder packaging recommended

DIALKYLSILYL REDUCING AGENTS

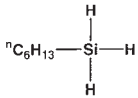
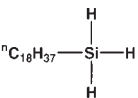
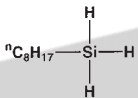
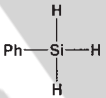
TABLE 4

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SIT4230.0 DIMETHYLSILANE [1111-74-6] TSCA		Very low boiling point silane that is a gas at atmospheric conditions.	50g/\$160.00 + cylinder
SID3342.0 DI-tert-BUTYLSILANE [30736-07-3]		Sterically-hindered silane reducing agent.	5g/\$60.00
SID3368.0 DICHLOROSILANE [4109-96-0] TSCA		Gives improved yields in reduction of imines over that of trichlorosilane. ⁵⁶	250g/\$150.00 1.5kg/\$720.00 + cylinder
SIB3368.2 DICHLOROSILANE 25% in xylene [4109-96-0] TSCA		Easier to handle form of dichlorosilane.	400g/\$94.00 2kg/\$368.00
SID3415.0 DIETHYLSILANE [542-91-6] TSCA		Used in the 'in-situ' preparation of diborane and haloboranes. ⁸⁹	10g/\$40.00 50g/\$160.00 2kg/\$3680.00
SID4559.0 DIPHENYLSILANE [775-12-2] TSCA		Used in the preparation of silyl-substituted alkylidene complexes of tantalum. ¹⁰⁹ Used in the ionic reduction of enones to saturated ketones. ¹¹⁰ Used in the reductive cyclization of unsaturated ketones. ^{111,112} Reduces esters in the presence of zinc hydride catalyst. ⁵³ Reduces α-halo ketones in presence of Mo(0). ¹¹³ Reduces thio esters to ethers. ²² Reduces esters to alcohols with Rh catalysis. ⁴⁹ Employed in the asymmetric reduction of methyl ketones ¹¹⁴ and other ketones ^{115,116} . Reductively cleaves allyl acetates. ¹¹⁷	25g/\$39.00 100g/\$127.00 2kg/\$1400.00
SIP6742.0 PHENYLMETHYLSILANE [766-08-5] TSCA		Used in the preparation of silyl-substituted alkylidene complexes of tantalum. ¹⁰⁹	10g/\$32.00 50g/\$128.00 2kg/\$1810.00

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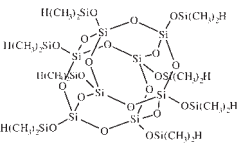
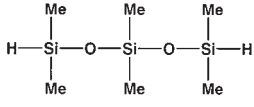
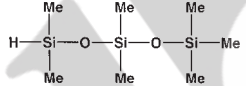
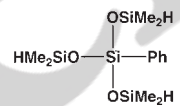
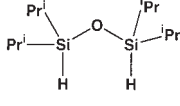
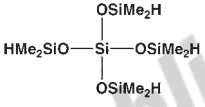
MONO-SUBSTITUTED SILANE REDUCING AGENTS

TABLE 5

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SIH6166.2 n-HEXYLSILANE [1072-14-6] TSCA			10g/\$34.00 50g/\$136.00
SIO6635.0 n-OCTADECYLSILANE [18623-11-5] TSCA			25g/\$40.00 100g/\$130.00
SIO6712.5 n-OCTYLSILANE [871-92-1] TSCA			10g/\$42.00 50g/\$168.00 1.5kg/\$1245.00
SIP6750.0 PHENYLSILANE [694-53-1] TSCA		Employed in the reduction of esters to ethers. ¹¹⁸ Reduces α,β -unsaturated ketones to saturated ketones in the presence of tri-n-butyltin hydride. ¹¹⁹ Reduces tin amides to tin hydrides. ¹²⁰ Used in the tin-catalyzed reduction of nitroalkanes to alkanes. ¹²¹ Reduces α -halo ketones in presence of Mo(0). ¹¹³	5g/\$21.00 25g/\$84.00 2kg/\$2400.00

SILOXANE-BASED SILANE REDUCING AGENTS

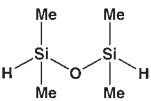
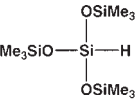
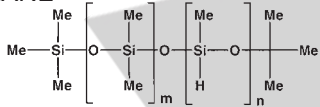
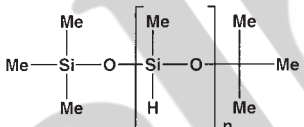
TABLE 6

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SIO6696.5 OCTAKIS (DIMETHYLSILOXY)- T8-SILSESIQUOXANE [125756-69-6]		Solid siloxane reducing agent. Offers 8 Si-H bonds. Potential for easy removal of silicon by-products.	2.5g/\$34.00 10g/\$114.00
SIH6117.0 1,1,3,3,5,5-HEXAMETHYL- TRISILOXANE [1189-93-1] TSCA		High molecular weight silane reducing agent.	50g/\$88.00 2kg/\$1950.00
SIP6718.0 PENTAMETHYLCYCLO- PENTASILOXANE, 90% [6166-86-5] TSCA	[MeHSiO] ₅		25g/\$39.00 100g/\$126.00 2kg/\$850.00
SIH5844.0 HEPTAMETHYLTRISILOXANE [2895-07-0]			25g/\$26.00 100g/\$85.00 1.5kg/\$525.00
SIP6736.5 PHENYLHYDROCYCLO- SILOXANES, contains linears.	[PhHSiO] ₄₋₆	High-boiling siloxane reducing agent.	5g/\$48.00 25g/\$192.00
SIP6826.0 PHENYLTRIS (DIMETHYLSILOXY)SILANE, 95% [18027-45-7] TSCA		High molecular weight silane reducing agent.	25g/\$42.00 100g/\$138.00 2kg/\$752.00
SIT7274.0 1,1,3,3-TETRAISOPRO- PYLDISILOXANE [18043-71-5]		Sterically-hindered silane reducing agent with potential for diastereoselective reductions.	5g/\$38.00 25g/\$152.00
SIT7278.0 TETRAKIS(DIMETHYLSILOXY) SILANE [17082-47-2] TSCA		High molecular weight silane reducing agent.	25g/\$26.00 100g/\$84.00
SIT7530.0 1,3,5,7-TETRAMETHYL- CYCLO-TETRASILOXANE [2370-88-9] TSCA	[MeHSiO] ₄	High molecular weight silane reducing agent.	25g/\$29.00 100g/\$94.00 3kg/\$1740.00

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SILOXANE-BASED SILANE REDUCING AGENTS

TABLE 6 (cont.)

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SIT7546.0 1,1,3,3-TETRAMETHYL-DISILOXANE [30110-74-8] TSCA		Reduces aromatic aldehydes to benzyl halides. ³⁸ Used in the reductive halogenation of aldehydes and epoxides. ¹²²	25g/\$15.00 250g/\$105.00 1.5kg/\$279.00
SIT8721.0 TRIS(TRIMETHYLSILOXY) SILANE [1873-89-8]		High molecular weight silane reducing agent.	25g/\$19.00 100g/\$62.00 2kg/\$700.00
METHYLHYDROSILOXANE-DIMETHYLSILOXANE COPOLYMERS HMS-013 through HMS-501 having various MW's, viscosities, and hydride content. [68037-59-2] TSCA		Potential reducing agents in the mode of HMS-991 or HMS-992.	100g/\$39.00-68.00
HMS-991 or HMS-992 POLYMETHYL-HYDROSILOXANE [63148-57-2] TSCA		Reduces lactones to lactols. ⁵⁵ Reduces aldehydes, ketones, esters, lactones, triglycerides and epoxides to alcohols with zinc hydride catalysis. ⁵² With titanium tetraisopropoxide catalysis carries out reductive amination of ketones and aldehydes ⁸² and the reduction of acids or esters to 1° alcohols ⁵⁰ . With TBAF catalysis selectively reduces aldehydes over ketones. ⁴³ Used to generate tri-n-butyltin hydride 'in-situ' and in a one-pot hydrostannylation/Stille coupling sequence. ¹²³ Reduces esters to alcohols. ⁵⁴	For HMS-991 100g/\$14.00 3kg/\$96.00 For HMS-992 100g/\$24.00 3kg/\$168.00

GERMANIUM AND TIN-BASED REDUCING AGENTS

TABLE 7

REDUCING AGENT	STRUCTURE	COMMENTS	PRICING
SNT8130 TRI-n-BUTYL TIN HYDRIDE [688-73-3] TSCA	$\begin{array}{c} \text{}^n\text{Bu} \\ \\ \text{}^n\text{Bu}-\text{Sn}-\text{H} \\ \\ \text{}^n\text{Bu} \end{array}$	Has been reviewed. ⁸⁰ Catalyzes the Si-H reduction of α,β -unsaturated ketones. ¹¹⁹ Useful in the reductive amination of ketones and aldehydes to form 3° amines. ⁸¹	10g/\$15.00 50g/\$60.00 1kg/\$960.00 3kg/\$1575.00
GET8100 TRI-n-BUTYLGERMANE [998-39-0]	$\begin{array}{c} \text{}^n\text{Bu} \\ \\ \text{}^n\text{Bu}-\text{Ge}-\text{H} \\ \\ \text{}^n\text{Bu} \end{array}$	Reduces acid chlorides to aldehydes in presence of Pd(0). ⁸³ Effects free-radical reductive addition of alkyl halides to olefins. ¹²⁴ Reduces benzylic chlorides 70x faster than silyl hydrides. ¹²⁵	2.5g/\$39.00 10g/\$126.00
GET8660 TRIPHENYLGERMANE [2816-43-5]	$\begin{array}{c} \text{Ph} \\ \\ \text{Ph}-\text{Ge}-\text{H} \\ \\ \text{Ph} \end{array}$	Readily adds to terminal acetylenes and olefins. ¹²⁶ Used in the reductive alkylation of acrylonitrile and enones. ⁸⁴	2.5g/\$59.00 10g/\$192.00
GET8560 TRIMETHYLGERMANE [1449-63-4]	$\begin{array}{c} \text{Me} \\ \\ \text{Me}-\text{Ge}-\text{H} \\ \\ \text{Me} \end{array}$	Effects halogen displacement of alkyl halides with hydrogen when exposed to UV. ¹²⁷	0.5g/\$39.00 2.5g/\$160.00 25g/\$960.00

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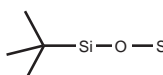


Figure 2

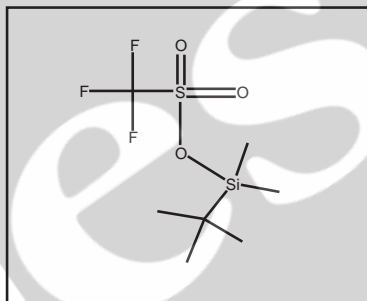


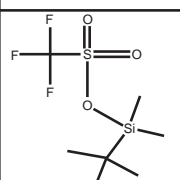
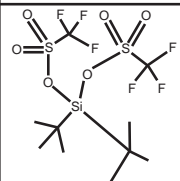
Figure 3

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10 g

Product Name	t-BUTYLDIMETHYLSILYLTRIFLUOROMETHANESULFONATE	Formula	C7H15F3O3SSi
Product Code	SIB1967.0	TSCA	No
CAS No.	69739-34-0	MP °C	
HMIS	3-3-1-X HMIS Key	Refractive Index	1.3848 /
M. W.	264.33	Flash Point	36° C (98° F)
BP °C/mm Hg	65 / 10		
Specific Gravity	1.151 /		
Purity			
Reactivity/Apps			
Addition Properties			
Fieser			
Reference	review: G. Simchen. Adv. Silicon Chem., 1, 189, 1991 JAI Press		
Application	powerful silylation reagent and Lewis acid		

Figure 4

No.	Structure	Name	Catnum	CAS	Formula
1		t-BUTYLDIMETHYLSILYLTRIFLUOROMETHANESULFONATE	SIB1967.0	69739-34-0	C7H15F3O3SSi
2		DI-t-BUTYLSILYLBIS(TRIFLUOROMETHANESULFONATE)	SID3345.0	85272-31-7	C10H18F6O6S2Si