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Chemistry of Alkynylsilanes

Gerald L Larson Gelest, Inc.

1 Introduction

Alkynylsilanes as discussed here are those wherein the silyl moiety is directly bonded to the sp-carbon of the triple bond. They are also oftentimes referred to as silylacetylenes. Alkynylsilanes such as propargylsilanes are, therefore, not included.

 $R_3Si - R^1$

where R¹ = alkyl, aryl, heteroaryl, vinyl, halogen, functional alkyl

Scheme 1 General structure of alkynylsilanes

Acetylene chemistry has been extensively reviewed over the years. Several of the more recent additions are noted here.¹

The vast majority of applications of 1-silylacetylenes occur where the silyl group, typically trimethylsilyl, serves as a group for the protection of the reactive terminal C-H bond. Supporting this silyl protection strategy is the fact that it is quite easy to remove the silyl group in high yield under a variety of mild conditions that are tolerant of other functional groups. A further advantage of the terminal silylacetylenes is that the presence of the silyl group, for both steric and electronic reasons, can often influence the regio- and stereochemistry of reactions at the triple bond. Finally, the trimethyl-silyl group has its own reactivity in the final product of a reaction at the triple bond. These often result in the generation of a vinylsilane unit, which can be further reacted under a number of conditions including protiodesilylation to generate the parent olefin.²

2 Safety

A report of an explosion using ethynyltrimethylsilane in an oxidative coupling under Glaser-Hay conditions was reported.³ The cause of the explosion was attributed to static electricity between the syringe needle used to introduce the copper catalyst and a digital thermometer inside the flask and not the thermal instability of the silane. It is interesting to note that the trimethylsilyl group can impart stability to alkynyl systems. A good example of this is bis(trimethylsilyl)-1,3-butadiyne, which shows excellent thermal stability compared to the parent 1,3-butadiyne. A flash explosion of trimethylsilyl-propyne during a bulk transfer from a metal drum has also been reported and was shown to be associated with static discharge.

3 Protiodesilylation

Because trialkylsilyl groups are very commonly used to protect the terminal C-H of an alkyne, protiodesilylation back to the parent alkyne is an important transformation. This can be accomplished with a number of mild reaction conditions. Among these is the simple reaction of the

Abbreviat	ions:		
BIPHEP DABCO DDQ	1,1'-bis(diphenylphosphino)biphenyl 1,4-diazabicyclo[2.2.2]octane 2,3-Dichloro-5,6-dicyano-1, 4-benzoquinone	<i>i-</i> PrI MPM NIS SIPr	Isopropylimidazole 4-Methoxybenzyl <i>N</i> -Iodosuccinimide 1,3-Bis(2,6-diisopropylphenyl)-
DIH	1,3-Diiodohydantoin		imidazolidinium chloride
DIPA	Diisopropylamine	TBAF	Tetra- <i>n</i> -butylammonium fluoride
DMI	1,3-Dimethyl-2-imidazolidinone	TBS	Tert-butyldimethylsilyl
DMEDA	Dimethylethylenediamine	TES	Triethylsilyl
DMSO	Dimethylsulfoxide	TMS	Trimethylsilyl
Dppe	1,2-Bis(diphenylphosphino)ethane	TMSI	Trimethyliodosilane

alkynyltrimethylsilane with $K_2CO_3/MeOH$ or, for more hindered silanes, TBAF/THF. Examples of these are to be found throughout this short review. The selective protiodesilylation of an alkynylTMS group in the presence of an alkynylTIPS group with $K_2CO_3/THF/MeOH$ illustrates the potential for selective protection/deprotection.⁴

Bis(trimethylsilyl)-1,3-butadiyne was selectively relieved of one of the trimethylsilyl groups by reaction with MeLi/LiBr in diethyl ether.





Bis(trimethylsilyl)-1,3-butadiyne was metalated with one equivalent of MeLi and reacted with acrolein and subsequently protiodesilylated to yield vinyl diynyl carbinol **1**. The trans metalation with five equivalents of MeLi and reaction with acrolein gave the diol **2** in excellent yield. These key intermediates were carried forth in syntheses of (+)- and (-)-falcarinol and (+)- and (-)-3-acetoxy falcarinol.⁵



Scheme 3 Desilylative lithiation and reactions of bis(trimethylsilyl)-1,3-butadiyne

5 Sonogashira Reactions: Formation of Conjugated Enynes and Arylalkynes

The Sonogashira reaction has proven to be a very important synthetic entry into aryl alkynes and conjugated enynes.⁶ These approaches typically make use of the Pd-catalyzed or Pd/Cu-catalyzed protocols employed in most cross-coupling reactions. The Au-catalyzed use of alkynylsilanes in Sonogashira cross-coupling has been reviewed.⁷

Of the many reactions at the terminal C-H of the simple alkynylsilanes, the Sonogashira reaction stands among the most important. Under the standard Sonogashira reaction conditions the C-Si bond

does not react, providing excellent protection of this position along with adding more desirable physical properties. Moreover, it provides an excellent entry into a variety of substituted alkynylsilanes. Though the silyl group nicely provides protection of a terminal position in the Sonogashira crosscoupling, under modified conditions wherein the silyl group is activated, a Sonogashira-type conversion at the C-Si bond is possible, thus providing an alternative to a two-step protiodesilylation/Sonogashira sequence.

In an example of the use of the TMS group as a protecting group eventually leading to an unsymmetrically arylated system, trimethylsilylbutadiyne was coupled with aryl iodide **3** to diyne **4**, which was protiodesilylated and further cross-coupled to **5**, a potential hepatitis C NS5A inhibitor.^{8,9}



Scheme 4 Sonogashira cross-coupling sequence employing desilylation

Modest yields of symmetrical1,4-diaryl-1,3-butadiynes resulted from the Sonogashira reaction of an aryl bromide and ethynyltrimethylsilane followed by treatment with NaOH in MeCN. The reaction sequence combined a Sonogashira cross-coupling and a Glaser coupling in a two-step single-flask operation. The second step did not require the further addition of catalyst. The reaction was tolerant of HO, CO₂H, and CHO functionalities.¹⁰



The Beller group developed a copper-free protocol for the Sonogashira reaction with the more available and less costly aryl chlorides. Both ethynyltrimethyl- and ethynyltriethylsilane reacted without loss of the silyl group. The key to the success of the reaction proved to be the sterically hindered ligand 6.¹¹

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The ethynylsilane (CPDMSA) **7** with the 3-cyanopropyl moiety was prepared and utilized in the synthesis of arene-spaced diacetylenes. The purpose of this particular ethynylsilane was two-fold, firstly it could be selectively deprotected in the presence of the ethynyl-TIPS group and, secondly, it provided polarity allowing for a facile chromatographic separation of the key intermediates in the syntheses of the diethynyl arenes. The arene groups were introduced via Sonogashira cross-coupling.¹²



Scheme 7 Sonogashira cross-coupling and selective protiodesilylation

In a good example of the use of ethynyltrimethylsilane as a precursor to the 1,2,4,5-tetraethynylbenzene, 1,2,4,5-tetraiodobenzene was reacted with ethynyltrimethylsilane under Sonogashira conditions to give 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene. The trimethylsilyl groups were then converted to bromides with NBS in greater than 90% over the two steps. The tetrakis(bromoethynyl)benzene was reacted with 1,4-cyclohexadiene to give 2,3,6,7-tetrabromoanthracene.¹³



In related chemistry the direct ethynylation of tautomerizable heterocyclics under Sonogashira conditions without the need for conversion of the heterocyclic to an aryl halide was reported. These worked well for ethynyltrimethylsilane and ethynyltriethylsilane.¹⁴



Scheme 9 Direct Sonogashira ethynylation of tautomerizable heterocycles

In an interesting and useful approach, ethynyltrimethylsilane cross-coupled with aryl iodides, bromides and triflates in the presence of an amidine base and water. If water was held out until the second stage of the reaction, i.e. reaction at the C-Si terminus, the result was the synthesis of unsymmetrical diarylacetylenes.¹⁵



Scheme 10 Symmetrical and unsymmetrical diarylation of ethynyltrimethylsilane

The Sonogashira reaction of ethynyltrimethylsilane with 2,6-dibromo-3,7-ditriflatoanthracene was investigated as an intermediate in a route to anthra[2,3-b:6,7-b']-difuran (*anti*-ADT). In this reaction the Sonogashira cross-coupling occurred selectively at the triflate leaving the bromine groups available. This route did not result in a synthetic approach to the desired anthracene difuran. Success was realized via the Sonogashira cross-coupling of ethynyltrimethylsilane with 2,6-dibromo-3,7-diacetatoanthracene followed by desilylative cyclization. The thiofuran analog, *anti*-ADT, was prepared via cross-coupling of **8** with ethynyltrimethylsilane, I_2 cyclization and reduction. A Suzuki-Miyaura cross-coupling and protiodesilylation gave the phenyl-substituted *anti*-ADT **2**. In an analogous manner the *anti*-diselenophene **10** was prepared from **9** in 62% yield over three steps.¹⁶





Scheme 11 Sonogashira cross-coupling in the synthesis of thiophenes and selenophenes

The relatively simple and economical catalyst system of FeCl₃ and N,N'-dimethylethylenediamine was used in the synthesis of arylethyltriethylsilanes. The reaction conditions were not mild requiring 135 °C and 72 h for completion.¹⁷



Scheme 12 Sonogashira cross-coupling with iodopyridine

The Sonogashira reaction of several terminal alkynes with *o*-nitrofluorobenzene gave the *o*-alkynylnitrobenzene. The use of ethynyltriethylsilane gave a considerably higher yield than other terminal alkynes. The TES group was not further reacted in this study.¹⁸



Scheme 13 Sonogashira cross-coupling with *o*-nitrofluorobenzene

7 Cross-Coupling with the C-Si Bond

Hatanaka and Hiyama were the first to report the cross-coupling of alkynyltrimethylsilanes. This they accomplished with cross-coupling with β -bromostyrene to form conjugated enynes with TASF promotion. It bears mentioning that under the same conditions vinyltrimethylsilanes were cross-coupled in high yield with aryl and vinyl iodides.¹⁹

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3-Aryl-*tert*-propargyl alcohols reacted with bis(trimethylsilyl)acetylene under Rh catalysis to give the enyne regio- and stereoselectively with loss of benzophenone and one equivalent of the starting arylethynyl group as its TMS-substituted derivative. Under Pd catalysis this silylated enyne could be cross-coupled with an aryl iodide, which was converted to the alkylidene dihydrofuran, which showed fluorescent properties.²⁰



Scheme 15 Silyl Sonogashira cross-coupling of propargyl alcohols

Seeking a practical entry into 1,4-skipped diynes as potential precursor to polyunsaturated fatty acids, the Syngenta group investigated the cross-coupling of alkyltrimethylsilanes with propargyl chlorides. Under the best conditions the reaction of an alkynyltrimethylsilane with a propargyl chloride gave the 1,4-skipped diyne under promotion with fluoride ion and CuI catalysis. The method avoids the need for protiodesilylation to the parent acetylene that is required in other copper catalyzed coupling protocols. The reaction failed with nitrogen containing groups on the alkynylsilane. The reaction proceeded well with phenylethynyltri-*n*-butyltin (70%) and phenethylethynyltrimethylgermanium (90%).²¹





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Denmark and Tymonko demonstrated the cross-coupling of alkynyldimethylsilanols with aryl iodides with potassium trimethylsilanolate promotion. This protocol avoids the typical necessity of fluoride ion promotion and the associated disadvantages of cost and low tolerance for silicon-based protecting groups. The alkynylsilanols were prepared in a two-step reaction sequence. Interestingly, a direct comparison of the reaction rates of 1-heptyne, heptynyldimethylsilanol, and heptynyltrimethylsilane under the potassium trimethylsilanolate promotion conditions showed the heptynyldimethylsilanol to be considerably faster than 1-heptyne and the heptynyltrimethylsilane to be unreactive. This strongly suggests a role of the silanol group in the cross-coupling. A similar experiment with TBAF promotion showed all three to react with the silanol derivative being the fastest. Under the same conditions 4-bromotoluene gave a 25% conversion showing the need for the iodoarene.²² The TBAF-promoted cross-coupling of alkynylsilanols with aryl iodides had previously been shown.²³





The bis(trimethylsilyl)enyne **11** was nicely prepared via a Suzuki cross-coupling with bromoethynyltrimethylsilane. The ethynylsilane **11** cross-coupled with aryl iodides in a sila-Sonogashira reaction to provide the silylated conjugated enyne **12**. Similar cross-coupling reactions with vinyl iodides led to 1,5-dien-3-ynes **13**. Cyclic vinyl triflates also reacted well to form the 1,5-dien-3-ynes **14**.²⁴





Scheme 18 Suzuki cross-coupling with bromoethynyltrimethylsilane and cross-coupling of the alkynyltrimethylsilane

8 Stille Cross-Coupling

Ethynyltrimethylsilane was deprotonated and reacted with tributylchlorotin to give the stannylated ethynylsilane **15** in good yield.²⁵



Tributylstannylethynyltrimethylsilane **15** was prepared directly from ethynyltrimethylsilane and tributylmethoxytin in 49% isolated yield.²⁶

$$n-Bu_{3}SnOMe + //TMS \xrightarrow{ZnBr_{2} (5 \text{ mol}\%)}{THF, \text{ rt, 3 h}} 15$$

$$49\%$$
Scheme 20 Alternative synthesis of tri-*n*-butylstannylethynyltrimethylsilane

The bis(silyl)enyne **17** was prepared by cross-coupling tri-*n*-butylstannylethynyltrimethylsilane with vinyl iodide **16** in 75% yield. In another approach to this end in the same paper vinylstannane **18** reacted with bromoethynyltrimethylsilane and bromoethynyltriisopropylsilane to give the bissilylated conjugated enynes in good yield.²⁷



Scheme 21 Stille cross-coupling reactions

The alkynylation of anomeric position of the benzyl-protected glucose derivatives **19** was accomplished with tributylstannylethynyltrimethylsilane.²⁸



Scheme 22 sp³-sp cross-coupling of **18** with a sugar derivative

Tri-*n*-butylstannylethynyltrimethylsilane was cross-coupled with **20** and found to be tolerant of a ketal, and a cyclopropene. The TMS group was removed along with deacetoxylation of the ester upon treatment with $K_2CO_3/MeOH$.²⁹



Tributylstannylethynyltrimethylsilane was cross-coupled with the highly substituted aryl bromide **21** in a synthesis of (+)-kibdelone A. The TMS group was removed in 93% yield with AgNO₃•pyridine in aqueous acetone.³⁰





Similarly to the Sonogashira reaction of ethynyltrimethylsilane where the cross-coupling occurs at the C-H bond the cross-coupling of tributylstannylethynyltrimethylsilane occurs at the C-Sn bond rather than the C-Si bond. This was employed in the synthesis of the indole piece of sespendole.³¹



Scheme 25 Stille cross-coupling with a highly-substituted aryl triflate

In an approach to the synthesis of Lactonamycins, a model glycine was prepared wherein a critical step was the addition of an ethynyl group onto a highly substituted arene. Thus, bromoarene 22 was subjected to a Stille cross-coupling with tributylstannylethynyltrimethylsilane to give the ethynylarene 23 in 91% yield. This compared favorably with a three-step sequence.³²



9 **Reaction at Terminal Carbon**

Under Co-catalysis triisopropylsilylacetylene reacted with enones to form β-ethynylketones in high yields. The reaction worked well with ethynylTBS, ethynylTBDPS as well, although ethynylTES gave only 40% yield. Under the reaction conditions the non-silvlated terminal acetylenes phenylacetylene and 1-octyne gave alkyne oligomerization. An asymmetric version of the reaction, which gave good yields and acceptable ee's, was also presented.³³





Carreira and coworkers reacted terminal acetylenes including ethynyltrimethylsilane with aldehydes in the presence of (+)-*N*-methylephedrine to give the propargyl alcohol in high yield and high enantiomeric excess.³⁴



Scheme 28 Asymmetric ethynylation of an aldehyde

The aldehyde **24** was reacted with ethynyltrimethylsilane under Carreira conditions to give a single diastereomer of **25**, which was O-silylated followed by protiodesilylation of the TMS group. This material was carried forth in a synthesis of hyptolide and 6-*epi*-hyptolide.³⁵



In keeping with the common use of ethynylsilanes as surrogates for the simple ethynyl organometallics, an 'in situ' process for the ethynylation of aldehydes was developed. In this chemistry a combination of ZnBr₂, TMSOTf and Hünig's base was used to generate the ethynylzinc reagent in situ and along with a silylating agent this was reacted with the aldehyde to generate the doubly silylated propargyl alcohol.³⁶



Scheme 30 'In situ' ethynylation of aldehydes

The aminomethylation of terminal alkynes was applied to a variety of acetylene derivatives including one example with ethynyltriethylsilane, which provided the triethylsilylated propargyl amine in good yield. This was subsequently protiodesilylated and the resulting propargyl amine converted to a mixed bis(aminomethyl)alkyne in a 49% yield over the three steps.³⁷



Scheme 31 Aminomethylation of terminal alkynes

Ethynyltriisopropylsilane was employed in a Ni-catalyzed, three-component reaction of the ethynylsilane, an alkyne and norbornene. A variety of norbornene derivatives were reacted with good success. When ethynyltriisopropylsilane was used as the sole acetylene reactant the bis(triisopropylsilyl)-1,5enyne was produced. One example with a bicyclo[2.2.2]octane gave only a 12 percent yield when reacted with ethynyltriisopropylsilane.³⁸



Scheme 32 Three-component reaction of norbornene with and ethynylTIPS and an alkyne

Ethynyltrimethylsilane could be directly alkylated to 1-trimethylsilyldodec-1-yne on modest yield. The yield of this sole silicon example was comparable to the direct alkylation of other terminal alkynes.³⁹

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Scheme 33 Copper-catalyzed alkylation of ethynyltrimethylsilane

The Formation of Aromatic Rings

The tricyclization of alkynes to aromatic rings has long been known as has the use of silylacetylenes in this practice.⁴⁰

Silyl-protected arylacetylenes reacted with *o*-phenylethynylbenzaldehyde under acid catalysis to produce the 2-aryl-3-silylnaphthalene in good yield. The TMS-protected arylalkynes resulted in the 2-arylnaphthalene with protiodesilylation taking place under the reaction conditions. However, the more hindered TES, TBS, and TIPS-protected derivatives gave the corresponding 3-silylnaphthalenes allowing for the ICl ipso iodination of the silyl group to provide the naphthyl iodide for further elaboration via cross-coupling chemistry. The chemistry was applied to the synthesis of several highly encumbered polyaromatic systems.⁴¹



Scheme 34 Cyclization to aromatic rings from ethynylarenes

The rhodium-catalyzed reaction of trimethylsilylacetylenes with cyclobutenols gave 1,2,3,5-tetrasubstituted benzenes with the trimethylsilyl group regioselectively positioned in the 2-position. No conversions of the trimethylsilyl group were carried out in this work, however.⁴²



Scheme 35 Cyclobutenol to a TMS-substituted arene

Methyl trimethylsilylpropynoate was successfully employed in the synthesis of 2*H*-quinolizin-2-ones. In this approach the trimethylsilyl group conveniently served the purpose of protecting the acidic hydrogen of the parent terminal acetylene.⁴³



Scheme 36 Quinolizin-2-ones from TMSpropynoate

The cationic rhodium catalyst, [Rh(cod)₂]BF₄/BIPHEP, brought about the cyclotrimerization of ethynyltrimethylsilane with unsymmetrical electron-deficient acetylenes. Unfortunately, neither the stoichiometry nor the regioselectivity of the cyclization was optimal. Larger silyl groups tended to favor the addition of one of the silylacetylene moieties and two of the electron-deficient alkynes, whereas increasing the steric bulk of the electron-deficient alkyne resulted in the reaction of two equivalents of the silylacetylene. Ethynyltriisopropylsilane failed to react. Protiodesilylation of a mixture of regioisomers was able to simplify the reaction mixture, but reaction with ICl gave a synthetically challenging mixture of isomers in modest yield.⁴⁴





with ethyl propynoate

The cyclotrimerization of ethyl trimethylsilylpropynoate gave the single regioisomers 28 in 92% yield.⁴⁵



Scheme 38 Homocyclization of ethyl TMS-propynoate

Complete regioselection in the formation of 2-aryl-1,3,5-tris(silyl)benzene was realized in the Pdcatalyzed reaction of two equivalents of a terminal alkyne, including ethynyltrimethylsilane, and an equivalent of a β -iodo- β -silyl styrene. The nature of the silylstyrene proved crucial as the trialkylsilyl (TMS, TES, TBS, Me₂BnSi) groups gave poor yields, and the phenylated silyl groups giving better yields with the β -Ph₂MeSi-substituted styrene proving to be optimal. Selective electrophilic substitution of the 5-trimethylsilyl, para position relative to the aromatic substituent, proved possible. In a demonstration of the potential synthetic utility of the highly silylated systems a number of conversions of the silyl groups were carried out including protiodesilylation, acylation, iodination and a Denmark cross-coupling. It is noteworthy that the iododesilylation of **29** is selective for the formation of **30** and that iododesilylation of a phenyl group from the Ph₂MeSi group does not occur. Comparable selectivity was noted in the acetylation of **29** to acetophenone **31**, which could be desilylated to 4-phenylacetophenone in good yield.⁴⁶



Scheme 39 Cyclotrimerization with a vinyl iodide and subsequent conversions

Diels-Alder Cyclizations of Alkynylsilanes

1-Trimethylsilylacetylenes were shown to provide excellent regiochemical control in the cobalt-catalyzed Diels-Alder reaction with 1,3-dienes. In the un-substituted case various Si-substituted ethynylsilanes were reacted with 2-methyl-1,3-butadiene under cobalt catalysis. It turned out that the regioselectivity was highly dependent on the accompanying ligand employed with $CoBr_2(mesityl$ pyridin-2-yl-methyleneamine) favoring the *meta* regioisomers **32** after DDQ oxidation to the aromatic derivative. On the other hand, the use of $CoBr_2(1,2-bis-diphenylphosphinoethane)$ favored the *para* isomer **33**. In addition a number of alkynyltrimethylsilanes were reacted with 2-methyl-1,3-butadiene. Here the yields were very high, but the regioselectivity was less than that observed with the simple ethynylsilanes. Of particular interest was the result from the reaction of 1-trimethylsilylpropargyl acetate with Danishefsky's diene, 2-trimethylsilyloxy-1,3-butadiene **36**.⁴⁷



Scheme 40 Diels-Alder cyclization of alkynylsilanes with 1,3-dienes

The synthesis of aryl and vinyl iodides has taken on increased importance due to their facility as electrophilic partners in various cross-coupling reactions. Building on the Diels-Alder chemistry of butadienes with ethynyltrimethylsilanes the Hilt group devised an efficient route to highly substituted aryl iodides wherein the TMS group served nicely to define the regiochemistry and provide the iodide functionality. The complete reaction sequence could be carried out in a single flask although consid-

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erable effort was placed on the oxidation-iodination step. For example, ICl/CH_2Cl_2 gave only 5% of the iodide **38**, NIS/MeCN gave modest yields of the iodide in 5 cases, but the reaction was very slow and product decomposition led to purification difficulties. The combination of H_2O_2/ZnI_2 gave modest yields, but again in a slow reaction that required further oxidation with DDQ for completion. Finally, the use of *tert*-butylhydroperoxide with ZnI_2 and K_2CO_3 was found to give high yields of the desired iodides.⁴⁸



Scheme 41 Diels-Alder cyclization to cyclic 1,4-dienes

Formation of 1,2,3-Triazines

A series of 1,4-disubstituted-1,2,3-triazines **42** was prepared in a one-pot, three-step sequence involving first a Sonogashira preparation of an arylethynyltrimethylsilane from ethynyltrimethylsilane, reaction with an alkyl azide and, finally, deprotection of the 5-trimethylsilyl group.⁴⁹

Arylethynyltrimethylsilanes, readily formed via a Sonogashira reaction from ethynyltrimethylsilane, reacted with sodium azide and an alkyl bromide in a three-step, one-pot sequence to yield a desily-lated 1-alkyl-4-aryl-1,2,3-triazole **43** or **44**. The reaction took place via initial deprotection of the trimethylsilyl group followed by the [3+2] click cycloaddition. This represents a safe and scalable process for the formation of 1,4-disubstituted 1,2,3-triazoles.

The reaction of alkynyltrimethylsilanes with CuBr/Et₃N served to directly prepare the alkynylcopper reagent without prior desilylation. The resulting copper reagent underwent reaction with various azides to form the 1,2,3-triazenes **45** in excellent yield. When the reaction was carried out with ethynyltrimethylsilane or ethynyltriisopropylsilane the reaction occurred at the C-H terminus. TIPS and TBS-terminated acetylenes failed to react.⁵⁰

The dichloropyridazine **46** was converted to the [1,2,3]triazole-fused pyrazinopyridazindione **47** in a three-step sequence with ethyl trimethylsilylpropynoate. The TMS group is lost in the last step of the sequence, but provides the desired regioselectivity in the azide click step of the sequence.⁵¹



Addition to the Triple Bond

The Ru-catalyzed hydroacylation of 4-methoxybenzaldehyde with trimethylsilylpropyne gave a mixture of isomeric trimethylsilyl dienol ethers **47** and **48**.⁵²

The reaction of a tertiary amine with methyl trimethylsilylpropynoate gave addition of the amine to the triple bond and the formation of an allenoate ion. This, in the presence of an aldehyde, gave predominantly bis addition of the aldehyde resulting in two products **49** and **50**. When the aldehyde was an aliphatic group addition at the C-H terminus of the triple bond occurred to give **51**. No reaction occurred with ethyl 3-methylpropionate indicating that the trimethylsilyl group was necessary.



Scheme 43 Aldehyde addition to an alkynylsilane

Ethynyltrimethylsilanes were reacted under nickel catalysis with phthalimides to give decarbonylation and alkylidenation of one of the carbonyl groups. Although the reaction appears to be potentially general all but two of 11 examples were with N-(1-pyrollidino)phthalimide. The use of a catalytic amount of the strong and sterically demanding methylaluminum bis-(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) was crucial in the success of the reaction. In the absence of MAD the major products were isoquinolones. Only phenylethynyltrimethylsilane and *p*-anisylethynyltrimethylsilane were reported to give mixtures of (Z) and (E) alkylidene isomers. Two additional examples were presented, where the PhMe₂Si and *t*-BuMe₂Si acetylenes were reacted, albeit in lower yield. Two dialkylacetylenes failed to react indicating that the presence of the TMS group is necessary for the reaction.⁵³





The torquoselective olefination of alkynoates was accomplished. The silylalkynoates gave excellent selectivity for the (E)-enyne formed. Silver catalyzed cyclization of the resulting enynes was carried

out to give either the 5-exo tetronic acid derivatives or the 6-endo pyrones. The TES-silylated tetronic acid **52** was stereoselectively converted to the corresponding iodide **53**, which was in turn subjected to phenylation via a Suzuki cross-coupling and to ethynylation via Sonogashira cross-coupling.⁵⁴



Scheme 45 Addition to silylpropynoates

A series of silvlated propargylic alcohols was prepared via the straightforward reaction of the lithiated ethynylsilane and a variety of aldehydes and ketones. These were subjected to conditions for the Meyer-Schuster rearrangement in the preparation of acylsilanes. The reaction of the propargyl alcohols derived from aromatic aldehydes underwent the rearrangement in good yield under either of two catalyst systems, *p*-TSA•H₂O/*n*-Bu₄•ReO₄ or Ph₃SiOReO₃. The *p*-TSA•H₂O/*n*-Bu₄•ReO₄ system did not work for electron donating aryl systems, though the Ph₃SiOReO₃ catalyst worked well for these. Aliphatic aldehydes failed with the exception of that obtained from pivaldehyde. The reactions from the propargylic alcohols prepared from diaryl ketones showed mixed pathways.⁵⁵



Scheme 46 rearrangement and oxidation of silylpropargyl alcohols

A one-step hydroiodation of ethynylsilanes to the vinyl iodide, highly useful substrates for crosscoupling applications, was found to occur upon treatment of the ethynylsilane with trimethyliodosilane. The reaction sequence of a Sonogashira cross-coupling of ethynyltrimethylsilane and an aryl halide followed by the hydroiodation resulted in a facile synthesis of α -iodostyrene derivatives. In the end the reaction resulted in the Markovnikov addition of HI to the triple bond. It was further found that the terminal acetylene itself would undergo the reaction as well. More hindered silyl groups gave a lower yield of the vinyl iodide.⁵⁶



A three-component with methyl trimethylsilylpropiolate, an amine and an imine is directed by both the ester and the trimethylsilyl moieties. The reaction involves a 1,4-silyl shift. When applied to salicyl imines chromenes were generated. This reaction was shown to proceed through the aminal **54**, which could be trapped with allyltrimethylsilane or the TMS-enol ether of acetophenone.⁵⁷



Scheme 48 Reaction of silylpropynoates with imines

A variety of 1-silylethynyl aldehydes and ketones, prepared via a silylation, deprotection, oxidation sequence, were converted to the silyl-1,3-dithianes, which are useful synthons via their potential for Anion Relay Chemistry (ARC).⁵⁸ Although 8 different R₃Si groups showed good results, the dithia-tion did not occur when R₃Si was sterically hindered as with TBDPS, TIPS, (*t*-)Bu₂HSi, or *i*-Pr₂HSi.⁵⁹



Scheme 49 Dithiation of silylpropynals

The LAH reduction of the 4-silylbutyn-2-ones provided the 4-silylbuten-2-ol in good yields and high Z:E ratios.⁶⁰



Scheme 50 LAH reduction of silylpropargyl alcohols

The β -silyl effect to stabilize β -cationic intermediates was employed in the regioselective addition of ICl to ethynylsilanes. The diastereoselectivity of the addition is the opposite that found for the reaction of ICl with the simple terminal alkyne. The Z:E selectivity is higher with aryl-substituted ethynylsilanes, though the Z selectivity of the alkyl-substituted ethynylsilanes increases with an increase in the size of the silyl group.⁶¹



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The addition of the halogens to ethynyltrimethylsilane in the absence of light produced the E-isomer, which could be equilibrated to a mixture of both stereoisomers. In the cases of the E-dichloride or E-dibromide the equilibration was brought about by exposure to light in the presence of a trace of bromine. In the case of the E-diiodide, prolonged refluxing in cyclooctane produced a 9:1 E:Z mixture.⁶²



The reaction of Weinreb amides with internal acetylenes under promotion via a Kulinkovich-type titanium intermediate gave α , β -unsaturated ketones in modest yield. The reaction conditions were mild with activation of the titanium promoter as the last step at room temperature. With the TMS-terminated alkynes the yields were comparable to those of other alkynes investigated, though with slightly lower regioselectivity.⁶³



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The syn addition of two aryl groups from an arylboronic acid to an internal alkyne resulted in the formation of 1,2-diaryl tetrasubstituted olefins. In the single silicon example the reaction of ethyl trimethylsilylpropiolate with *p*-tolylboronic acid under Pd catalysis formed the trisubstituted corresponding vinylsilane via the addition of two equivalents of the *p*-tolyl group. The reaction provided a route to a highly substituted β -trimethylsilyl- α , β -unsaturated ester.⁶⁴

The highly regio- and stereoselective addition of a boronic acid to alkynylsilanes was reported. The reaction occurred under mild conditions and in high yields. Interesting points found were that 1-hexynyltriethylsilane was more regioselective than 1-hexynyltrimethylsilane, which gave a mixture of isomeric vinylsilanes indicating that the steric effect of the silyl group plays a role and extended reaction times gave reduced stereoselectivity. The resulting arylated vinylsilanes could be converted to their corresponding iodide and bromide. In the case of the iodide this could be done in a two-step, one-pot reaction sequence, whereas with the bromide two independent steps were required. In a further extrapolation of the chemistry the region- and stereoselective synthesis of (Z)-1-(4-tolyl)-2-(4-anisyl)styrene **55** was accomplished in 3 steps from phenylethynyltrimethylsilane. The reaction was also possible with the addition of a vinylboronic acid giving a dienylsilane.⁶⁵



Scheme 54 Addition of a boronic acid to alkynylsilanes



Scheme 54 Addition of a boronic acid to alkynylsilanes. (cont.)

The Oshima group reported the syn-hydrophosphination of terminal and internal alkynes. With aryl terminal alkynes the regioselectivity was approximately 9:1 and with ethynyltriethylsilane, the sole silicon example, it was 94:6 slightly less than that with alkylacetylene substrates, which showed a 100:0 regioselectivity all placing the phosphine on the terminal position. The products were isolated as their sulfides.⁶⁶

Ph₂PH + // TES
$$TES$$
 $Co(acac)_2 (10 \text{ mol}\%)$ H H H Ph_2PS S_8 69%

Scheme 55 Hydrophosphination of an alkynylsilane

A chiral NHC catalyst was employed in the enantioselective conjugate addition of trimethylsilylalkynes to 3-substituted cyclopentenones and 3-substituted cyclohexenones. Thus, the alkynylsilane was reacted with diisobutylalane to form the 1-trimethylsilylvinylaluminum reagent, which was then reacted with the enone under catalysis with the chiral NHC complex **56**. In the reactions with the cyclopentenones up to 10% of addition of the isobutyl group from aluminum was observed. This increased to up to 33% in the case of the cyclohexenones reacted. The er values were excellent ranging from 92.5:7.5 to 98.5:1.5. Of considerable importance the resulting vinylsilanes were further reacted. Oxidation with *m*-chloroperbenzoic acid gave the ketone. NCI converted it to the vinyl iodide and protiodesilylation to the parent olefin. This chemistry was applied to a short synthesis of riccaardiphenol B **57**.⁶⁷



Scheme 56 Hydroalumination of alkynylsilanes and asymmetric vinylation of enones

The reaction of indoles with halophenylethynyltrimethylsilanes under copper (I) catalysis gave addition of the indole to the triple bond and, under the basic conditions, protiodesilylation to form the corresponding olefin as a mixture of stereoisomers. Very little amination of the aryl halogen bond occurred. In fact, a control experiment wherein indole was reacted with a mixture of 4-bro-mophenylethynyltrimethylsilane and 4-iodoanisole a 50% yield of addition to the triple bond and only 6% reaction of the iodophenyl bond was observed.⁶⁸

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Scheme 57 Hydroamination of alkynylsilanes in presence of aryl halides

The hydrosilylation of various propiolate esters was carried out and served to prepare α -silylated- α , β -unsaturated esters in good yields. When this reaction was done with trimethylsilylpropiolate esters the product formed was the (E)- α , β -bis(silyl)acrylate. Other similar systems such as an ynone and a sulfone gave good addition products.⁶⁹



Scheme 58 Hydrosilylation of functional alkynylsilanes

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Bis(trimethylsilyl)-1,3-butadiyne underwent carbomagnesiation of one of the triple bonds with arylmagnesium bromide reagents. The resulting vinylmagnsium bromide intermediate could be further reacted, including cross-coupling to form various substituted silylated enynes. Phenyl-(trimethysilyl)butadiyne underwent the carbomagnesiation at the phenyl substituted triple bond.⁷⁰



Scheme 59 Addition of Grignard reagents to alkynylsilanes

Kimura and coworkers reported on the nickel-catalyzed, four-component coupling of internal acetylenes, 1,3-butadiene, dimethylzinc, and carbon dioxide. The reaction of the TMS-substituted alkynes gave lower yields and poorer regioselectivity than those of alkyl- or aryl-substituted alkynes.⁷¹



Scheme 60 Four-component coupling involving an alkynylsilane

The three-component coupling of acetylenes, vinyloxiranes and dimethylzinc was reported to give 2-vinyl-5,6-unsaturated alcohols. The bis(trimethylsilyl)acetylene and ethynyltrimethylsilane gave lower yields than trimethylsilylpropyne and alkyl- or arylalkynes. In a similar manner vinylcyclo-propanes were reacted to provide the 1,4-dienes.⁷²



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Scheme 61 Alkylative three-component coupling of an alkynylsilane with a vinyloxiranes
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The reaction of ethynylsilane **58** with ruthenium catalyzed addition of acetic acid gave a mixture of the desired enol acetate **59** along with **60**. A longer reaction time gave **60** in good yield. Although **59** was the initial desired intermediate it was **60** that was in fact carried forward in a synthesis of Clavosolide A.⁷³



Scheme 62 Hydroacetation of an alkynylsilane

An iron-catalyzed imine-directed C2-alkenylation of indole with internal alkynes produced the 2–alkenylated derivative in good yield and regioselectivity. Terminal acetylenes did not react under the conditions employed. This was, however, circumvented by the use of a TMS-terminated acetylene, which was reacted with high regioselectivity forming the C_2 - C_{vi} bond beta to the TMS group. These conditions also proved useful for the formation of C_2 - C_{sp}^3 bonds when the reaction was carried out with olefins. Here again the reaction did not occur with terminal olefins.⁷⁴





The dibal-H addition to 1-trimethylsilylpropyne followed by conversion to the lithium alanate and reaction with formaldehyde resulted in vinylsilane **61**. This was in turn used to generated vinylsilane **62** and, from that, vinyliodide **63**, which was then converted in two steps to norfluorocurarine **64**.⁷⁵



Scheme 64 Dibal-H addition to propargyITMS and further reaction to norfluorocurarine

Reaction at the Si-C Bond

A study on the iododesilylation of a series of vinylsilanes wherein the silyl group was TIPS, TBS, and TBDPS was carried out. This was the first report of the iododesilylation of a vinylsilane with sterically hindered silyl moieties. Interestingly, it was found that the rate of the reaction with TIPS or TBS groups was about the same, but that of TIPS was faster than that of the vinylTBDPS. Four different sources of I+, N-iodosuccinimide (NIS), N-iodosaccharin (NISac), 1,3-diodo-5,5-dimethylhydantoin (DIH), and bis(pyridine)iodonium tetrafluoroborate (Ipy₂BF₄) were investigated with comparable results for each. The success of the reaction depended on the solvent system including hexafluoroisopropanol. The reaction was tolerant of epoxides, olefins, esters, TIPS ethers, and a TIPS acetylene.⁷⁶

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Bis-(trimethylsilyl)butadiyne was reacted with MeLi•LiBr to prepare the mono-lithiated diyne, which was reacted in a Sonogashira cross-coupling with *o*-iodoaniline.⁷⁷



Scheme 66 Lithiation and reaction of bis(trimethylsilyl)butadiyne

Pan and coworkers were able to conjugate add alkynyl groups to acrylate derivatives via the reaction of the trimethylsilylalkyne under InCl₃ catalysis. Silyl moieties other than that of the TMS group were not investigated. The reaction worked best for alkynes with a strongly electron donating aryl group attached. Thus, 4-CN, 4-CO₂Me and 4-CF₃-substituted arylalkynes failed to react. In direct comparison of the TMS-terminated alkyne and the H-terminated the yields were better with the TMS derivatives. Chlorobenzene was found to be the best solvent and Et₃N the best base. Bis(trimethylsi-lylethynyl)benzene **65** could be reacted to furnish the mono- or di-substituted γ , δ -ethynyl ester. The reaction was also occurred with methylvinyl ketone as the acceptor.⁷⁸

This protocol compares well with the conjugate addition of terminal alkynes to acrylates catalyzed with $Ru_3(CO)_{12}/bis(triphenylphosphine)iminium chloride^{79}$ and with $Pd(OAc)_2$.⁸⁰





Scheme 67 Ethynylation of α , β -unsaturated esters with alkynyltrimethylsilanes

Miscellaneous

 β -Amino enone **66** was converted in a two-step, single-pot sequence to enol ether **67** via reaction with trimethylsilylpropargyllithium in 51% overall yield. Propargylmagnesium bromide gave a 40% yield of **67**. Enol ether **67** was carried on in a synthesis of 7-hydroxycopodine.⁸¹



Scheme 68 Reaction of trimethylsilylpropargyllithium with an iminium salt

Trialkylsilylethynylcyclopropanols were ring expanded to alkylidene cyclobutanones under the promotion of ruthenium catalyst **68**. Interestingly, the favored stereoisomer was the (Z)-isomer. Similar results were obtained with the electron deficient alkynyl cyclopropanols. On the other hand, alkylethynylcyclopropanols reacted to give expansion to cyclopentenones. Stabilization of a β -carbocation in the silyl-substituted examples, and a favored Michael addition in the electron deficient examples help explain the formation of the four-membered ring in these cases.⁸²



Scheme 69 Rearrangement of silylethynylcyclopropanols

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Trimethylsilylpropynal was nicely used in a convenient synthesis of ethynyl- β -lactone **69** Propynal did not undergo the requisite chemistry to this key synthon. The silylated enantiomerically enriched β -lactone 1 has been applied to synthetic approaches to leustroducsin B and the protiodesilylate ethnyl lactone **70** to (-)-murictacin, (-)-Japonilure and (-)-Eldamolide.^{83,84,85}



Scheme 70 Synthesis of silylethynyl-β-lactone

Corey and Kirst were the first to report on the synthesis and utility of lithio(trimethylsilyl)propyne **71**. The direct lithiation occurred with BuLi/TMEDA in 15 minutes. The reagent reacted with primary alkyl halides in diethyl ether to form the desired alkyne with only small amounts of the isomeric allene, a common side product found with propargylmagnesium chloride reagent.⁸⁶

Corey and Rucker followed this work up with propynyltriisopropylsilane **72**, which was readily lithiated to give the more sterically encumbered TIPS propargyllithium reagent. This was converted via lithium reagent to the bis(triisopropyl)propyne **74** in quantitative yield. Reaction of **73** with cyclohexenone gave 1,4-addition in THF/HMPA and 1,2-addition in THF. Bis-TIPS reagent **77** was reacted with *n*-BuLi/THF to give lithiated **78**, which was reacted with aldehydes in a Peterson reaction to form an enynes.⁸⁷

Trimethylsilylpropargyllithium **71** was used to introduce the propargyl group onto epoxy geranyl chloride. The yield was 85% over three steps from geraniol. The TMS group was removed with TBAF and the envne carried on to the triterpene limonin.⁸⁸

Trimethylsilylpropargyllithium 71 was reacted with lactone 75 followed by mesylation/elimination to give enynes 76 and 77 in good yield. The TMS group was removed with $AgNO_3/EtOH_{aq}$ en route to stereoisomers of bis(acetylenic) enol ether spiroacetals of artemisia and chrysanthemum.⁸⁹





Scheme 71 Formation and reactions of silylpropargyllithium reagents

Fu and Smith demonstrated the enantioselective nickel-catalyzed, Negishi cross-coupling arylation of racemic trimethylsilylpropargylic bromides. The yields and the ee values were excellent. The protocol was applied to the synthesis of **79** which had been shown to be a precursor to pyrimidine **80**, an inhibitor of dihydrofolate reductase.⁹⁰





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►►► Gelest, Inc.

 D_4^{20} n_D^{20}

1.4390

1.413

Acetylenic Product List

MW

bp °C/mm (mp)

	SIB1760.0					
	BIS(PHENYLETHYNYL)DIMETHYLSILANE					
	C ₁₈ H ₁₆ Si		260.41	180° / 4	(78-81°)	
	Reductive cyclization yields siloles, olig	osiloles.1				
	Useful in silicon-mediated Sonogashira	cross-coupling reactio	ns. ²			
Si	1. Tamao, K. <i>J. Am. Chem. Soc.</i> 1994 ,	116, 11715.				
	2. Larson, G. L. "Silicon-Based Cross-C	oupling Reagents" Ge	lest, Inc. 2011.			
	HYDROLYTIC SENSITIVITY: 4: no rea	LIMIS: 2.2.1 V	neutral conditio	ons 5a		
	[2170-08-3]	HIWII 3. 2-2- 1-A		Jy		
	SIB1816.3					
	1,2-BIS(TRIETHOXYSILYL)ACETYLENE, te	ech-95				
o-si-si-o	4,4,7,7-TETRAETHOXY-3,8-DIOXA-4,4-DISILA	DEC-5-YNE	050 50	00 408 / 0 05		4 404
	Eorme mosoporous structures		300.00	38-40 / 0.05		1.101
				50		
		HIVII5: 2-2-1-X		эy		
			170 40	133-5°	(22°)	0 770
	08118012		Flashpoint: 2	°C (36°F)	(22)	0.110
	Versatile reagent for introducing unsatur	ation		· · /		
—si——si—	Key reviews. ^{1,2,3}					
	Used to prepare 1 2-bis(aryl)acetylenes	3				
	Reacts with internal acetylenes to form	1 2 4 5-tetrasubstituted	henzenes ⁴			
	Liseful in silicon-mediated Sonorashira	cross-coupling reaction	ne ⁵			
	Used to propare 4 alkypylthiazolos ⁶	cross-couping reactio	115.			
				00 - 100		
	1. Weber, W. In Silicon Reagents for Or	ganic Synthesis; Sprin	iger-verlag: 19	83, p129.		
	2. Vollhardt, P. Acc. Chem. Res. 1977,	10, 1.				
	3. Nishihara, Y. et al. J. Org. Chem. 200	0, 65, 1780.				
	4. Li, S. et al. <i>Org. Lett.</i> 2009 , <i>11</i> , 3318.					
	5. Larson, G. L. "Silicon-Based Cross-C	oupling Reagents" Ge	lest, Inc. 2011.			
	6. Arunkukmar, K. et al. Tetranedron Let	t. 2012 , 53, 3885.			07 000 141	
	F&F: Vol. 4, p 42; Vol. 5, p 44; Vol. 8, p 1	46; VOI.9, p 142; VOI. 10	J, p 126; Vol. 10	J, p 126; Vol. 13,	p 97, p 309; voi.	14, p 116.
	HYDROLYTIC SENSITIVITY: 2: reacts	with aqueous acid		10	=0	
	[14630-40-1] ISCA EC 238-671-9	HMIS: 2-4-1-X		10g	50g	
	SIB1852.0					
\backslash	BIS(TRIMETHYLSILYL)ACETYLENEDICA	RBOXYLATE				
—śi—o o	$C_{10}H_{18}O_4Si_2$		258.42	78-80° / 0.05		0.988
			Flashpoint: 6	7°C (153°F)		
0 0 <u>-si</u>	Synthetic intermediate with readily clear	able silyl groups.				
	HYDROLYTIC SENSITIVITY 7 reacts	slowly with moisture/v	vater			
	[76734-92-4]	HMIS: 3-2-1-X	rator	10g		
		111110.0217		iog		
	SIB1854.0					
	BIS(TRIMETHYLSILYL)BUTADIYNE		404.40		(407.0%)	
	$C_{10}\Pi_{18}$ Stable crystalling form of butadiving: cyr	then for botoroovalos ¹	194.42		(107-9)	
	Used to propare multideptate 1.2.3 triaz	alo cholato ligande 2				
	Lindergoes 6+2 cycloaddition with cyclo	hentatriene ³				
	1. Jacobs, P. M. et al. Heterocycl. Chem	n. 1977. <i>14</i> . 1115.				
	2. Fuller, T. J. et al. Organometallics 20	08 , 27, 5430.				
	3. Hilt, G. et al. Synthesis 2009, 3305.					
	See also SIT8597.0					
	HYDROLYTIC SENSITIVITY: 4: no rea	ction with water under	neutral conditio	ons		
	[4526-07-2]	HMIS: 2-3-1-X		10g		

Name



Name

	SIB1858.0						
	1,3-BIS[(TRIMETHYLSILYL)ETHYNYL]BENZEI	NE					
si	C ₁₆ H ₂₂ Si ₂		270.52		(57-9°)		
	HYDROLYTIC SENSITIVITY: 4: no reaction	n with water under i	neutral conditions				
	[38170-80-8]	HMIS: 3-3-0-X	store <5°C	5a			
	SID1050 2						
	5161658.2						
	1,4-BIS[(TRIMETHYLSILYL)ETHYNYL]BENZEI	NE					
	$C_{16}H_{22}Si_2$		270.52		(119-121°)		
	HYDROLYTIC SENSITIVITY: 4: no reaction	n with water under i	neutral conditions				
	[17938-13-5]	HMIS: 3-3-0-X		5g			
	SIB1899.0						
	Carthe BrSi		253 22	60-80° / 0 2	(61-3°)	1 192	
			200.22	00 00 7 0.2	(010)	1.102	
Br————————————————————————————————————							
	HYDROLYTIC SENSITIVITY: 1: no significa	ant reaction with ac	lueous systems				
	[16116-78-2]	HMIS: 2-2-0-X		10g			
	SIB1907.0						
	3-BROMO-1-(TRIMETHYLSILYL)-1-PROPYNE	- 95%					
	CeH44BrSi	_, 0070	191 15	44-5°/2		1 351	1 4950
			Flashpoint: 62°C	(144°F)			
/	Reagent for preparation of terminal conjugat	ed envnes ¹		. ()			
	Lead to property homoproperty/lie and allon	d clocholo ²					
	1 Ciboop A st el Symbolio 1001 5 414	aconois.					
Br'	2 Liu M Litch T B L Am Cham Son	2002 125 12042					
	2. Liu, MJ., Lon, TF. J. Am. Chem. Soc.	2003, 723, 13042.					
	HYDROLYTIC SENSITIVITY: 4: no reaction	with water under i	neutral conditions				
				F			
	[38002-45-8]	HIVIIS: 3-2-1-X		bg			
1	SIB1931.0						
	3-BUTEN-1-YNYLTRIMETHYLSILANE						
Si	C ₇ H ₁₂ Si		124.26	52-3° / 80		0.7714	1.4512
	Cycloannulation reagent						
	HYDROLYTIC SENSITIVITY: 4: no reaction	n with water under i	neutral conditions				
~	[2696-32-4]	HMIS: 2-3-1-X		5a			
	SIB1939 5						
\ \	4-(t-BUTYLDIMETHYLSILOXY)BUTYNE		404.05	70 48 / 40		0.000	1 1000
	C ₁₀ H ₂₀ OSI		Flooppoint: 59°C	70-4 / 10 (126°E)		0.695	1.4300
S1	Directorated by the sel		Flashpoint: 56 C	(130 F)			
· · · · · · · · · · · · · · · · · · ·	Protected bulynoi Detertial for the surtheasis of silvel protected by		1				
	Potential for the synthesis of singl-protected i	utyrioi derivatives.	Inat Ing. 2011				
•	HVDDOI VTIC SENSITIVITV 7 roasts alar	why with projecture h	vator				
	HIDROLING SENSITIVITY. 7. Teacts slow		valer				
	[/8092-82-2]	HMIS: 2-3-1-X		iug			
	SIC2325.6						
	(5-CHLORO-1-PENTYNYL)TRIMETHYLSILAN	IE					
	1-CHLORO-5-TRIMETHYLSILYL-4-PENTYNE						
			474 75	75-6° / 20		0.077	1.4560
1	C ₈ H ₁₅ CISi		1/4./5	10 0 120		0.977	
	C ₈ H ₁₅ CISi		Flashpoint: 65°C	C (149°F)		0.977	
Si	$C_{\theta}H_{16}CISi$ Forms functionalized triazoles by"click" che	mistry	Flashpoint: 65°C	C (149°F)		0.977	
Si	C₅H₁₅ClSi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0	mistry	Flashpoint: 65°C	C (149°F)		0.377	
CI	C ₈ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reactior	emistry n with water under I	Flashpoint: 65°C	C (149°F)		0.977	
CI	C ₉ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reactior [77113-48-5]	mistry n with water under n HMIS: 2-2-0-X	Flashpoint: 65°C	5 <u>g</u>		0.911	
CI	C ₉ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reaction [77113-48-5]	mistry h with water under n HMIS: 2-2-0-X	Flashpoint: 65°C	5g		0.917	
CI	C ₆ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reaction [77113-48-5] SIC2326.4	mistry h with water under h HMIS: 2-2-0-X	Flashpoint: 65°C	5g		0.977	
CISi	C ₆ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reactior [77113-48-5] SIC2326.4 (4-CHLOROPHENYLETHYNYL)TRIMETHYLS	mistry n with water under i HMIS: 2-2-0-X	Flashpoint: 65°C	5g		0.977	
CISi	C ₆ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reactior [77113-48-5] SIC2326.4 (4-CHLOROPHENYLETHYNYL)TRIMETHYLS C ₁₁ H ₁₃ CISi	mistry n with water under n HMIS: 2-2-0-X	208.76	5g 75-9° / 2.5	(47-51°)	0.977	
	C ₆ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reaction [77113-48-5] SIC2326.4 (4-CHLOROPHENYLETHYNYL)TRIMETHYLS C ₁₁ H ₁₃ CISi See also SID4000.0	mistry n with water under n HMIS: 2-2-0-X IILANE	Flashpoint: 65°C neutral conditions 208.76 Flashpoint: 105°	5g 75-9° / 2.5 C (220°F)	(47-51°)	0.977	
	C ₈ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reaction [77113-48-5] SIC2326.4 (4-CHLOROPHENYLETHYNYL)TRIMETHYLS C ₁₁ H ₁₃ CISi See also SIB1899.0 UNPDOLYTID OFNICTION (1)	mistry n with water under n HMIS: 2-2-0-X	Flashpoint: 65°C neutral conditions 208.76 Flashpoint: 105°	5g 75-9° / 2.5 C (220°F)	(47-51°)	0.911	
	C ₈ H ₁₅ CISi Forms functionalized triazoles by"click" che See also SIE4901.87, SIH5848.0 HYDROLYTIC SENSITIVITY: 4: no reaction [77113-48-5] SIC2326.4 (4-CHLOROPHENYLETHYNYL)TRIMETHYLS C ₁₁ H ₁₃ CISi See also SIB1899.0 HYDROLYTIC SENSITIVITY: 4: no reaction [72704.40.41	mistry h with water under i HMIS: 2-2-0-X	Flashpoint: 65°C neutral conditions 208.76 Flashpoint: 105°	5g 75-9° / 2.5 C (220°F)	(47-51°)	0.977	

MW

bp °C/mm (mp)

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 D_4^{20} n_D^{20}

 ${\sf D_4}^{20}$

bp °C/mm (mp)

 n_D^{20}

	SID3425.0					
	1,3-DIETHYNYLTETRAMETHYLDISILOXANE					
	C ₈ H ₁₄ OSi ₂		182.37	122-8°	0.842	1.4104
	//,		Flashpoint: 20°C	C (68°F)		
	End-capper for acetylene functional silicone	s				
Si Si	Useful in silicon-mediated Sonogashira cros	ss-coupling reactio	ins.1			
	1. Larson, G. L. "Silicon-Based Cross-Coup	<i>ling Reagents</i> " Ge	lest, Inc. 2011.			
/	HYDROLYTIC SENSITIVITY: 4: no reaction	n with water under	neutral conditions			
	[4180-02-3]	HMIS: 2-4-0-X	Store <5°C	10g		
1	SID3610.0					
	1-DIMETHYLAMINO-3-(TRIMETHYLSILYL)-2-	PROPYNE				
-S1	N,N-DIMETHYL-3-(TRIMETHYLSILYL)-2-PROPYN-	1-AMINE				
	C ₈ H ₁₇ NSi		15531		0.774	
	HYDROLYTIC SENSITIVITY: 7: reacts slow	wly with moisture/\	water			
	[56849-88-8]	HMIS: 3-3-1-X		5g		
	SIE4901.8					
	ETHYL 3-(TRIMETHYLSILYL)PROPYNOATE					
<u> </u>	C ₈ H ₁₄ O ₂ Si		170.29	95-9° / 30	0.897	1.4410
	_		Flashpoint: 71°C	C(160°F)		
	HYDROLYTIC SENSITIVITY: 3: reacts with	n aqueous base				
0	[16205-84-8]	HMIS: 3-2-0-X		5g		
	SIE4901.83					
	ETHYNYL-t-BUTYLDIMETHYLSILANE					
	t-BUTYLDIMETHYLSILYLACETYLENE					
<u> </u>	· C ₈ H ₁₆ Si		140.30	116-7°	0.751 25	1.451
			Flashpoint: 6°C	(43°F)		
	HYDROLYTIC SENSITIVITY: 4: no reaction	n with water under	neutral conditions			
	[86318-61-8]	HMIS: 2-3-0-X		5g		
\frown	SIE4901.85					
	ETHYNYLCYCLOHEXYLDIETHYLSILANE					
	C ₁₂ H ₂₂ Si		194.39	74-7° / 3	0.869 25	1.4705 ²⁵
S1						
	HYDROLYTIC SENSITIVITY: 3: reacts with	n aqueous base				
		HMIS: 2-3-1-X		1.0g		
\frown	SIE4901.87					
	ETHYNYLCYCLOPENTYLDIETHYLSILANE				25	25
	C ₁₁ H ₂₀ Si		180.36	82-3° / 8	0.858 25	1.4166 23
SI SI						
	HYDROLYTIC SENSITIVITY: 3: reacts with	n aqueous base				
		HMIS: 2-3-1-X		1.0g		
	SIE4901.9					
	ETHYNYLDIPHENYLMETHYLSILANE					
Si	C ₁₅ H ₁₄ Si		222.37	86° / 0.5	1.010	1.575
			Flashpoint: 113°	C (235°F)		
	See also SIE4901.83					
	HYDROLYTIC SENSITIVITY: 4: no reaction	n with water under	neutral conditions			
	[17156-65-9]	HMIS: 2-2-1-X		2.5g		
	SIE4902.0					
	ETHYNYLTRIETHYLSILANE					
	TRIETHYLSILYLACETYLENE					
	C ₈ H ₁₆ Si		140.30	136°	0.783	1.4430
			Flashpoint: 17°C	2 (63°F)		
≡ Si ¬	Reacts with enol silyl ethers to form α, α -bis	s- <i>trans</i> -β-triethylsi	lylethenyl ketones			
	Useful in Sonogashira cross-coupling reacti	ons w/ more stable	e silyl group than t	he trimethylsilyl group. [∠]		
, Y	1. Amemiya, K. et al. Tetrahedron Lett. 200	0, 47, 1797. Juna Resconte " Co	lest Inc. 2011			
	Z Larson G L SUICON-Based Cross-COUR	NUM READEDIS (SE	NEST INC. ZUTT			

MW

2. Larson, G. L. "Silicon-Based Cross-Coupling Reagents" Gelest, Inc. 2011.

See also SIE4903.0

Name

HYDROLYTIC SENSITIVITY: 4: no reaction with water under neutral conditions [1777-03-3] HMIS: 2-4-1-X 5g





Name		MW	bp °C/mm (n	np)	D_4^{20}	n _D ²⁰	
SIE4903.0							
ETHYNYLTRIISOPROPYLSILANE							
TRIISOPROPYLSILYLACETYLENE							
C ₁₁ H ₂₂ Si		182.38	50-2° / 0.6		0.813	1.4527	
		Flashpoint: {	56°C (133°F)				
See also SIE4902.0							
HYDROLYTIC SENSITIVITY: 4: no read	ction with water under	neutral conditi	ons				
[89343-06-6]	HMIS: 2-3-0-X		25g				
SNE4900							
ETHYNYLTRI-n-BUTYLTIN, 95%							
TRIBUTYLSTANNYLACETYLENE							
C ₁₄ H ₂₈ Sn		315.07	71° / 0.2		1.092	1.4760	
		Flashpoint:	73°C (163°F)				
Undergoes reactions at triple bond. ¹							
Pd catalyzed reactions with alkenyl and	aryl iodides yields ace	etylenes. ^{2,3}					
1. Stamm, W. <i>J. Org. Chem.</i> 1963 , 28, 3	3264.						
2. Stille, J. et al. J. Am. Chem. Soc. 198	7 , <i>10</i> 9, 2138.						
3. Stille, J. et al. J. Org. Chem. 1989, 54	, 5856.						
[994-89-8]	HMIS: 2-2-1-X		2.5g	10g			
SIE4904.0							
ETHYNYLTRIMETHYLSILANE, 98%							
TRIMETHYLSILYLACETYLENE							
C ₅ H ₁₀ Si		98.22	52°		0.709	1.3880	
Vapor pressure, 20°: 214 mm		Flashpoint: ·	-26°C (-15°F)				
		Autoignition	temperature: 310°C				
Doped polymer films are conductive							
Review of synthetic utility.1							
Ethynylates aromatic compounds.2							
Precursor to trimethylsilylethynyl coppe	r reagent. ³						
Lithiated derivative (n-BuLi treatment) re	eacts with halotriazine	s to produce m	onomers.4				
Employed in ortho ethenylation of phenol	s. ⁵						

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Undergoes Diels-Alder reactions with butadienes.6

Converts imines to propargyl amines.7

Forms propargylic amines from aldehydes and amines in aqueous system. $^{\rm 8}$

Regioselectively forms either regioisomeric enyne upon addition to propargyl amines depending on catalyst employed.⁹



Reacts w/ aryl aldehydes to form diethynylmethane derivatives.¹⁰ Useful in the preparation of unsymmetrical diarylacetylenes.¹¹



1. Handbook of Reagents for Organic Synthesis, Reagents for Silicon-Mediated Organic Synthesis Fuchs, P. L. Ed., John Wiley and Sons, Ltd., 2011, p. 569-580.

- 2. Austin, W. et al. *J. Org. Chem.* **1981**, *46*, 2280.
- 3. Sakata, H. et al. *Tetrahedron Lett.* **1987**, *28*, 5719.
- 4. Kouveetakis, J. et al. *Chem. Mater.* **1994**, 6, 636.
- 5. Kobayashi, K.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 241.
- 6. Paik, S.-J. et al. *Org. Lett.* **1999**, *1*, 2045.
- 7. Fischer, C.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 4319.
- 8. Wei, C.; Li, C.-J. J. Am. Chem. Soc. **2003**, *125*, 9584.
- 9. Matsuyama, N. et al. J. Org. Chem. 2009, 74, 3576.
- 10. Girard, D. et al. Tetrahedron Lett. 2007, 48, 6022.

11. Mio, M. et al. Org. Lett. 2002, 4, 3199.

- 1. Handbook of Reagents for Organic Synthesis, Reagents for Silicon-Mediated Organic Synthesis, Fuchs, P. L. Ed., John Wiley and Sons, Ltd., : See also SIT8606.5
- HYDROLYTIC SENSITIVITY: 4: no reaction with water under neutral conditions

[1066-54-2]	TSCA	EC 213-919-9	HMIS: 2-4-1-X	5g	25g

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	Name	MW	bp °C/mm (mp)	D4 ²⁰	n _D ²⁰
	SIH5848.0				
	1-HEPTYNYLTRIMETHYLSILANE				
	C ₁₀ H ₂₀ Si	168.35 Flashpoint: 4	176° 2°C (108°E)		1.4344
Si	Useful in silicon-mediated Sonogashira cross-coupling 1. Larson, G. L. " <i>Silicon-Based Cross-Coupling Reagen</i> See also SIC2325.6 HYDROI YTIC SENSITIVITY 4: no reaction with water	reactions. ¹ ts" Gelest, Inc. 2011.	005		
	[15719-56-9] HMIS: 2-2	-1-X	10g		
	SII6452.2				
/	C ₅ H ₉ ISi	224.11	130°	1.460	1.511
I—————————————————————————————————————	Light sensitive Intermediate for benzofused nitrogen heterocycles. ¹ 1. Mak, X. et al. <i>J. Org. Chem.</i> 2011 , 76, 1852. See also SIB1907.0				
	HYDROLYTIC SENSITIVITY: 4: no reaction with water	under neutral condition	ons		
	[18103-47-8] HMIS: 2-3	- I-X Store < 5 C	1.0g		
		drofuran (12,13 wat ⁰	(1)		
1	C_8H_9LiSi	104.15 Flashpoint: -	°) 14°C (7°F)	0.829	
L'	Forms conductive anisotropic films on reaction with hal	otriazines. ¹			
Li————————————————————————————————————	 Intermediate for synthesis of alkylgalliumacetylides.² 1. Kouvetakis, J. <i>Chem. Mater.</i> 1994, 6, 636. 2. Lee, K. et al. <i>J. Organomet. Chem.</i> 1993, 449, 53. See also SIT8594.1 				
	HYDROLYTIC SENSITIVITY: 8: reacts rapidly with mo	isture, water, protic s _1_X	olvents	Da	
			209 10	-9	
	CtoHtaSi	160.29	33-4°/0.3	0.906	1.5407
	H	Flashpoint: 7	′6°C (169°F)	0.000	
	HYDROLYTIC SENSITIVITY: 3: reacts with aqueous ba	ase			
	[87290-97-9] HMIS: 2-2	-1-X	5g		
	SNP6734				
	PHENYLETHYNYLTRI-n-BUTYLTIN, 95%				
	$C_{20}H_{32}Sn$	391.17		1.116	1.5320
Sp C ₄ H ₉		Flashpoint: 1	13°C (235°F)		
C4H9 C4H9	[3757-88-8] HMIS: 3-2	510 1-X	10a		
	SIP6736.0				
	C ₁₁ H ₁₄ Si	174.32	67° / 5	0.896	1.5284
		Flashpoint: 8	32°C (180°F)		
	Reacts with tetraphenylcyclopentadienone to form penta	phenylphenyltrimethy	/Isilane. ¹		
	Cross couples with aryl halides and triflates as well as h	nomocouples to 1,2-d	iynes. ²		
	Undergoes alkynyl cross metathesis reactions. ³				
	Provides the ethynyl silver acetylide. ⁴	_			
	Reacts w/ propargyl chlorides to form 1,2-diene-4-ynes	5			
Si-Si-	— Ethynylsilanes react w/ propargyl halides to form 1,4-dig	/nes. ⁶			
	1. Jianhua, C. et al. In <i>Silicon Chemistry;</i> Corey, J., et a	I. Ed.; Wiley: 1988: p.	. 105.		
	2. Nashihara, Y. et al. <i>J. Org. Chem.</i> 2000 , 65, 1780.				
	5. Fulstner, A., Matnes, C. Org. Lett. 2001, 5, 221. 4. Vitérisi A. et al. <i>Tetrahedron Lett.</i> 2006 , 47, 2779				
	5. Montel, F. et al. <i>Org. Lett.</i> 2006 . <i>8</i> . 1905.				
	6. Kuninobu, Y.; Ishii, E.; Takai, K. Angew. Chem., Int. E	d. Engl. 2007 , 46, 329	96.		
	See also SIB1760.0 BIS(PHENYLETHYNYL)DIMETHY	LSILANE			
	HYDROLYTIC SENSITIVITY: 1: no significant reaction	with aqueous system	S		
	[2170-06-1] HMIS: 2-2	-1-X	5g 2	5g	

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	Name		MW	bp °C/mm (mp)	D4 ²⁰	n _D ²⁰				
	SIT8588.6			,		_				
	4-(TRIMETHYLSILYL)DIPHENYLACETYLENE									
	[4-(PHENYLETHYNYL)PHENYL]TRIMETHYLSILANE									
	C ₇ H ₁₈ Si		250.42	(37-41°)						
	HYDROLYTIC SENSITIVITY: 4: no reaction with water under neutral conditions									
	[136459-72-8] H	IMIS: 2-2-1-X	store <5°C	5g						
	SIT8588.63									
	4-[(TRIMETHYLSILYL)ETHYNYL]BENZALDEHYD	DE								
	$C_{12}H_{14}OSi$	202.33 (66-70								
	1. McDonald, A. et al. <i>J. Organomet. Chem.</i> . 2009 , 694, 2153.									
	HYDROLYTIC SENSITIVITY: 7: reacts slowly	with moisture/w	vater							
	[77123-57-0] H	IMIS: 2-2-1-X		5g						
	SIT8588.7									
/	2-[(TRIMETHYLSILYL)ETHYNYL]TOLUENE									
	C ₁₂ H ₁₆ Si		188.34	50-58° / 0.5	0.88	1.5320				
si-	See also SIP6736.0		Fiashpoint: 90*	U (194 F)						
	HYDROLYTIC SENSITIVITY: 4: no reaction with	ith water under r	neutral condition	s						
	[3989-15-9] H	IMIS: 2-2-0-X	store <5°C	5g						
Sn	SIT8588.8									
	TRIMETHYLSILYLETHYNYLTRI-n-BUTYLTIN									
	1-TRIBUTYLSTANNYL-2-TRIMETHYLSILYLACETYLE	ENE	387.26	128-8° / 22	1 055	1 475				
	Converts vinvl mesulates to envnes. ¹		307.20	120-0 / 22	1.000	1.475				
· · ·	1. Barret, D. et al. <i>J. Antibiotics</i> 1997, <i>50</i> , 100.									
	HYDROLYTIC SENSITIVITY: 4: no reaction with	ith water under r	neutral condition	S						
-	[81353-38-0] H	IMIS: 3-1-0-X		10g						
	SIT8589.7									
	1-TRIMETHYLSILYL-1-HEXYNE		154 33	155°	0 770	1 431				
1	C3110Ci		Flashpoint: 37°	°C (99°F)	0.110	1.101				
Si	Undergoes Pd-catalyzed hydroesterification to	form β-ethoxyvi	nylsilanes.1							
	1. Takeuchi, R. J. Chem. Soc., Perkin. Trans.	1 1993, 1031.	and a second	_						
	HYDROLYTIC SENSITIVITY: 4: no reaction wi [3844-94-8] H	ith water under r	neutral condition	5a						
	SIT8597 0			~3						
	1-TRIMETHYLSILYL-14-PENTADIYNE									
			136.27	42° / 25	0.789					
Si			Flashpoint: 8°C	C (46°F)						
	See also SIB1854.0	: 41- · · · - 4 - · · · · · - 1 - · · ·		_						
	HYDROLYTIC SENSITIVITY: 4: no reaction with water under neutral conditions [71789-10-1] HMIS: 2-4-1-X 5-9									
	SIT8604 0			09						
	3-TRIMETHYLSILYL-2-PROPYN-1-OL									
/	C ₆ H ₁₂ OSi		128.25	170-2°	0.875	1.4518				
			Flashpoint: 65°	°C (149°F) al rat I D50: 150 mg/kg						
	I UXICITY: oral rat, LD50: 150 mg/kg Hydromagnesiation of triple bond vields intermediates for terpene synthesis									
но́∖	Useful in silicon-mediated Sonogashira cross-coupling reactions to give substituted propargyl alcohols. ¹									
	1. Larson, G. L. "Silicon-Based Cross-Coupling	g Reagents" Gel	est, Inc. 2011.							
	F&F: Vol. 10, p 70; Vol. 11, p 164. HYDROLYTIC SENSITIVITY: 4: no reaction wi	ith water under r	neutral condition	s						
	[5272-36-6] TSCA FC 226-094-5 H	IMIS: 3-2-0-X		- 5α	25a					
				-9	J					

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	Name	MW	MW bp °C/mm (mp)		D₄ ²⁰	n _D ²⁰				
	SIT8605.0			,		5				
	3-TRIMETHYLSILYLPROPARGYLMETHACRYLATE 95%									
	3-METHACRYLOXYPROP-2-YNYLTRIMETHYLSILANE									
0	$C_{10}H_{16}O_2Si$	196.32								
$\rightarrow 0$	/	CAUTION: SE	NSITIZER							
	Forms polymers that undergo "click" chemistry. ¹²									
	1. Quemener, D. et al. J. Polym. Sci., Part A: Polym. Chem. 3 2. Ladmiril V. et al. J. Am. Chem. Soc. 2006 , 128, 4823	2008, 46, 155.								
	HYDROLYTIC SENSITIVITY: 4: no reaction with water under	neutral conditions								
	[214268-06-1] HMIS: 3-3-1-X	store <5°C	2.5g							
	SIT8606 3									
	CeHtoQSi	126.23	52° / 30		0.862	1.443				
,		Flashpoint: 29°0	C (84°F)							
	Used in the preparation of 1,3,5-triynes. ¹									
	Potential for the synthesis of 3-substituted alkynals. ²									
ő	1. Mukai, C. et al. <i>J. Org. Chem.</i> 2001, 66, 5875.									
0	2. Larson, G. L. "Silicon-Based Cross-Coupling Reagents" Gelest, Inc. 2011									
	HYDROLY HC SENSITIVITY: 4: no reaction with water under neutral conditions									
			209							
		112 25	99-100°	(-69°)	0 758	1 4091				
	C0.120	Flashpoint: -3°C	C (27°F)	(00)	0.100	1.1001				
	Forms polymers with very high oxygen permeability. ¹		- /							
	Polymerization catalyzed with TaCl ₅ /(C_6H_5) ₃ Bi ²									
	Converts aldehydes to 1,3-dienes in presence of $Cp_2Zr(H)CI$	3								
/	Synthetic reagent. ⁴									
/	Used in the preparation of alkynylxenon fluoride. ⁵									
Si	Useful in silicon-mediated Sonogashira cross-coupling reacti	ons.°								
\ \	1. Masuda, I. et al. J. Am. Chem. Soc. 1983 , 105, 1413. 2. Masuda, T. et al. J. Polym. Sci. Part A. Polym. Chem. 19	87 25 1353								
X	3. Maeta, H. et al. <i>Tetrahedron Lett.</i> 1992, 33, 5969.	57, 20, 1000.								
	4. F&F: Vol. 2, p 239; Vol. 6, p 638.									
	5. Schmidt, H. et al. Inorg. Chem. 2004, 43, 1837.									
	6. Larson, G. L. "Silicon-Based Cross-Coupling Reagents" G	elest, Inc. 2011.								
	See also SIB1931.0, SIT8386.0									
	HYDROLYTIC SENSITIVITY: 4: no reaction with water under [6224-91-5] TSCA EC 228-314-5 HMIS: 2-4-0-X	r neutral conditions	50	25a						
			Jy	ZJY						
	S118606.6									
		140.00	105 0° / 10	(47.0%)						
HO /	C6H10O2SI	Flashpoint: 96°(C (205°E)	(47-9)						
>	Potential for the preparation of propiolic acid derivatives. ¹		5 (200 1)							
	1. Larson, G. L. "Silicon-Based Cross-Coupling Reagents" G	elest. Inc. 2011.								
0 ,	See also SIT8623.0									
	HYDROLYTIC SENSITIVITY: 4: no reaction with water under	r neutral conditions	;							
	[5683-31-8] HMIS: 3-1-1-X		5g							
	SIT8606.7									
	(3-TRIMETHYLSILYL-2-PROPYNYL)TRIPHENYLPHOSPHONI	UM BROMIDE								
	C ₂₄ H ₂₆ BrPSi	453.44		(166-7° dec)						
	Wittig Reagent									
	Employed in synthesis of terminal enynes. ^{1,2}									
Si	1. Corey, E. J.; Ruden, R. A. <i>Tetrahedron Lett.</i> 1973 , <i>14</i> , 1495 2. Corey, E. J. et al. <i>Tetrahedron Lett.</i> 1973 , <i>14</i> , 3963).								
	HYDROLYTIC SENSITIVITY: 6: forms irreversible hydrate									
	[42134-49-6] HMIS: 3-2-1-X		5g							
	SIT8623.0									
	TRIMETHYLSILYL (TRIMETHYLSILYL)PROPYNOATE									
	C ₉ H ₁₈ O ₂ Si ₂	214.42	64-5° / 1.5			1.4400				
/	/	Flashpoint: 43°0	C (109°F)							
∖ o—si	 Potential for the synthesis of 3-substituted propiolic acid deriv 	atives.1								
si	1. Larson, G. L. "Silicon-Based Cross-Coupling Reagents" G	elest, Inc. 2011								
	HYDROLYTIC SENSITIVITY: 7: reacts slowly with moisture	/water	0.5							
0	[9/92/-35-0] HMIS: 3-2-1-X	store <5°C	2.5g							

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