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SHORT COMMUNICATION

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Activation of Si–Si Bonds for Copper(I)-Catalyzed Conjugate Silylation

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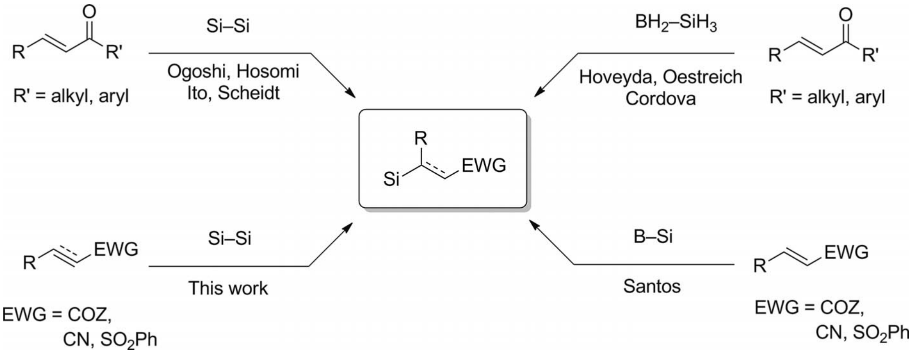
Several alkyl- and vinylsilanes were prepared through the copper(I)-catalyzed conjugate silylation of α,β-unsaturated compounds. Optimal reaction conditions were first investigated to realize the conjugate addition of a nucleophilic silicon species to poorly electrophilic acceptors such as phenylvinyl sulfone by cleavage of the Si–Si bond of a disilane reagent. The scope of this reaction was extended to various electrophiles bearing different electron-withdrawing groups and afforded the desired substituted alkyl- and vinylsilanes. Among the wide range of commercially available disilanes, the reactivities of alkyl-, aryl-, and ethoxydisilane were also examined.

Introduction

New methods for the preparation of organosilicon compounds have received increased attention owing to the applications of organosilicon compounds as reagents in organic synthesis and their interesting properties in functional materials.[1] Among the different methods, the metal-mediated conjugate addition of nucleophilic silicon is particularly attractive, because it leads to the formation of functionalized β-silyl carbonyl compounds.[2] Although the use of commercially available disilanes has been studied, the generation of nucleophilic silicon by activation of a Si–Si bond[3] from disilanes is limited to Pd-[4] and Cu-catalyzed[5] conjugate silylation of enones and enals. More recently, Scheidt reported an extension of this method to α,β-unsaturated esters, but that study was restricted to the case of highly electrophilic alkylidene malonates.[6] This limitation can be overcome by the use of silylboranes such as Suginome's dimethylphenylsilylpinacolatoboron.[7] Very recently, Santos successfully applied this strategy to various α,β-unsaturated compounds.[8] However, despite the efficiency of the activation of the Si–B bond[9] by transition metals (Cu, Rh)[10,11] or N-heterocyclic carbenes,[12] this approach suffers from a lack of atom economy,[13] as these reagents required an additional step for their synthesis.[7]

In connection with our recent efforts on the development of Cu-catalyzed 1,4-additions[14] and on the use of organosilicon reagents,[15] we report herein a general method for the conjugate silylation of various α,β-unsaturated compounds using disilanes (Scheme 1).



Scheme 1. General route to β-silyl carbonyl compounds by 1,4-addition.

Results and Discussion

The catalytic system was first optimized on the model reaction of commercially available diphenyltetramethyldi-

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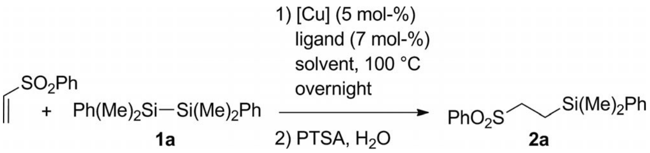
silane (**1a**) with phenylvinyl sulfone in the presence of Cu^I salts (5 mol-%) followed by an acidic workup. After screening the copper sources with the use of cataCXiumA as the ligand in DMF at 100 °C (Table 1, Entries 1–3), $(CuOTf)_2{\cdot}C_6H_6$[16] appeared as the most efficient salt, yielding **2a** in 38 % yield, whereas CuI gave a lower yield of 33 %. Surprisingly, no reaction occurred with CuCl. Subsequently, a wide range of ligands (phosphanyl and amino ligands, Figure 1) was explored (Table 1, Entries 4–9). CyJohnPhos and phenanthroline provided similar results, affording desired silylated compound **2a** in 52 and 53 % yield, respectively. Given the low price of phenanthroline, it was selected as the ligand of choice. Finally, the influence of the solvent was found to be crucial to activate the disilane,[5] and we were delighted to observe that, among the aprotic polar solvents tested, *N*,*N′*-dimethyl-*N*,*N′*-propylene urea (DMPU; Table 1, Entry 12) dramatically improved the yield of the reaction, providing **2a** in 80 % yield.

Table 1. Optimization of the reaction conditions.



Entry	[Cu]	Ligand	Solvent	Yield [%]
1	$(CuOTf)_2{\cdot}C_6H_6$	cataCXiumA	DMF	38
2	CuI	cataCXiumA	DMF	33
3	CuCl	cataCXiumA	DMF	–[a]
4	$(CuOTf)_2{\cdot}C_6H_6$	PBu_3	DMF	40
5	$(CuOTf)_2{\cdot}C_6H_6$	SPhos	DMF	47
6	$(CuOTf)_2{\cdot}C_6H_6$	CyJohnPhos	DMF	52
7	$(CuOTf)_2{\cdot}C_6H_6$	2-ethylpyridine	DMF	47
8	$(CuOTf)_2{\cdot}C_6H_6$	di-*tert*-butylbipyridine	DMF	43
9	$(CuOTf)_2{\cdot}C_6H_6$	phenanthroline	DMF	53
10	$(CuOTf)_2{\cdot}C_6H_6$	phenanthroline	HMPA	54
11	$(CuOTf)_2{\cdot}C_6H_6$	phenanthroline	DMI	40
12	$(CuOTf)_2{\cdot}C_6H_6$	phenanthroline	DMPU	80

[a] No reaction.

Diphenyltetramethyldisilane (**1a**) was subjected to the previously optimized cleavage conditions by using Cu^I salts [$(CuOTf)_2{\cdot}C_6H_6$ (5 mol-%), phenanthroline (7 mol-%), in DMPU at 100 °C, overnight, followed by acidic workup using *p*-toluenesulfonic acid in water] to generate a nucleophilic silicon species, which was then trapped with several 1,4-acceptors such as sulfono, cyano, amido, and phosphonato groups (Table 2, Entries 1–4). Phenyl vinyl sulfone emerged as a very efficient acceptor for this reaction, as previously reported, yielding the corresponding silylated product in 80 % yield (Table 2, Entry 1). Acrylonitrile was also found to be a suitable partner for this transformation, affording desired **3a** in 60 % yield (Table 2, Entry 2). In the case of less electrophilic substrates such as amides and phosphonates, more limited results were obtained. A moderate yield of 38 % was observed with unsaturated amide **4a** (Table 2, Entry 3), and no reaction occurred with α,β-unsaturated diethylvinylphosphonate **5a** (Table 2, Entry 4).

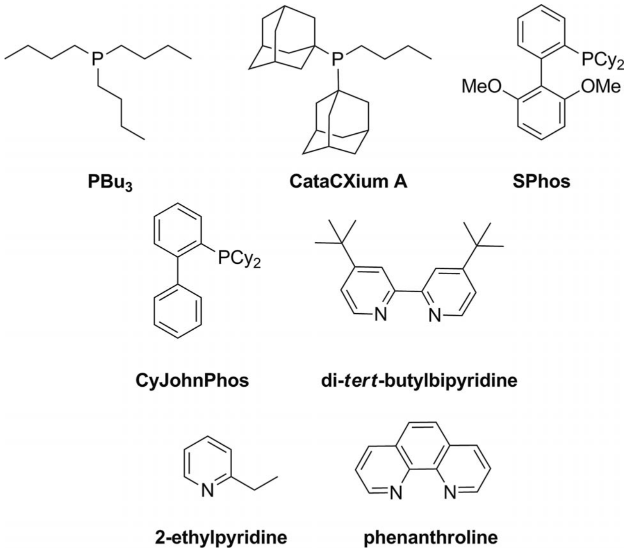
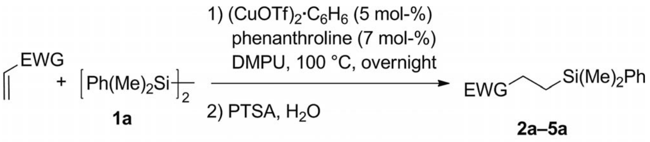
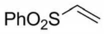
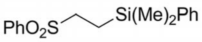
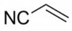
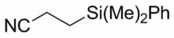
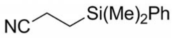


Figure 1. Ligands utilized in optimization studies.

Table 2. Scope of the α,β-unsaturated substrates.

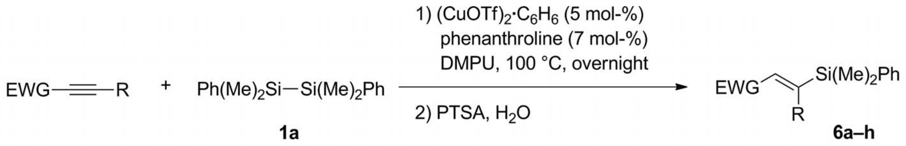


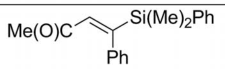
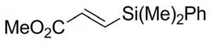
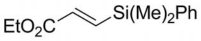
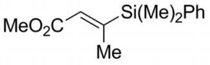
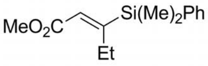
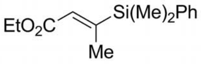
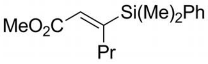
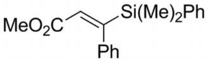
Entry	EWG 	Product		Yield [%]
1			**2a**	80
2			**3a**	60
3			**4a**	38
4		–	**5a**	–[a]

[a] No reaction.

Interestingly, the designed conditions could be extended to the use of alkynes, leading to a new route for the preparation of vinylsilanes (Table 3).[17] Hence, phenylbutynone allowed the formation of the corresponding silylated compound **6a** in 74 % yield (Table 3, Entry 1). Less-reactive alkynyl esters also proved to be suitable partners, and methyl and ethyl propiolates afforded desired **6b** and **6c** in 51 and 41 % yield, respectively (Table 3, Entries 2 and 3). A mixture of two inseparable isomers was obtained with a predominant *E* configuration, as determined by ^{1}H NMR spectroscopy. The same trend was observed for the other alkyl-substituted alkynes, which led to the formation of functionalized vinylsilanes **6d**–**g** in moderate yields with various *E*/*Z* ratios (Table 3, Entries 4–7). Complete stereoselectivity in favor of the *E* isomer was only observed in the cases of phenyl-substituted alkynes, albeit in a reduced yield in the case of the propiolate (Table 3, Entries 1 and 8).

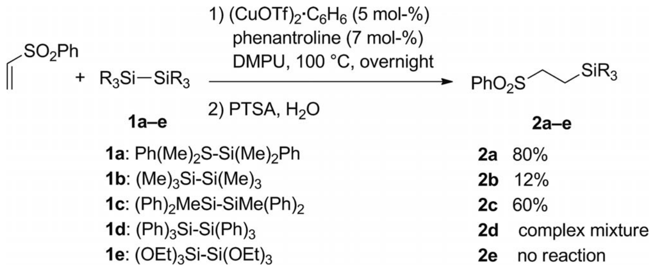
Table 3. Scope of the alkynes.



Entry	$EWG{-}{\equiv}{-}R$	Product		Isomeric ratio (E/Z)[a]	Yield [%]
1	$Me(O)C{-}{\equiv}{-}Ph$		**6a**	100:0	74
2	$MeO_2C{-}{\equiv}$		**6b**	90:10	51
3	$EtO_2C{-}{\equiv}$		**6c**	87:13	41
4	$MeO_2C{-}{\equiv}{-}Me$		**6d**	66:34	53[b]
5	$MeO_2C{-}{\equiv}{-}Et$		**6e**	55:45	60
6	$EtO_2C{-}{\equiv}{-}Me$		**6f**	73:27	40
7	$MeO_2C{-}{\equiv}{-}Pr$		**6g**	63:37	31
8	$MeO_2C{-}{\equiv}{-}Ph$		**6h**	100:0	27

[a] Isomeric ratio determined by ^1H NMR spectroscopy. [b] Mixture of **6d** and silane (trace amounts).

Finally, owing to the ability of diphenyltetramethyldisilane (**1a**) to generate a nucleophilic silicon species in the 1,4 addition reactions, we decided to expand the scope of our method to other commercially available disilanes by using phenyl vinyl sulfone as the acceptor (Scheme 2). We started our investigation with hexamethyldisilane (**1b**), and expected alkylsilane **2b** was detected in a low yield of 12%, probably because of the volatility of the disilane reagent. Tetraphenyldimethyldisilane (**1c**) emerged as a suitable partner for this transformation, leading to **2c** in 60% yield. Unfortunately, the use of hexaphenyldisilane (**1d**) only led to a complex mixture of unidentified products, and no reaction occurred with hexaethoxydisilane (**1e**), as the starting materials were recovered.



Scheme 2. Variation of disilanes.

Conclusions

In summary, we have demonstrated that the copper-catalyzed conjugate silylation by using disilanes can be applied to a good range of α,β-unsaturated compounds. Various electrophiles bearing different electron-withdrawing groups were successfully used, and this method appears as a useful and direct route for the preparation of substituted alkyl- and vinylsilanes.

Experimental Section

Procedure for Silylation: $Cu(OTf)_2{\cdot}C_6H_6$ (0.025 mmol, 12.5 mg) and phenanthroline (0.035 mmol, 6.3 mg) were placed in a Biotage microwave vial under an atmosphere of argon and DMPU (1 mL) was added. After stirring for 5 min at room temperature, the α,β-unsaturated compound (0.5 mmol) and disilane (0.6 mmol) were added, and the reaction mixture was heated conventionally to

100 °C overnight. After cooling to room temperature, water (100 µL) and *p*-toluenesulfonic acid (5 mg) were added, and the reaction mixture was stirred for 30 min. Then, the crude mixture was dissolved in Et$_2$O and washed several times with H$_2$O, dried (Na$_2$SO$_4$), concentrated in vacuo, and purified by flash column chromatography (hexanes/EtOAc).

Supporting Information (see footnote on the first page of this article): General considerations, characterization data, and copies of the ^{1}H NMR and ^{13}C NMR spectra.

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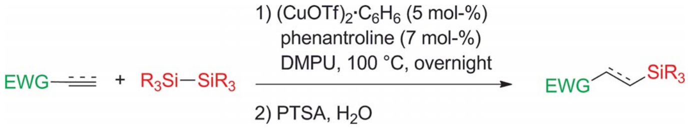
Conjugate Addition



Alkyl- and vinylsilanes were prepared through copper(I)-catalyzed conjugate addition through activation of Si–Si bonds. Electrophilic substrates such as activated alkenes containing sulfono, cyano, and amido groups were used as acceptors for this transformation, and ester-substituted alkynes also emerged as suitable partners, leading to a new method for the generation of vinylsilanes.

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Activation of Si–Si Bonds for Copper(I)-Catalyzed Conjugate Silylation

Keywords: Silanes / Copper / Nucleophilic addition / Alkenes / Silicon

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