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One-Step Preparation of Functionalized (*E*)-Vinylsilanes from Aldehydes

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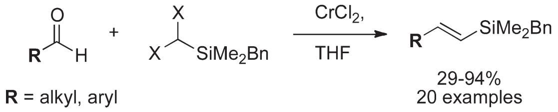
ABSTRACT



Functionalized (*E*)-vinylsilanes have been prepared in one step from a wide range of aldehydes, via a chromium(II)-mediated olefination with novel dihalomethylsilane reagents, in moderate to excellent yields and with excellent stereoselectivity.

Organosilanes are versatile functionalities in the synthetic chemist's toolbox, offering a convenient and inexpensive means to create new carbon–carbon[1] or carbon–heteroatom[1b,2] bonds while remaining compatible with a range of chemical manipulations.[3] For example, vinylsilanes have been employed with great efficacy in organic synthesis, as direct mediators of carbon–carbon bond formation through the nucleophilic capture of cations,[1b,4] in Hiyama cross-coupling reactions,[1c,5] and also as substrates for Tamao-Fleming oxidations in which they represent masked carbonyl groups.[6]

Hiyama cross-coupling in particular represents an extremely important application, which usually requires the silane to be functionalized with a heteroatom (or other readily substituted group)[7] so that it can be activated toward transmetalation on treatment with a fluoride source or a base.[8] "Safety-catch" silanols, which are stable to conditions

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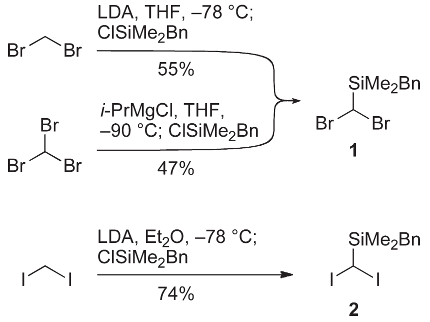
that heteroatom-substituted silanes may not tolerate but which can nonetheless be activated toward cross-coupling in a similar manner, are a particularly important subclass.[8k,9]

Regio- and stereoselective access to functionalized vinylsilanes has primarily been achieved via the transition metal-catalyzed hydrosilylation of alkynes[10] and from vinyl halides via metal–halogen exchange/carbanion silylation.[11] As these vinylsilane precursors are themselves often prepared from aldehydes, a direct synthesis of functionalized vinylsilanes from aldehydes would represent a valuable means to bypass an additional functional group manipulation. To our knowledge, the only direct preparation of functionalized vinylsilanes from aldehydes has been reported by Yoshida and coworkers and involves the formation of 2-pyridyldimethylsilyl alkenes through the Peterson olefination of a *bis*-pyridylsilyl carbanion.[12] While this route affords (*E*)-vinylsilanes in good yields and excellent stereoselectivity, the reaction is necessarily conducted under strongly basic conditions, which may limit functional group tolerance. In contrast, the preparation of nonfunctionalized vinylsilanes (i.e., trialkylvinylsilanes) from aldehydes has much greater precedent. In particular, the Takai silylolefination of aldehydes with chromium(II) chloride and Me$_3$SiCHBr$_2$, which affords (*E*)-vinylsilanes with high stereoselectivity,[13] is well-recognized as a valuable and reliable tool for the stereoselective synthesis of alkenyl trimethylsilanes.

Scheme 1. Preparation of Dihalomethyl Benzyldimethylsilane Reagents **1** and **2**



In the course of investigations into the total synthesis of polyene-containing natural products, we required a mild and selective method for the synthesis of a vinylsilane suitable for Hiyama coupling and recognized that application of a Takai-type olefination using a functional dihalomethylsilane reagent might offer a solution to this problem. While the Takai olefination has been extended to the synthesis of vinylboronic esters using pinBCHBr$_2$,[13c,14] an analogous "functionalized" silylation has not yet been realized but would certainly represent a powerful means to access such useful vinylsilanes. We report herein the development of this process and its application to a wide range of aldehydes.

Our investigations began with the selection of the benzyldimethylsilyl group as a representative "safety-catch" silanol, which has been shown to possess stability toward acidic and basic reaction conditions but can be activated by a fluoride source to participate in cross-coupling[8k,9a−9f] and oxidation reactions.[6e,9c,15] The dihalomethyl benzyldimethylsilane reagents **1** and **2** (Scheme 1) were conveniently prepared on a multigram scale by treating the corresponding dihalomethanes with LDA, followed by trapping of the lithium carbanion with benzylchlorodimethylsilane (Scheme 1).[16] Dibromide **1** could also be prepared from the Grignard reagent formed *in situ* from treatment of bromoform with *iso*-propylmagnesium chloride.[17] Although **1** can be stored indefinitely at room temperature without decomposition, diiodide **2** gradually turns

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(15) Trost, B. M.; Ball, Z. T.; Laemmerhold, K. M. *J. Am. Chem. Soc.* **2005**, *127*, 10028–10038.

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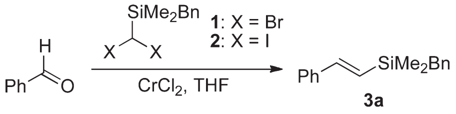
(17) Seyferth, D.; Lambert, R. L.; Hanson, E. M. *J. Organomet. Chem.* **1970**, *24*, 647–661.

from a colorless to brown oil on storage for a month in the dark at 4 °C.

Reaction optimization studies were performed on benzaldehyde (Table 1), which we initially subjected to standard Takai olefination conditions of 2 equiv of **1** and 8 equiv of chromium(II) chloride in dry THF.[13a,18] To our delight, this resulted in complete consumption of benzaldehyde after 16 h and provided the desired vinylsilane **3a** in 74% isolated yield, with exclusive formation of the (*E*)-vinylsilane (entry 1). Reducing the equivalents of **1** and $CrCl_2$ to 1.3 and 6.0, respectively, resulted in complete conversion on the same time scale and a slightly improved yield (entry 2), although further efforts to lower the stoichiometry of either reagent led to incomplete conversion even after 24 h (entries 3 and 4).[19]

In an effort to reduce the reaction time scale, we next tested the olefination at elevated temperatures. Pleasingly, reaction at 50 °C led to complete conversion in just two hours, with no detriment to the stereoselectivity (E:Z > 99:1, entry 5). We anticipated that the diiodosilane reagent **2** might offer benefits over **1** in terms of reactivity and indeed found that this reagent maintained both the yield and selectivity of the olefination, but significantly reduced the reaction time at room temperature (entry 6). The most rapid silylolefination could be achieved using **2** at 50 °C, which reduced the reaction time to just 45 min (77%, E:Z > 99:1, entry 7). In our subsequent substrate evaluations, conditions corresponding to entries 2, 5, and 7 were employed.

Table 1. Silylolefination Optimization Studies

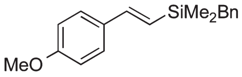
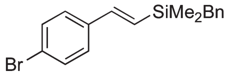
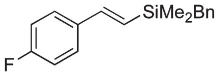
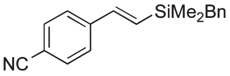
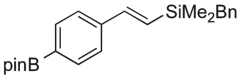
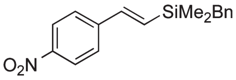
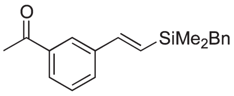
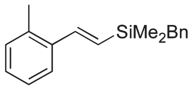
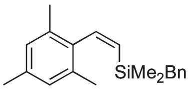
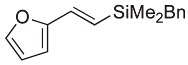
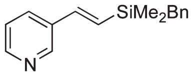


entry	silane (equiv)	$CrCl_2$ (equiv)	temp (°C)	time (h)	yield (%)[a] (conversion (%))[b]	E:Z[b]
1	**1** (2.0)	8.0	25	16	74 (100)	>99:1
2	**1** (1.3)	**6.0**	**25**	**16**	**82 (100)**	**> 99:1**
3	**1** (1.2)	6.0	25	24	74 (92)	>99:1
4	**1** (1.3)	4.0	25	24	53 (71)	>99:1
5	**1** (1.3)	**6.0**	**50**	**2**	**75 (100)**	**> 99:1**
6	**2** (1.3)	6.0	25	6.5	76 (100)	>99:1
7	**2** (1.3)	**6.0**	**50**	**0.75**	**77 (100)**	**> 99:1**

[a] Isolated yield. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

With this set of optimal reaction conditions established, a range of aldehydes were tested to determine the scope of the silylolefination. Initial screening of aromatic aldehydes (Table 2) revealed that *para*-substituted benzaldehydes generally afforded good to excellent yields of the corresponding vinylsilanes **3b**–**f** when treated with **1** (entries 1–5), with electron-rich, electron-poor, halogen, and boronic ester substituents all tolerated by the mild reaction conditions. In the latter case, heating of the reaction mixture (Conditions B) led to a slightly improved yield, and in all instances, complete selectivity for the (*E*)-vinylsilane was observed. The exception to this selection of substrates was *p*-nitrobenzaldehyde, for which no product was detected in the crude reaction mixture despite complete consumption of the starting material (entry 6), likely reflecting the susceptibility of the nitro group to reduction by chromium(II).[20]

Table 2. Preparation of (*E*)-Vinylsilanes from Aromatic and Heteroaromatic Aldehydes

entry		vinylsilane	condn[a]	time (h)	yield (%)[b] (conversion (%))[c]
1	**3b**		A	16	90 (100)
2	**3c**		A	36	82 (91)
3	**3d**		A	24	65 (100)
4	**3e**		B	4	75 (100)
5	**3f**		A B	24 3	78 (92) 86 (100)
6	**3g**		A	16	0 (100)
7	**3h**		A	24	92 (100)
8	**3i**		B	5	83 (100)
9	**3j**		B	24	29 (40)[d]
10	**3k**		A B	24 2	86 (100) 86 (100)
11	**3l**		A A C	16 16 1	0 (100) 45 (100)[e] 49 (100)[e]

[a] Reaction conditions: **A**: $BnMe_2SiCHBr_2$ (1.3 equiv), $CrCl_2$ (6.0 equiv), THF, 25 °C; **B**: $BnMe_2SiCHBr_2$ (1.3 equiv), $CrCl_2$ (6.0 equiv), THF, 50 °C; **C**: $BnMe_2SiCHI_2$ (1.3 equiv), $CrCl_2$ (6.0 equiv), THF, 50 °C. [b] Isolated yields; [c] Determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [d] Z:E = 13:1. [e] Quenched with aqueous EDTA.Na_2.

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(19) Chromium(II) chloride from a variety of sources (Sigma Aldrich (anhydrous, 99.99%) and Alfa Aesar (anhydrous, 97%)) was used.

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(21) The geometry of the alkene was characterised by a $^3J_{HH}$ value of 15.0 Hz, which is typical for (*Z*)-vinylsilanes; see ref 10e.

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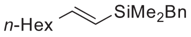
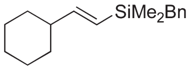
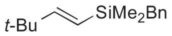
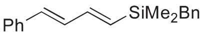
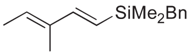
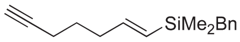
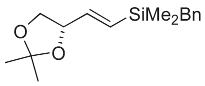
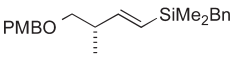
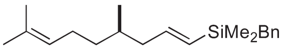
(23) See the Supporting Information for details.

Table 3. Preparation of (*E*)-Vinylsilanes from Conjugated and Aliphatic Aldehydes

entry		vinylsilane	condn[a]	time (h)	yield (%)[b] (conversion (%))[c]
1	**3m**		A	16	77 (100)
2	**3n**		A B	16 2	80 (100) 78 (100)
3	**3o**		A	24	77 (100)
4	**3p**		A	24	94 (100)
5	**3q**		A	16	82 (100)
6	**3r**		A	18	79 (100)
7	**3s**		A	16	61 (100)[d]
8	**3t**		A B	24 3	68 (100)[e] 79 (100)[f]
9	**3u**		B	3	81 (100)

[a] Reaction conditions: **A**: BnMe$_2$SiCHBr$_2$ (1.3 equiv), CrCl$_2$ (6.0 equiv), THF, 25 °C; **B**: BnMe$_2$SiCHBr$_2$ (1.3 equiv), CrCl$_2$ (6.0 equiv), THF, 50 °C. [b] Isolated yields. [c] Determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [d] 99% *ee*. [e] 74% *ee*; the aldehyde was prepared in 80% *ee* . [f] 60% *ee*.

In a manner reminiscent of other Takai olefinations, the reaction proved selective for aldehydes in the presence of ketones, as illustrated by the conversion of 3-acetylbenzaldehyde to **3h** (Table 2, entry 7). The presence of *ortho* substituents on the arene necessitated the use of heated reaction conditions (entries 8 and 9), with mesitaldehyde giving a low yield of silane **3j**, which intriguingly was formed in a 13:1 (*Z*:*E*) ratio.[21]

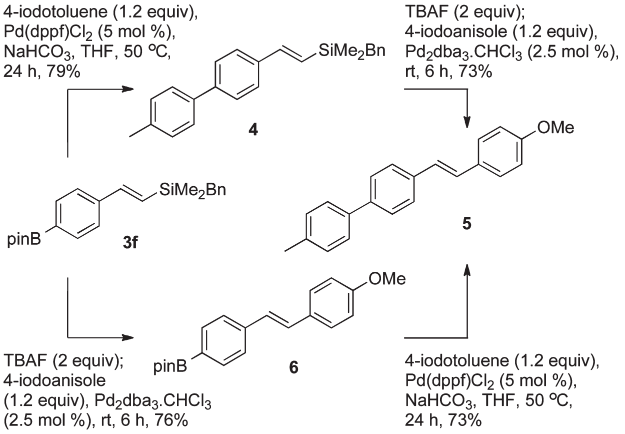
The reaction of heteroaromatic aldehydes proved more challenging; furfural required an extended reaction time to achieve a satisfactory yield of **3k** (Table 2, entry 10), although this could be improved to 2 h by employing Conditions B. In the case of nicotinaldehyde (entry 11), no product was detected despite complete consumption of starting material. Broadening of signals in the ^{1}H NMR spectrum of the crude reaction mixture suggested complexation of the pyridine to chromium, and pleasingly, quenching the reaction mixture with aqueous EDTA-Na$_2$ to sequester the chromium(III) salts successfully liberated the pyridyl group,[22] enabling the isolation of **3l** in moderate yields.

We next screened a range of nonaromatic aldehydes in the silylolefination (Table 3). Simple aliphatic aldehydes gave excellent yields (entries 1–3) with pivaldehyde being a particularly notable substrate that underwent complete conversion to **3o**. α,*β*-Unsaturated aldehydes readily provided dienes **3p** and **3q**, which are valuable building blocks for the synthesis of polyunsaturated compounds (entries 4 and 5). Vinylsilane **3r**, bearing a terminal alkyne and which would likely prove challenging to prepare via hydrosilylation, was isolated from hex-5-ynal in good yield (entry 6). To demonstrate the applicability of the reaction in more complex settings, a series of aldehydes containing other functional groups or stereogenic centers were subjected to the olefination. Vinylsilanes **3s**–**3u** were obtained with excellent stereoselectivity (E/Z > 99:1), with little or no epimerization of the adjacent stereocenters,[23] suggesting the reaction to be well suited for applications in synthesis.

Finally, we aimed to demonstrate the utility of the silylolefination through an application of a vinylsilane in cross-coupling. We selected the boronic ester product **3f**, which we could subject to sequential Hiyama and Suzuki cross-couplings. The orthogonal nature of the activation of silicon and boron cross-coupling partners enabled us to perform these operations in either order (Scheme 2). Thus, Suzuki coupling of **3f** with 4-iodotoluene gave the intermediate silane **4** in 79% yield; subsequent fluoride activation of the benzyldimethylsilyl group and Hiyama coupling with 4-iodoanisole provided the arylated product **5** (73%). Switching the order of these events resulted in an equally efficient synthesis (76 and 73% for the Hiyama and Suzuki couplings, respectively).

In conclusion, we have developed a mild and highly stereoselective method for the preparation of vinylsilanes suitable for cross-coupling or oxidation chemistry, via the chromium-mediated coupling of dihalomethylsilanes with aldehydes. Applications of this method in complex molecule synthesis will be reported in due course.

Scheme 2. Applications of Benzyldimethylvinylsilanes



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Supporting Information Available. Experimental procedures and spectroscopic data for reagents **1** and **2** and vinylsilanes. This material is available free of charge via the Internet at http://pubs.acs.org.