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# Stereoselective Synthesis of Allyl- or Alkynyl-Substituted (*Z*)-Vinylsilanes via Organoboranes

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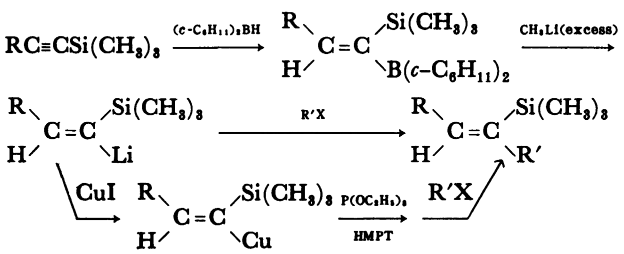
**Synopsis.** Copper(I) iodide-catalyzed cross-coupling reactions of (*Z*)-(1-trimethylsilyl-1-alkenyl)dicyclohexylboranes with allyl bromide or 1-bromo-1-hexyne gave stereoselectively (*Z*)-1,4-dienes or conjugated (*Z*)-enynes having a trimethylsilyl group on the internal carbon atom of the double bond.

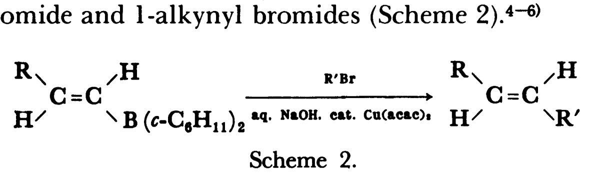
Vinylsilanes are versatile intermediate in organic synthesis.[1] There have been several approaches to the synthesis of these useful compounds. Uchida et al. reported a stereoselective synthesis of (*Z*)-vinylsilanes via (*Z*)-(1-trimethylsilyl-1-alkenyl)dicyclohexylboranes (**1**) starting from 1-trimethylsilyl-1-alkynes.[2] As depicted in Scheme 1, **1** were once transformed to the corresponding vinyllithium or vinylcopper(I) compounds before the cross-coupling reactions with organic halides while the reactions were carried out in situ. In the vinyllithium route, an excess amount of methyllithium, and in the vinylcopper(I) route, an excess amount of methyllithium and a small excess amount of copper(I) iodide were employed.



Scheme 1.

A similar cross-coupling reaction of (*Z*)-(1-trimethylsilyl-1-nonenyl)dicyclohexylborane with allyl bromide was performed by using stoichiometric amount of copper(I) bromide–methyl sulfide.[3]

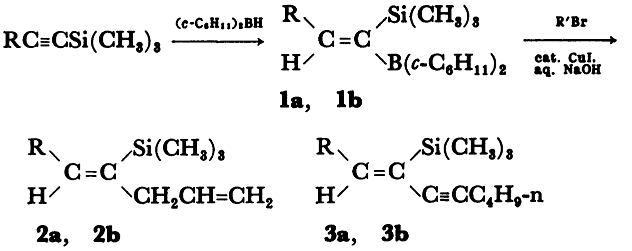
On the other hand, the authors have found that a catalytic amount of bis(acetylacetonato)copper(II) catalyzed a stereoselective cross-coupling reactions of alkenyldialkylboranes with organic bromides including allyl bromide and 1-alkynyl bromides (Scheme 2).[4–6]



Scheme 2.

Above facts suggested that it was probable to transform 1-trimethylsilyl-1-alkenyldicyclohexylboranes (**1a**) directly to (*Z*)-vinylsilanes by using catalytic amount of bis(acetylacetonato)copper(II).

As was suggested, (*Z*)-4-(trimethylsilyl)-1,4-nonadiene (**2a**) was obtained in 84% yield, uncontaminated by *E* isomer, in the reaction of **1a** with allyl bromide in the presence of 5 molar% of bis(acetylacetonato)copper(II). In further studies to increase the yield of **2a**, copper(I) iodide was found to be far more effective catalyst. Thus, **1a** was transformed to **2a** quantitatively in the presence of 10 molar% of copper(I) iodide (Scheme 3). The use of far less amount of copper(I) compound than in the reaction reported earlier seemed synthetically interesting.



**1a**, **2a**, **3a**; R=*n*-$C_4H_9$
**1b**, **2b**, **3b**; R=phenyl

Scheme 3.

Copper(I) chloride and copper(I) bromide showed little catalytic effect and the yields of **2a** could not exceed 76 and 78% respectively even in the presence of stoichiometric amount of these copper compounds.[2,3]

Similarly, (*Z*)-1-phenyl-2-(trimethylsilyl)-1,4-pentadiene (**2b**) was afforded in 92% yield from (*Z*)-(1-trimethylsilyl-2-phenylvinyl)dicyclohexylborane (**1b**) and allyl bromide.

The present reaction could be applied also to the synthesis of trimethylsilyl-substituted conjugated enynes which were expected to be interesting intermediates because of the unique position of the trimethylsilyl group in the molecule. Thus, similar reactions of **1a** and **1b** with 1-bromo-1-hexyne afforded (*Z*)-6-(trimethylsilyl)-5-dodecen-7-yne (**3a**) and (*Z*)-1-phenyl-2-(trimethylsilyl)-1-octen-3-yne (**3b**) in moderate yields respectively.

*Z*-Configuration was assigned to these compounds by direct comparisons of IR and $^1$H NMR spectra of 1,4-dienes and conjugated enynes, obtained by stereospecific desilylation of vinylsilanes[7] with those obtained by our previous work.[4]

These results are shown in Table 1.

All vinylsilanes obtained in the reactions were found to be isomerically pure by GLC using a glass capillary column and by $^1$H NMR spectra.

Reactions of **1a** and **1b** with alkyl bromides failed to give satisfactory results under the present reaction conditions.

## Experimental

**Instruments.** IR spectra (film) were recorded with a Hitachi 285 spectrometer. $^1$H NMR (60 MHz) spectra ($CCl_4$,

Table 1. Yields of Substituted (*Z*)-Vinylsilanes

| R | R′ | Cu compd | mol % | Product | Yield/%[a)] A | Yield/%[a)] B |
|---|---|---|---|---|---|---|
| *n*-$C_4H_9$ | $CH_2CH=CH_2$ | Cu-(acac)$_2$ | (5) | 2a | 47 | |
| | | CuCl | (100) | 2a | 76 | |
| | | CuBr | (100) | 2a | 78 | |
| | | CuI | (100) | 2a | 100 | |
| | | CuI | (10) | 2a | 100 | 91 |
| | | CuI | (5) | 2a | 93 | |
| $C_6H_5$ | | CuI | (10) | 2b | 92 | 86 |
| *n*-$C_4H_9$ | $C\equiv CC_4H_9$-n | CuI | (10) | 3a | 75 | 66 |
| $C_6H_5$ | | CuI | (10) | 3b | 78 | 70 |

a) The yields are based on 1-trimethylsilyl-1-alkynes. A; determined by GLC (5%-FFAP, supported on Diasolid M). B; isolated by column chromatography.

TMS) were run on a Hitachi R-20A spectrometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer.

**Reagents.** Cyclohexene and tetrahydrofuran (THF) were dried over lithium aluminium hydride and distilled under argon stream before use. 1-Trimethylsilyl-1-hexyne,[8)] 1-phenyl-2-(trimethylsilyl)acetylene[8)] and 1-bromo-1-hexyne[9)] were prepared as described in the literatures. Allyl bromide was dried over molecular sieves-4A. Commercial copper(I) iodide was used without any purification. THF solution of $BH_3$ was prepared by the method described in the literature.[10)]

**Reaction Procedure.** A 50-ml round bottomed flask, equipped with a gas inlet for argon, a sample inlet with a serum cap and a magnetic stirring bar, was flushed with argon. In the flask, 1-trimethylsilyl-1-alkyne (10 mmol) was added at 0 °C to the suspension of dicyclohexylborane (10 mmol) in THF, prepared by hydroboration of cyclohexene (20 mmol) with the THF solution of $BH_3$ (10 mmol) at 0 °C for 2 h, and then the reaction mixture was stirred at 0 °C for 1 h and then additional 1 h at room temperature in order to complete the reaction. Copper(I) iodide (1 mmol) and allyl bromide or 1-bromo-1-hexyne (10 mmol) were successively added to the solution at 0 °C and the solution was treated with 10 mmol of 3M[†]-NaOH at this temperature for 1 h. The residual boron compound was decomposed by oxidation with hydrogen peroxide. The reaction mixture was extracted three times with diethyl ether. The combined extracts were washed twice with NaCl-saturated water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was put on a column packed with silica gel (Wako-gel Q-50).

Spectral data of the products are as follows.

**(*Z*)-4-Trimethylsilyl-1,4-nonadiene (2a).** $^1$H NMR $\delta$=0.12 (s, 9H), 0.89 (m, 3H) 1.07—1.50 (m, 4H), 1.86—2.37 (m, 2H), 2.63—2.85 (m, 2H), 4.68—5.07 (m, 2H), and 5.40—6.07 (m, 2H). IR: 3075, 1640, 1615, 1250, 995, 910, 835, 760, and 685 cm$^{-1}$. MS: *m/z* 196 (M$^+$).

**(*Z*)-1-Phenyl-2-trimethylsilyl-1,4-pentadiene (2b).** $^1$H NMR $\delta$=0.15 (s, 9H), 3.03—3.24 (m, 2H), 5.00—5.40 (m, 2H), 5.68—6.39 (m, 1H), and 7.28 (s, 6H, one vinylic proton is contained). IR: 3075, 1645, 1595, 1495, 1440, 1260, 1000, 915, 840, 750, and 705 cm$^{-1}$. MS: *m/z* 216 (M$^+$).

**(*Z*)-6-Trimethylsilyl-5-dodecen-7-yne (3a).** $^1$H NMR $\delta$=0.12 (s, 9H), 0.83 (m, 6H), 1.06—1.55 (m, 8H), 1.84—2.34 (m, 4H), and 6.33 (t, *J*=7 Hz, 1H). IR: 1250, 840, and 755 cm$^{-1}$. MS: *m/z* 236 (M$^+$).

**(*Z*)-1-Phenyl-2-trimethylsilyl-1-octen-3-yne (3b).** $^1$H NMR $\delta$=0.13 (s, 9H), 0.99 (m, 3H), 1.18—1.76 (m, 4H), 2.23—2.60 (m, 2H), 7.23 (s, 5H), and 7.61 (s, 1H). IR: 1250, 840, 755, and 700 cm$^{-1}$. MS: *m/z* 256 (M$^+$).

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[†] 1 M = 1 mol dm$^{-3}$.