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Synthesis of *E*-Vinylsilanes from Olefins with Vicinal Silyl and Stannyl Substituents

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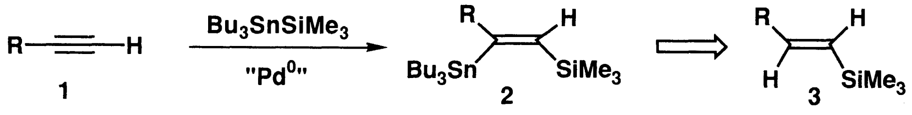
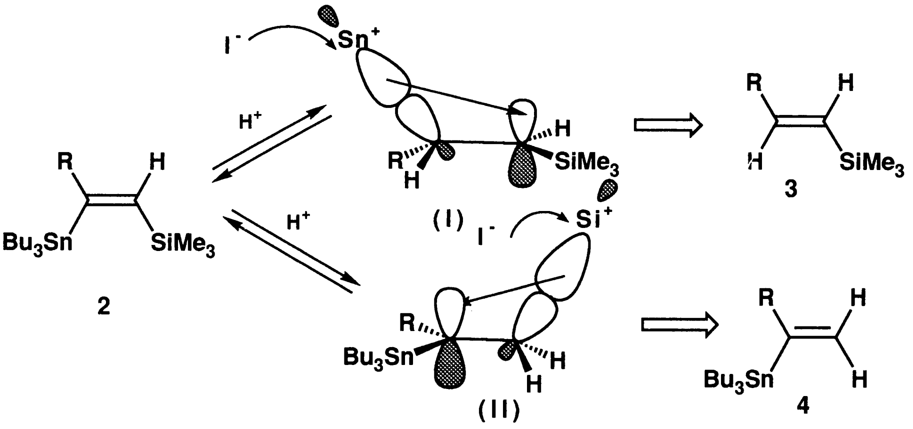
E-Vinylsilanes were synthesized regioselectively from olefins with vicinal silyl and stannyl substituents, prepared from the corresponding terminal alkynes, by destannylation with HI.

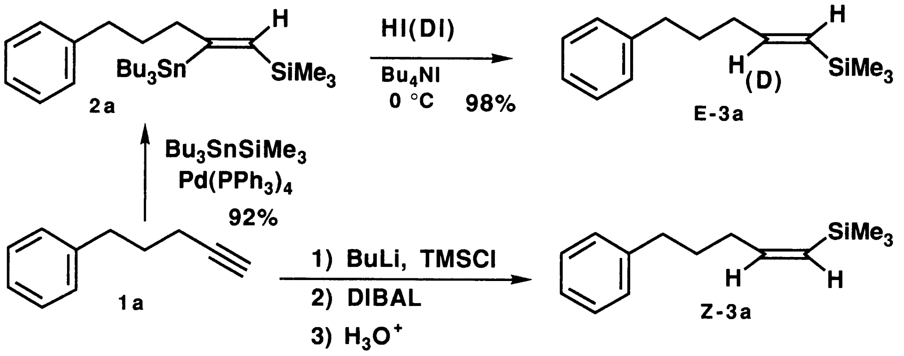
Bisfunctionalization of alkyne is quite interesting in synthetic organic chemistry because each functional group can be used for organic synthesis. Recently, Mitchell1) and Chenard2) independently reported that the reaction of terminal alkyne with $Bu_3SnSiMe_3$ in the presence of palladium catalyst gave bisfunctionalized alkene in good yields. During the course of our study of new cyclization by use of $Bu_3SnSiMe_3$ and R_4NX,3) we required isomeric pure *Z*-vinyl halide which was easily prepared from *E*-vinylsilane.4) Utimoto et al.5) reported that stereospecific exchange of Me_3Si for H proceeded on the olefin carbon by the action of hydriodic acid. They explained that protonation gives rise to carbocation stabilized and fixed by β-trimethylsilyl group. Then iodide ion attacks the silicon atom to produce the olefin with retention of configuration. If compound **2** prepared from terminal alkyne and $Bu_3SnSiMe_3$ in the presence of Pd(0) was treated with hydriodic acid, two intermediates (I) and (II) should be formed because of the stabilization effect of β-cation by silicon or tin.6) However, iodide ion would attack to stannane because of a reflection of the softness of a stannyl group compared to a silyl group toward the soft iodide ion.



Thus, to a toluene solution of compound **2a**, which was prepared from **1a** and $Bu_3SnSiMe_3$ in the presence of a catalytic amount of $Pd(PPh_3)_4$ (3 mol%) in THF, was added hydriodic acid (57%, 10 equiv.) at 0 °C and the solution was stirred at the same temperature for 1 h. After usual work up, we obtained destannylated compound **E-3a** in 98% yield. In order to confirm the stereochemistry of **E-3a**, 1-trimethylsilyl derivative of **1a** was treated with DIBAL followed by hydrolytic workup to give **Z-3a**. The chemical shifts and the coupling constants of vinylic proton of **Z-3a** on NMR spectrum were apparently different from those of **E-3a**[**E-3a**; 6.40(dt, J=18.6, 6.5 Hz, 1H), 5.65(dt,

J=18.6, 1.2 Hz, 1 H). **Z-3a**; 6.36(dt, J=13.0, 8.0 Hz, 1 H), 5.54(dt, J=13.0 Hz, 2.0 Hz, 1 H)]. Instead of hydriodic acid, deuterium iodide was used for the reaction to give deuterated compound **E-3a-D**, whose NMR spectrum shows that stereospecific exchange of Bu_3Sn for D proceeded on the stannylated carbon of **2a** [**E-3a-D**; 5.65(t, J=1.2 Hz, 1 H)].





Likewise, other E-vinylsilanes **3** are produced from various bisfunctionalized alkenes **2** in excellent yields as shown in Table 1. This reaction was superior for the synthesis of E-vinyl silane **3** having various functional groups such as ether, amine, ketone and ester groups. It was quite interesting that though desilylation of vinylsilane with HI proceeded smoothly at room temperature,4) E-vinylsilane was obtained in quantitative yield under the similar reaction conditions. This observation was in sharp contrast to the case of the reaction of **5** with Bu_4NF reported by Ritter7) where the corresponding vinyl stannane was exclusively formed. These results indicate that each group of bisfunctionalized olefin **2** by $R_3SnSiR'_3$ can be used for further reaction.

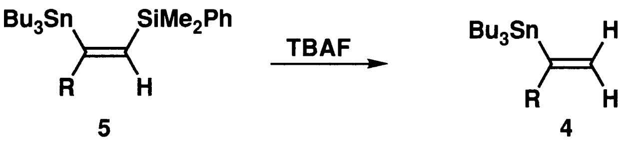
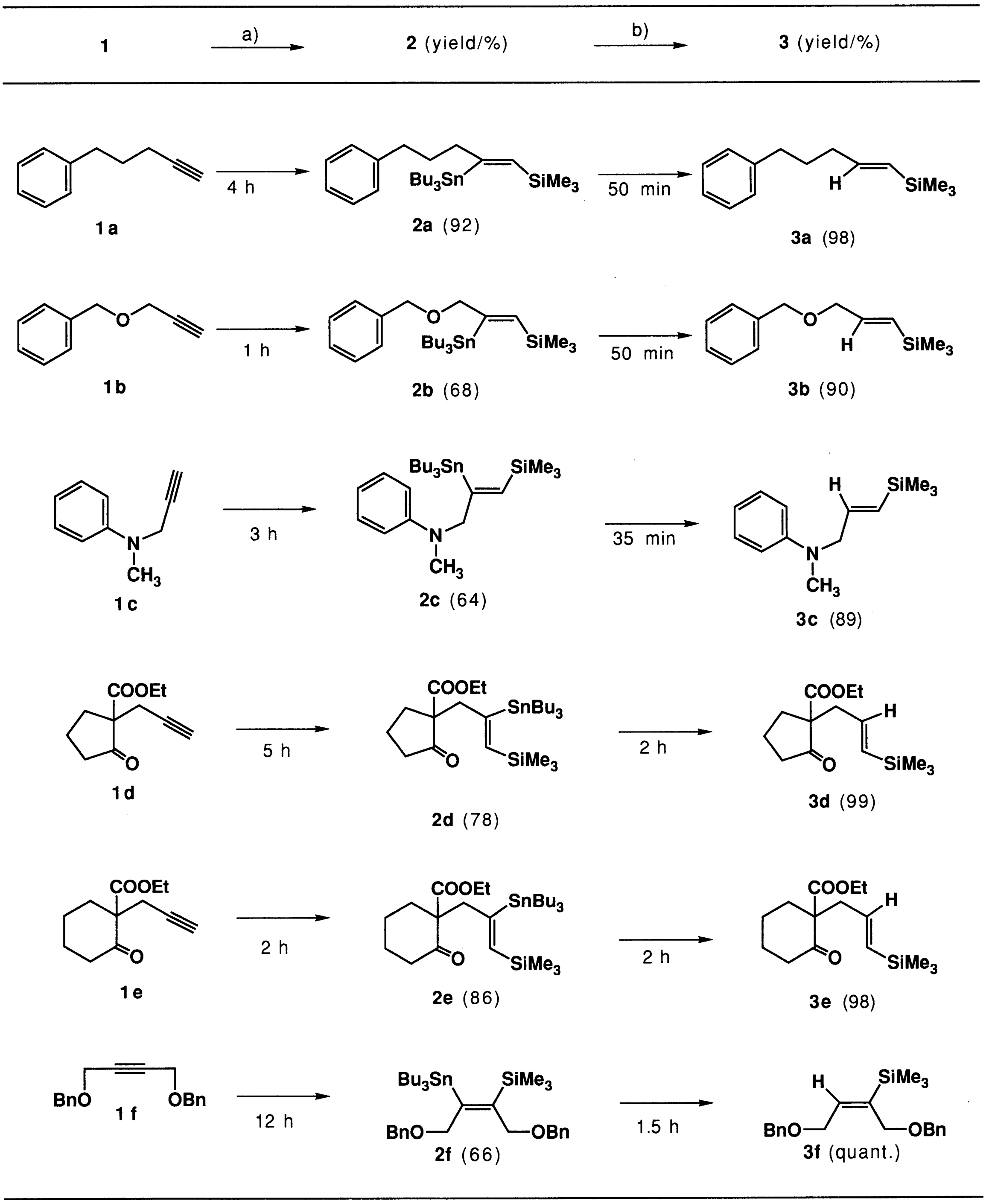


Table 1. Synthesis of Various *E*-Vinylsilanes from the Corresponding Olefins with Vicinal Silyl and Stannyl Substituents



a) Reactions were carried out in the presence of $Bu_3SnSiMe_3$ and a catalytic amount of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ in THF at 60 °C.
b) Reactions were carried out in the presence of HI (10 equiv.) and Bu_4NI (1 equiv.) in toluene at 0 °C.

In a typical procedure, to a solution of **1d** (300 mg, 1.58 mmol) and $PdCl_2(PPh_3)_2$ (34 mg, 0.049 mmol, 3 mol%) in THF (2.3 mL) was added $Bu_3SnSiMe_3$ (700 mg, 1.9 mmol) under argon atmosphere at 0 °C. After the solution was warmed at 60 °C for 30 min, the solution was cooled and concentrated. The residue was purified by column chromatography on silica gel eluted with hexane to afford **2d** as a colorless oil (685 mg, 78%). To a solution of **2d** (130 mg, 0.23 mmol) and Bu_4NI (86 mg, 0.23 mmol) in toluene (1 mL) was added HI (57%, 0.3 mL, 2.3 mmol) at 0 °C and the solution was stired at the same temperature for 50 min. Sat. $NaHCO_3$ solution was added and the mixture was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel eluted with hexane-AcOEt (1/0 then 5/1) to afford **3d** as a colorless oil (62 mg, 99%).

References

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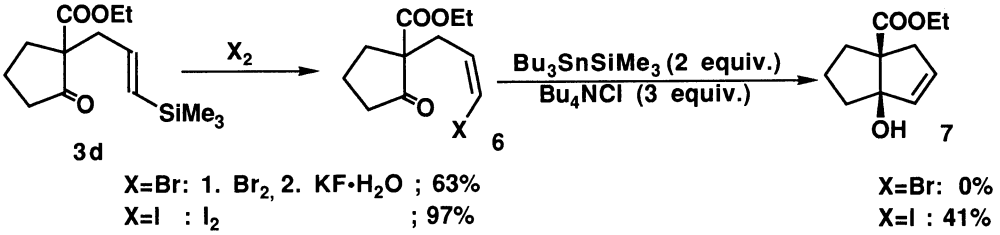

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