A Convenient Synthesis of (*E*)-β-Ethoxycarbonylvinylsilanes by Palladium-catalysed Regio- and Stereo-specific Hydroesterification of Trimethylsilylacetylenes

Ryo Takeuchi,* Masaharu Sugiura, Naomi Ishii and Nobuhiro Sato

Department of Chemistry, Yokohama City University, Kanazawa-ku, Yokohama 236, Japan

Palladium-catalysed hydroesterification of trimethylsilylacetylenes **1** gives (*E*)-β-ethoxycarbonylvinylsilanes **2** exclusively in excellent yields.

Vinylsilanes have attracted much attention because of their synthetic utility.[1] Their electrophilic substitution reaction provides a useful procedure for the stereoselective synthesis. Vinylsilanes that bear the alkoxycarbonyl group on one of the vinylic carbons should be useful synthetic intermediates, because they contain both the vinylsilane and α,β-unsaturated ester functionalities in the same molecule sharing the same carbon–carbon double bond.[2] Zweifel *et al.* reported the high yield and stereodefined synthesis of (*Z*)-α-ethoxycarbonylvinylsilanes *via* the stereo- and regio-specific hydroalumination of silylacetylene.[2a] Although (*E*)-3-trimethylsilylprop-2-enoic acid with the carboxy group on β-position in vinylsilane, was obtained in 86% *via trans*-β-trimethylsilylvinyllithium, the generality of the reaction is lacking.[2d] A general synthesis of vinylsilanes that bear the alkoxycarbonyl or carboxy group on the β-position of the vinylic carbons from easily accessible materials is desired. Transition metal complex catalysed carbonylation is a useful method for introducing a carbonyl functionality into organic compounds.[3] In our previous paper, we demonstrated the selective synthesis of α- or β-silyl esters by the highly regioselective carbonylation of vinylsilanes.[4] We now report a general method for the synthesis of (*E*)-β-ethoxycarbonylvinylsilanes **2** by the Pd-catalysed regio- and stereo-specific hydroesterification of easily accessible trimethylsilylacetylenes **1**.

The results are summarized in Table 1. The Pd-catalysed hydroesterification of **1** gave (*E*)-β-ethoxycarbonylvinylsilanes **2** exclusively except for entry 1 [eqn. (1)]. $PdCl_2$(dppf) combined with $SnCl_2 \cdot 2H_2O$ was the most effective catalyst with regard to the selectivity and the yield of the reaction [dppf = 1,1′-bis(diphenylphosphino)ferrocene];[5] addition of $SnCl_2 \cdot 2H_2O$ as a cocatalyst was essential for the reaction. Dicarbonylation or polymerization of **1** was not observed under the chosen conditions. The stereochemistry of **2** shows that the reaction proceeds in a *syn* manner.† A typical procedure is as follows. A mixture of trimethylsilylacetylene **1** (5 mmol), ethanol (10 ml), $PdCl_2$(dppf) (0.1 mmol), and $SnCl_2 \cdot 2H_2O$ (0.5 mmol) was heated in a 50 ml stainless steel autoclave and stirred at 90 °C for 15 h under 20 kg cm^{-2} of carbon monoxide. Products were isolated by distillations under reduced pressure. The silylacetylenes substituted by a primary or a secondary alkyl group as well as a phenyl group afforded the corresponding vinylsilanes in excellent yields (entries 2–5). This hydroesterification is also successful with trimethylsilylacetylenes bearing a functional group away from the triple bond (entries 6 and 7). The reduction of the carbon–chloro bond or ethoxycarbonyl group did not occur during the reaction.

The selectivity of the present reaction can be rationalized as follows. The hydropalladation of **1** proceeds in a *syn* manner to give complex **3** or **4**.[6] The steric repulsion between a trimethylsilyl substituent and ligands on palladium would yield **3** in preference to **4**. Insertion of carbon monoxide into the carbon–palladium bond would yield acylpalladium species. Subsequent nucleophilic attack by ethanol would yield the corresponding products.

As shown here, the present reaction provides an efficient route to (*E*)-β-ethoxycarbonylvinylsilanes. Further application and mechanistic studies of the reaction are in progress.

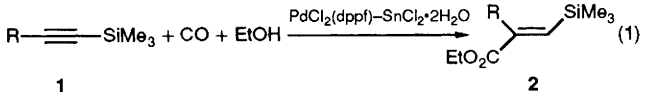
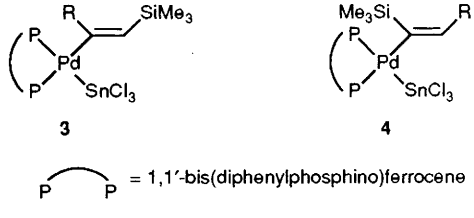


Table 1 Hydroesterification of trimethylsilylacetylenes **1**[a]

Entry	Substrate R	Product	Yield of **2**(%)[b]
1 **1a**	H	**2a**	84[c]
2 **1b**	Bu^n	**2b**	78
3 **1c**	Oct^n	**2c**	91
4 **1d**	Cy[d]	**2d**	85
5 **1e**	Ph	**2e**	88
6 **1f**	Cl	**2f**	82
7 **1g**	EtO_2C, CO_2Et	**2g**	90

[a] For conditions see test. [b] Isolated yield. [c] Determined by GLC. Ethyl 2-trimethylsilylprop-2-enoate was obtained in 1% yield. [d] Cy = cyclohexyl



† *Selected spectroscopic data*: Ethyl (*E*)-3-(trimethylsilyl)prop-2-enoate **2a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.29 (t, *J* 7.25 Hz, 3H), 4.20 (q, *J* 7.25 Hz, 2H), 6.23 (d, *J* 18.80 Hz, 1H), 7.24 (d, *J* 18.80 Hz, 1H): ^{13}C NMR (67.8 MHz) δ −2.03, 14.13, 60.33, 133.94, 149.31, 165.75: IR ν/cm^{-1} 1720.

Ethyl (*E*)-2-(n-butyl)-3-(trimethylsilyl)prop-2-enoate **2b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.17 (s, 9H), 0.92 (t, *J* 7.26 Hz, 3H), 1.30 (t, *J* 7.26 Hz, 3H), 1.34–1.44 (m, 4H), 2.38 (t, *J* 7.59 Hz, 2H), 4.19 (q *J* 7.26 Hz, 2H), 6.77 (s, 1H): ^{13}C NMR (67.8 MHz) δ −0.38, 13.89, 14.20, 22.91, 31.90, 32.26, 60.61, 140.23, 148.23, 167.44 ($^3J_{C=O,H}$ 9.8 Hz): IR ν/cm^{-1} 1715.

Ethyl (*E*)-2-(phenyl)-3-(trimethylsilyl)prop-2-enoate **2e**: ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.12 (s, 9H), 1.25 (t *J* 7.26 Hz, 3H), 4.20 (q, *J* 7.26 Hz, 2H), 7.17–7.23 (m, 3H), 7.29–7.34 (m, 3H): ^{13}C NMR (67.8 MHz) δ −0.76, 14.16, 61.10, 127.58, 127.62, 129.34, 138.33, 144.91, 147.87, 166.76 ($^3J_{C=O,H}$ 9.8 Hz): IR ν/cm^{-1} 1720.

Ethyl (*E*)-2-(3-chloropropyl)-3-(trimethylsilyl)prop-2-enoate **2f**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.20 (s, 9H), 1.31 (t, *J* 7.26 Hz, 3H), 1.87–1.98 (m, 2H), 2.54 (m, 2H), 3.57 (t, *J* 6.59 Hz, 2H), 4.20 (q, *J* 7.26 Hz, 2H), 6.89 (s, 1H): ^{13}C NMR (67.8 MHz) δ −0.45, 14.16, 29.65, 32.65, 44.89, 60.77, 142.25, 146.09, 166.86 ($^3J_{C=O,H}$ 9.7 Hz): IR ν/cm^{-1} 1710.

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