

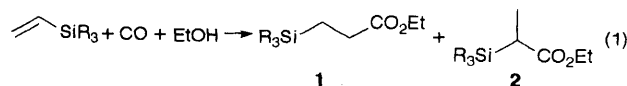
Department of Chemistry, Yokohama City University, Kanazawa-ku, Yokohama 236, Japan

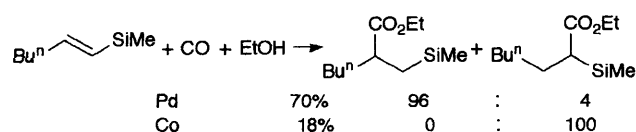
The results are summarized in Table 1. The Pd-catalysed reaction of vinyltrimethylsilane gave the corresponding β -silyl

Table 1 Hydroesterification of vinylsilanes^a

| Entry | SiR ₃ | Cat. ^b | Conditions | | Yield (%) ^c | 1 ^d : 2 ^d |
|-------|--------------------------------|-------------------|------------|-------------------------------|---------------------------|---------------------------------|
| | | | T/°C | Solvent | | |
| 1 | SiMe ₃ | Pd | 90 | THF ^e | 94 ^d | 98 : 2 |
| 2 | | Co | 140 | MeCN | 81 ^d | 7 : 93 |
| 3 | SiBu ⁿ ₃ | Pd | 120 | C ₆ H ₆ | 92 | 99 : 1 |
| 4 | | Co | 150 | MeCN | 79 | 7 : 93 |
| 5 | SiPh ₂ Me | Pd | 120 | C ₆ H ₆ | 82 | 100 : 0 |
| 6 | | Co | 150 | MeCN | 64 | 5 : 95 |
| 7 | Si(OEt)Me ₂ | Pd | 120 | C ₆ H ₆ | 70 | 97 : 3 |
| 8 | | Co | 160 | MeCN | 46 | 11 : 89 |
| 9 | Si(OMe) ₃ | Pd | 120 | C ₆ H ₆ | 70 | 91 : 9 |
| 10 | | Co | 160 | MeCN | 27 | 28 : 72 |
| 11 | SiPh ₂ F | Pd | 120 | C ₆ H ₆ | 87 | 100 : 0 |
| 12 | SiPhF ₂ | Pd | 120 | C ₆ H ₆ | 44 | 100 : 0 |

^a Vinylsilane (5 or 10 mmol), ethanol (25 or 50 mmol), solvent (10 ml), 14–24 h. ^b Pd: PdCl₂(PPh₃)₂ (1–2 mol%) CO 60 kg cm⁻², Co: Co₂(CO)₈ (2–4 mol%) CO 70 kg cm⁻². ^c Isolated yield. ^d Determined by GLC. ^e THF = tetrahydrofuran. ^f MeOH (50 mmol).

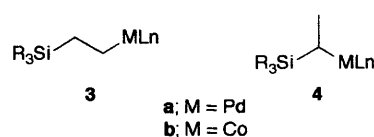




Scheme 1 Conditions: Pd: $\text{PdCl}_2(\text{PPh}_3)_2$, 100 °C, THF, 30 h; Co: $\text{Co}_2(\text{CO})_8$, 150 °C, MeCN, 17 h

follows. A mixture of vinylsilane (10 mmol), ethanol (50 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ or $\text{Co}_2(\text{CO})_8$ (0.1 or 0.2 mmol), and solvent (10 ml) was heated in a 50 ml stainless steel autoclave and stirred at 90–160 °C under 60–70 kg cm^{-2} of carbon monoxide. The Co-catalysed reaction required more rigorous conditions than that of the Pd-catalysed one. As the solvent, acetonitrile is essential for the high yield and selectivity in the Co-catalysed reaction. Other solvents gave less satisfactory results. Similar products and yields were obtained from the reaction of vinyltri-*n*-butylsilane and vinylphenylmethylsilane. Even in the case of the bulky diphenylmethylsilyl substituent, the Co catalyst carbonylated the α -position to the silicon atom; the more sterically hindered position. We previously reported that the Co-catalysed hydroformylation of vinyltrimethylsilane exclusively afforded the β -silylaldehyde⁴ but a quite different regioselectivity was obtained in this hydroesterification. (*E*)-1-Trimethylsilylhex-1-ene was less easily carbonylated (Scheme 1). The selectivity for the products was the same in the above cases with both catalysts. This carbonylation was also applicable to vinylalkoxysilanes (entries 7–10). For fluorosilanes, only the palladium catalyst was effective. The selectivity in the reaction of fluorosilanes was the same as in the case of vinyltrimethylsilane (entries 11 and 12).

The observed dependency of regioselectivity on the metal species can be explained reasonably as follows. Regardless of the metal species, the steric hindrance of the organosilicon substituent leads to the formation of **3** during the addition of the metal hydride complex to vinylsilanes. Complex **3a** is carbonylated to afford β -silyl ester **1**, while **3b** undergoes isomerization to afford **4b** before the CO insertion. α -Silyl esters **2** are obtained *via* the carbonylation of **4b**. Complex **4b**



would be more stable than **3b** because of the stabilization of the negative charge adjacent to silicon by the (p-d) π conjugation.⁵ Similar isomerization during the hydroesterification was observed to a considerable extent in the Co-catalysed reaction,⁶ whereas very little isomerization occurred in the Pd-catalysed reaction.⁷ The isomerization ability of **3b** would be much higher than that of **3a**.

As shown here, an appropriate choice of catalyst in the carbonylation of vinylsilanes can achieve the complete control of the regioselectivity. Further application and mechanistic studies of the reaction are in progress.

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