Highly Regioselective Carbonylation of Vinylsilanes: a Remarkable Effect of Organosilicon Substituent

Ryo Takeuchi,* Naomi Ishii and Nobuhiro Sato

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

The Pd-catalysed hydroesterification of vinylsilanes affords β-silyl esters **1** in high yields with high selectivity, whereas α-silyl esters **2** are obtained in high yields with high selectivity by the Co catalyst.

In the carbonylation of substituted alkenes[1] the major problem in this reaction is that at least two isomeric products are obtained. A great deal of work has been devoted to the designing of a catalyst system for the precise control of the regioselectivity. The carbonylation of alkenes substituted by various functional groups has been extensively studied. Recently, Perlmutter *et al.* reported that a *tert*-butyldiphenylsilyl substituent directed the formation of a β-silylaldehyde in Rh(0)-catalysed hydroformylation with high selectivity.[2] However, in the carbonylation of vinylsilanes high β-selectivity controlled by the less hindered trimethylsilyl substituent, or high α-selectivity, has not yet been reported. α- or β-Silyl esters, products of the hydroesterification of vinylsilanes, are potential building blocks in organic synthesis.[3] In the course of our study on the carbonylation of organosilicon compounds,[4] we have succeeded in a nearly quantitative control of the isomeric product composition in the hydroesterification of vinylsilanes by an appropriate choice of the catalyst [eqn. (1)].

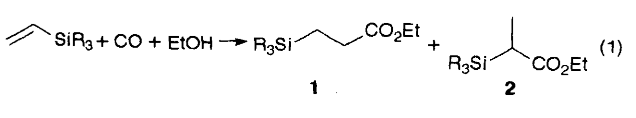
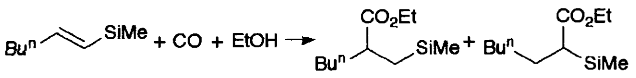


Table 1 Hydroesterification of vinylsilanes[a]

Entry	SiR_3	Cat.[b]	Conditions		Yield	
			T/°C	Solvent	(%)[c]	**1**[d] : **2**[d]
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_6H_6	92	99 1
4		Co	150	MeCN	79	7 93
5	$SiPh_2Me$	Pd	120	C_6H_6	82	100 0
6		Co	150	MeCN	64	5 95
7	$Si(OEt)Me_2$	Pd	120	C_6H_6	70	97 3
8		Co	160	MeCN	46	11 89
9	$Si(OMe)_3$	Pd	120	C_6H_6	70	91 9
10		Co	160	MeCN	27	28 72
11	$SiPh_2F$	Pd	120	C_6H_6	87	100 0
12	$SiPhF_2$	Pd	120	C_6H_6	44	100 0

[a] Vinylsilane (5 or 10 mmol), ethanol (25 or 50 mmol), solvent (10 ml), 14–24 h. [b] Pd: $PdCl_2(PPh_3)_2$ (1–2 mol%) CO 60 kg cm^{-2}, Co: $Co_2(CO)_8$ (2–4 mol%) CO 70 kg cm^{-2}. [c] Isolated yield. [d] Determined by GLC. [e] THF = tetrahydrofuran. [f] MeOH (50 mmol).

The results are summarized in Table 1. The Pd-catalysed reaction of vinyltrimethylsilane gave the corresponding β-silyl ester **1** in high yield with high selectivity (entry 1). In sharp contrast to $PdCl_2(PPh_3)_2$, $Co_2(CO)_8$ exhibited high selectivity to form the α-silyl ester **2** (entry 2). A typical procedure is as

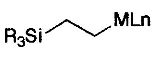


Pd	70%	96	:	4
Co	18%	0	:	100

Scheme 1 *Conditions*: Pd : $PdCl_2(PPh_3)_2$, 100 °C, THF, 30 h; Co : $Co_2(CO)_8$, 150 °C, MeCN, 17 h

follows. A mixture of vinylsilane (10 mmol), ethanol (50 mmol), $PdCl_2(PPh_3)_2$ or $Co_2(CO)_8$ (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 vinyldiphenylmethylsilane. 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-silylaldehyde[4] 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**.



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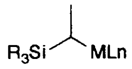

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a; M = Pd
b; M = Co

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.

We are grateful for financial support from a Grant-in-aid for Science Research (02750622) from the Ministry of Education, Science and Culture of Japan.

Received, 18th April 1991; Com. 1/01830B

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