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The Highly Regioselective Carbonylation of Vinylsilanes

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

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

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The hydroesterification of vinylsilanes, catalyzed by transition-metal complexes, afforded both β-silyl esters **2** and α-silyl esters **3** in high yield. The Pd(II) complex-catalyzed reaction showed high β-regioselectivity, whereas the $Co_2(CO)_8$-catalyzed reaction showed high α-regioselectivity. Vinylsilanes which bore trialkyl-, diphenylmethyl-, dimethylethoxy-, trimethoxy-, diphenylfluoro-, and difluorophenylsilyl groups were regioselectively, and some cases regiospecifically, hydroesterified. Pd(II) complexes were also shown to be effective catalysts of the hydrocarboxylation of vinylsilanes. Hydrocarboxylation was β-regiospecific and gave excellent yields of β-silyl carboxylic acids. Reasonable mechanisms for the reactions are described.

Introduction

The fact that carbon monoxide is more reactive when it is incorporated into a transition-metal complex has inspired the development of valuable methods for directly introducing carbonyl groups into organic molecules via the insertion of carbon monoxide into carbon–metal bonds.[1] The transition metal complex-catalyzed reaction of carbon monoxide with olefins in the presence of acidic nucleophiles like water (hydroxycarboxylation) or alcohols (hydroesterification) affords carboxylic acids or esters, respectively.[2] The major drawback of such reactions is that at least two isomeric products are usually formed. Consequently, a great deal of effort has been devoted to finding ways whereby the regioselectivity of the reactions can be controlled.

One of the most practical ways to synthesize an α- or β-functionalized carboxylic acid or esters is to regioselectively hydrocarboxylate or hydroesterify an olefin which bears the desired functional group on one of the vinylic carbons. Therefore, the hydrocarboxylation and hydroesterification of such olefins have been estensively studied.[3] However, few reports of the regioselective hydrocarboxylation or hydroesterification of members of one family of such olefins, the vinylsilanes, have appeared. The products of reaction would be valuable building blocks for use in organic synthesis.[4] For example, lithiated α-silyl esters have been used to prepare α,β-unsaturated esters via a Peterson-type reaction with aldehydes and ketones.[5]

Recently, it was reported[6] that a high degree of regioselectivity was achieved in a carbonylation reaction of vinylsilanes related to hydrocarboxylation and hydroesterification. Thus, the $RhH(CO)(PPh_3)_3/PPh_3$-catalyzed hydroformylation of 1-(*tert*-butyldiphenylsilyl)-1-alkenes gave, highly β-regioselectively (>96%), the corresponding 1-(*tert*-butyldiphenylsilyl)-2-formylalkanes. When, however, the vinylsilanes incorporated a trialkylsilyl group less bulky than t-$BuPh_2Si$–, e.g., Me_3Si–, Ph_3Si–, t-$BuMe_2Si$–, hydroformylation was not, except in the case of styrene derivatives, e.g., (*E*)- and (*Z*)-β-trimethylsilylstyrene, regioselective. What conditions, if any, under which a high degree of α-regioselectivity could be achieved were not determined. Here, we describe in detail the highly regioselective hydroesterification of vinylsilanes.[7] A high degree of either α- or β-regioselectivity could be achieved by using the appropriate catalyst. Also, conditions were found under which the highly β-regioselective hydrocarboxylation of vinylsilanes could be effected.

Table I. Pd(II) Complex- and Pt(II) Complex-Catalyzed Hydroesterification of Trimethylvinylsilane[a]

entry	catalyst	temp (°C)	solvent	yield[b] (%) of 2a + 3a	2a[b]:3a[b]
1	$PdCl_2(PhCN)_2$	90	benzene	1	95:5
2	$PdCl_2(PhCN)_2$ + PPh_3	90	benzene	89	97:3
3	$PdCl_2(PPh_3)_2$	90	benzene	92	97:3
4	$PdCl_2(PPh_3)_2$	90	THF	94	98:2
5	$PdCl_2(PPh_3)_2$	90	acetone	88	97:3
6	$PdCl_2(PPh_3)_2$	90	MeCN	79	97:3
7	$PdCl_2(PPh_3)_2$	90	EtOH	75	95:5
8[c]	$PdCl_2(PPh_3)_2$	70	benzene	82	98:2
9[d]	$PdCl_2$(dppe)	120	benzene	1	100:0
10[e]	$PdCl_2$(dppb)	120	benzene	0	–:–
11[f]	$PdCl_2$(dppf)	120	benzene	47	97:3
12	$PdCl_2(AsPh_3)_2$	120	benzene	14	96:4
13[g]	$PdCl_2(PCy_3)_2$	120	benzene	56	91:9
14[h]	$PtCl_2(AsPh_3)_2$	90	EtOH	68	100:0

[a] A stirred mixture of trimethylvinylsilane (10 mmol), catalyst (0.1 mmol), EtOH (50 mmol), and solvent (10 mL) was heated for 16 h under CO ($P_{initial}$ = 60 kg cm^{-2}). [b] Determined by GLC. [c] $P_{initialCO}$ = 30 kg cm^{-2}. [d] dppe = 1,2-bis(diphenylphosphino)ethane. [e] dppb = 1,4-bis(diphenylphosphino)butane. [f] dppf = 1,1′-bis(diphenylphosphino)ferrocene. [g] Cy = cyclohexyl. [h] $SnCl_2\cdot 2H_2O$ (0.5 mmol), [Sn]/[Pt] = 5.

Results and Discussion

The palladium(II) complex-catalyzed hydroesterification of trimethylvinylsilane (**1a**) in organic solution gave both

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[1] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 619–665 and 749–768. (b) Colquhon, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis*; Plenum: New York, 1984; Chapter 6, pp 195–253. (c) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: Berlin, 1980. (d) Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls*; John Wiley and Sons: New York, 1977; Vol 2. (e) Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, pp 101–223.

[2] (a) Anderson, G. K.; Davies, J. A. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley & Sons: New York, 1985; Vol. 3, p 335–359. (b) Fenton, D. M.; Moorehead, E. L. In *The Chemistry of The Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley & Sons: New York, 1985; Vol. 3, pp 435–445. (c) Stille, J. K.; James, D. E. In *The Chemistry of Double-Bonded Functional Groups, Part 1, Supplement A*; Patai, S., Ed.; John Wiley & Sons: New York, 1977; pp 1099–1166.

[3] See ref 1c, p 263.

[4] For the preparation of β-silyl esters via the conjugate addition of lithium disilyl cuprates to α,β-unsaturated esters, see: Fleming, I.; Waterson, D. *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1809. For the preparation of α-silyl esters via the reaction of Reformatsky reagents with cholorosilanes, see: Fessenden, R. J.; Fessenden, J. S. *J. Org. Chem.* **1967**, *32*, 3535.

[5] (a) Hartzell, S. L.; Sullivan, D. F.; Rathke, M. W. *Tetrahedron Lett.* **1974**, 1403. (b) Simoji, K.; Taguchi, K.; Ohshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 1620.

[6] Doyle, M. M.; Jackson, W. R.; Perlmutter, P. *Tetrahedron Lett.* **1989**, *30*, 233.

[7] A preliminary report of the work described here has appeared. See: Takeuchi, R.; Ishii, N.; Sato, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1247.

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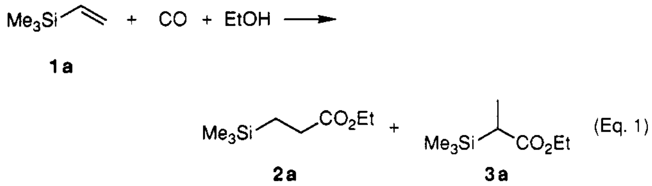
Table II. $Co_2(CO)_8$-Catalyzed Hydroesterification of Trimethylvinylsilane[a]

entry	solvent	yield[b] (%) **2a** + **3a**	**2a**[b]:**3a**[b]
1	EtOH	55	17:83
2	acetone	59	21:79
3	THF	29	9:91
4	benzene	36	2:98
5[c]	hexane	30	0:100
6	MeCN	81	7:93
7[d]	MeCN	80	4:96
8[e]	MeCN	82	8:92
9	*n*-PrCN	87	2:98
10	DMF	0	-:-
11	pyridine	3	84:16
12	Et_3N	1	0:100

[a] A stirred mixture of trimethylvinylsilane (10 mmol), $Co_2(CO)_8$ (0.1 mmol), EtOH (50 mmol), and solvent (10 mL) was heated at 140 °C for 7 h under CO (P_{initial} = 70 kg cm^{-2}). [b] Determined by GLC. [c] Reaction temperature = 160 °C. [d] Pyridine (0.4 mmol) was present; [pyridine]/[$Co_2(CO)_8$] = 4.0. [e] The reaction vessel was pressurized first with CO to 70 kg cm^{-2} and then with H_2 to 75 kg cm^{-2}.

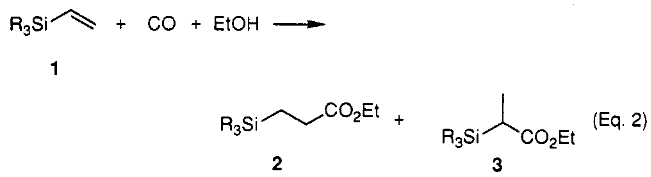
ethyl 3-(trimethylsilyl)propionate (the β-silyl ester **2a**, the major product) and ethyl 2-(trimethylsilyl)propionate (the α-silyl ester **3a**, the minor product) (eq 1). The results are summarized in Table I. Of the catalysts that were evaluated, $PdCl_2(PPh_3)_2$ proved to be the most effective. What solvent was used in the $PdCl_2(PPh_3)_2$-catalyzed reaction had little effect on either the yield of the products or the regioselectivity of hydroesterification. In every case (entries 3–8), a good to excellent yield and a high degree of β-regioselectivity were seen. In the presence of $PdCl_2(PPh_3)_2$, hydroesterification could be effected in benzene solution even under relatively mild conditions (entry 8). On the other hand, reaction was very slow, or did not occur at all, when the catalyst was a palladium(II) complex which did not incorporate monodentate phosphine ligands. For example, $PdCl_2(PhCN)_2$ showed negligible catalytic activity in benzene solution (entry 1). However, the species produced by introducing 1 equiv of triphenylphosphine into such a solution showed considerable catalytic activity (entry 2). $PdCl_2$(dppe) (entry 9) and $PdCl_2$(dppb) (entry 10), each of which incorporates a bidentate diphosphine ligand, were catalytically inactive. Both are stable chelate compounds. Yet, $PdCl_2$(dppf) (entry 11), which also incorporates a bidentate diphosphine ligand, did show some catalytic activity. Because the P–Pd–P bond angle in $PdCl_2$(dppf) is unusually large compared to that in $PdCl_2$(dppe) or $PdCl_2$(dppb),[8] it can be inferred that a great deal of strain exists in $PdCl_2$(dppf). Dissociation of one of the phosphino groups from the metal would relieve such strain and yield a catalytically active species. Various analogues of $PdCl_2(PPh_3)_2$ also proved to be fairly effective catalysts (entries 12–14). In the presence of $PtCl_2(AsPh_3)_2$, hydroesterification was β-regiospecific (entry 14).



(Eq. 1)

In sharp contrast to palladium(II) complex-catalyzed reaction, the $Co_2(CO)_8$-catalyzed hydroesterification of **1a** was highly α-regioselective. The results are summarized in Table II. The reaction proceeded smoothly at 140 °C after the reaction vessel had been pressurized to 70 kg cm^{-2} with carbon monoxide at room temperature. What the solvent was had a noticeable influence on both the yield of the products and the regioselectivity of the reaction. In THF (entry 3), benzene (entry 4), or hexane (entry 5), hydroesterification was highly α-regioselective, but the yield of the products was poor. However, in acetonitrile (entry 6) or butyronitrile (entry 9) the reaction was both highly α-regioselective and high yielding.[9] The presence of a small amount of either pyridine (entry 7) or molecular hydrogen (entry 8), both of which are well-known activators of the $Co_2(CO)_8$-catalyzed hydroesterifictaion of olefins,[11] had no effect on either yield or regioselectivity. In basic solvents like DMF (entry 10), pyridine (entry 11), and triethylamine (entry 12), reaction was slow. It should be noted that whereas the $Co_2(CO)_8$-catalyzed hydroesterification of **1a** is α-regioselective, the $Co_2(CO)_8$-catalyzed hydroformylation of the same compound has been reported to be β-regioselective.[12]

The hydroesterification of other vinylsilanes (eq 2) was also attempted. The results are summarized in Table III.



(Eq. 2)

The $PdCl_2(PPh_3)_2$-catalyzed reactions were all β-regioselective; indeed, in some cases (entries 5, 11, and 12) they were β-regiospecific. The $Co_2(CO)_8$-catalyzed reactions required more vigorous conditions than did those catalyzed by $PdCl_2(PPh_3)_2$ and were α-regioselective. Good to excellent yields of products were obtained from the reactions of **1a** (entries 1 and 2), tri-*n*-butylvinylsilane (**1b**, entries 3 and 4), and diphenylmethylvinylsilane (**1c**, entries 5 and 6) in the presence of either catalyst. It is noteworthy that the $Co_2(CO)_8$-catalyzed hydroesterification of **1c** (entry 6) was still highly α-regioselective despite the high degree of steric hindrance imposed by the diphenylmethylsilyl group. The alkoxyvinylsilanes **1d** (entries 7 and 8) and **1e** (entries 9 and 10) were also regioselectively hydroesterified, although as the number of alkoxy substituents on silicon was increased, the degree of regioselectivity decreased somewhat. The $PdCl_2(PPh_3)_2$-catalyzed hydroesterification of **1e** in the presence of ethanol afforded a complex mixture of products. This suggested that considerable ethanolysis of **1e** (or species derived therefrom) had occurred. When methanol was employed in place of ethanol, the expected products were formed in good yield (entry 9). The hydroesterification of fluorovinylsilanes was also examined.

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[8] Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

[9] The infrared spectrum of $Co_2(CO)_8$ in MeCN solution shows a CO band at 1890 (vs) cm^{-1}, characteristic of a tetracarbonylcobaltate. Treatment of $Co_2(CO)_8$ with MeCN causes disproponation to give [Co(CO)$_4$]$^-$ and Co(MeCN)$_6^{2+}$ (eq i).[10] Co(CO)$_4^-$ subsequently reacts with EtOH to give HCo(CO)$_4$, which is the active species in the hydroesterification (eq ii). The generation of HCo(CO)$_4$ from $Co_2(CO)_8$ occurs more rapidly in nitriles than in other solvents.

$$3Co_2(CO)_8 + 12\,MeCN \longrightarrow 2[Co(MeCN)_6][Co(CO)_4]_2 + 8CO \quad \text{(Eq. i)}$$

$$Co(CO)_4^- + EtOH \longrightarrow HCo(CO)_4 + EtO^- \quad \text{(Eq. ii)}$$

[10] Wender, I.; Sternberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1952**, *74*, 1216.

[11] (a) Sisak, A.; Ungavaray, F.; Marko, L. *J. Org. Chem.* **1990**, *55*, 2508. (b) Pesa, F.; Haase, T. *J. Mol. Catal.* **1983**, *18*, 237. (c) Matsuda, A. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2596. (d) Matsuda, A. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 135.

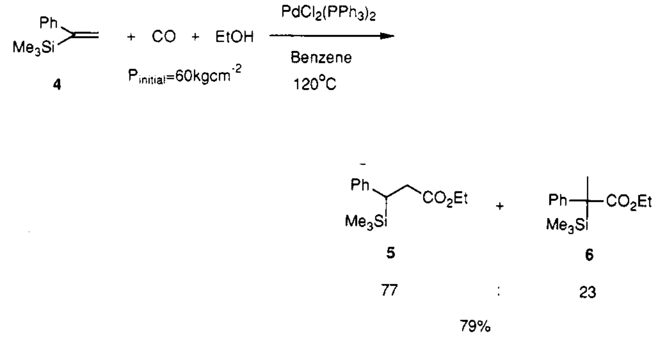
[12] Takeuchi, R.; Sato, N. *J. Organomet. Chem.* **1990**, *393*, 1.

Table III. Hydroesterification of Representative Vinylsilanes[a]

entry	substrate	SiR_3	catalyst[b]	condns	yield[c] (%) of **2** + **3**	**2**[d]:**3**[d]
1	**1a**	$SiMe_3$	Pd	90 °C, THF	94[d]	98:2
2			Co	140 °C, MeCN	81[d]	7:93
3	**1b**	Si(*n*-Bu)$_3$	Pd	120 °C, benzene	92	99:1
4			Co	150 °C, MeCN	79	7:93
5	**1c**	$SiPh_2Me$	Pd	120 °C, benzene	82	100:0
6			Co	150 °C, MeCN	64	5:95
7	**1d**	Si(OEt)Me_2	Pd	120 °C, benzene	70	97:3
8			Co	160 °C, MeCN	46	11:89
9[e]	**1e**	Si(OMe)$_3$	Pd	120 °C, benzene	70	91:9
10[e]			Co	160 °C, MeCN	27	28:72
11	**1f**	$SiPh_2F$	Pd	120 °C, benzene	87	100:0
12	**1g**	$SiPhF_2$	Pd	120 °C, benzene	44	100:0

[a] A stirred mixture of the vinylsilane (5 or 10 mmol), catalyst, EtOH (25 or 50 mmol), and solvent (10 mL) was heated for 14–24 h. [b] Pd = $PdCl_2(PPh_3)_2$ (1–2 mol %), $P_{initialCO}$ = 60 kg cm^{-2}, Co = $Co_2(CO)_8$ (2–4 mol %), $P_{initialCO}$ = 70 kg cm^{-2}. [c] Isolated yield. [d] Determined by GLC. [e] MeOH (50 mmol) was used in place of EtOH. The products were $(MeO)_3SiCH_2CH_2COOMe$ and $(MeO)_3SiCH(COOMe)CH_3$.

Scheme I



Scheme II

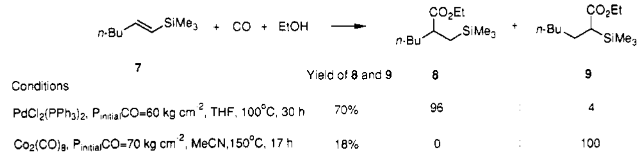


Table IV. Pd(II) Complex-Catalyzed Hydrocarboxylation of Trimethylvinylsilane[a]

entry	catalyst	temp (°C)	solvent	yield[b] (%) of **10a**
1	$PdCl_2(PPh_3)_2$	90	THF	95
2	$PdCl_2(PPh_3)_2$	90	benzene	87
3	$PdCl_2(PPh_3)_2$	90	acetone	87
4	$PdCl_2(PPh_3)_2$	90	DMF	3
5	$PdCl_2(PPh_3)_2$	120	acetic acid	10
6	$PdCl_2$(dppe)	120	THF	2
7	$PdCl_2$(dppb)	120	THF	46[c]
8	$PdCl_2$(dppf)	120	THF	49

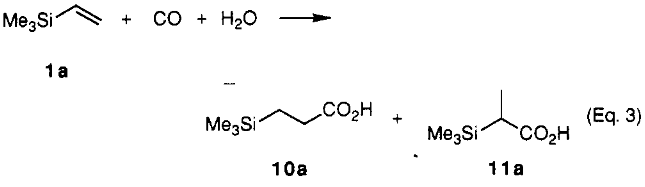
[a] A stirred mixture of trimethylvinylsilane (10 mmol), catalyst (0.1 mmol), H_2O (50 mmol), and solvent (10 mL) was heated for 16 h under CO ($P_{initial}$ = 60 kg cm^{-2}). [b] Determined by GLC. [c] $Me_3SiCH(CH_3)COOH$ was also obtained, in 1% yield.

The $PdCl_2(PPh_3)_2$-catalyzed reaction of diphenylfluorovinylsilane (**1f**) gave **2f** exclusively, in 87% yield (entry 11). Similarly, only **2g** was produced from difluorophenylvinylsilane (**1g**, entry 12). Neither compound was hydroesterified in the presence of $Co_2(CO)_8$. It appears that it is the presence in **1f** and **1g** of one or more fluorines attached to the atom (silicon in this case) adjacent to the olefinic carbon–carbon double bond that is responsible for the unusually high degree of β-regioselectivity that is seen. For example, it has been reported that 3,3,3-trifluoropropene, which possesses three fluorines on the allylic carbon, is both hydroformylated[13a] and hydroesterified,[13b] in the presence of various group-VIII transition-metal complexes, more regioselectively than other terminal alkenes.

The $PdCl_2(PPh_3)_2$-catalyzed hydroesterification of **4**, an α-phenylvinylsilane, gave a 77:23 mixture of compounds **5** and **6**, in 79% yield (Scheme I). In this case, the reaction was less β-regioselective than were the hydroesterifications of **1a–c**. Because it is known that the transition metal-complex-catalyzed hydroformylation of styrene and ring-substituted styrenes is more highly α-regioselective than that of other terminal alkenes,[14] it may be that it is the presence in **4** of the α-phenyl group which is responsible for the relatively high degree of α-regioselectivity that is seen. Compound **4** could not be hydroesterified in the presence of $Co_2(CO)_8$.

The β-alkylvinylsilane **7** was less easily hydroesterified (Scheme II). The $PdCl_2$ $(PPh_3)_2$-catalyzed reaction was highly β-regioselective, whereas the $Co_2(CO)_8$-catalyzed reaction was α-regiospecific. It is evident from the results of the hydroesterification of **1a–c**, **4**, and **7** that the yield of the expected products decreases as access to the carbon–carbon double bond of the vinylsilane becomes sterically more hindered. It also seems that the $Co_2(CO)_8$-catalyzed reaction is more sensitive to steric factors.

The palladium(II) complex-catalyzed hydrocarboxylation of a few representative vinylsilanes was also examined. The results of the reaction of trimethylvinylsilane (**1a**, eq 3) are summarized in Table IV. Whereas



Fenton[15] and Ojima[13b] reported that the palladium(II) complex-catalyzed hydrocarboxylation of olefins took place readily only in acetic acid, we found that **1a** could be hydroxylated in any of several solvents. Except when $PdCl_2$(dppb) was the catalyst (entry 7), **1a** was hydrocarboxylated β-regiospecifically to give **10a**. Compound **10a** was produced in nearly quantitative yield by the $PdCl_2(PPh_3)_2$-catalyzed reaction in THF (entry 1). Even reaction in a heterogeneous medium gave an excellent yield

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(13) (a) Ojima, I.; Kato, K.; Okabe, M.; Fuchikami, T. *J. Am. Chem. Soc.* **1987**, *109*, 7714. (b) Fuchikami, T.; Ohishi, K.; Ojima, I. *J. Org. Chem.* **1983**, *48*, 3803.

(14) (a) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674. (b) Lazzaroni, F.; Raffaelli, A.; Settambolo, R.; Bertozzi, S.; Vitulli, G. *J. Mol. Catal.* **1989**, *50*, 1. (c) Hayashi, T.; Tanaka, M.; Ogata, I. *J. Mol. Catal.* **1981**, *13*, 323.

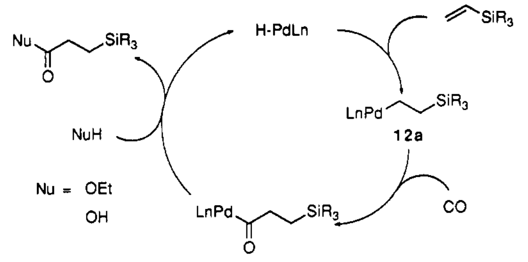
(15) Fenton, D. M. *J. Org. Chem.* **1973**, *38*, 3192.

Table V. $PdCl_2(PPh_3)_2$-Catalyzed Hydrocarboxylation of Vinylsilanes in THF Solution[a]

entry	substrate	SiR_3	temp (°C)	product	yield[b] (%)
1	**1a**	$SiMe_3$	90	**10a**	95[c]
2	**1b**	$Si(n\text{-}Bu)_3$	150	**10b**	73
3	**1c**	$SiPh_2Me$	150	**10c**	87

[a] A stirred mixture of the vinylsilane (5 or 10 mmol), H_2O (25 or 50 mmol), $PdCl_2(PPh_3)_2$ (1 mol %), and THF (10 mL) was heated for 14 h under CO ($P_{initial}$ = 60 kg cm^{-2}). [b] Isolated yield. [c] Determined by GLC.

Scheme III



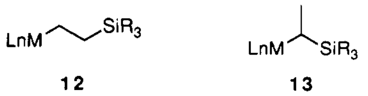
of product (entry 2). Interestingly, in acetic acid, hydrocarboxylation afforded **10a** in only poor yield (entry 5). It appears that, in this case, protiodesilylation of **1a** by acetic acid[16] takes place before hydrocarboxylation can occur. Palladium(II) complexes which incorporate cis-chelating diphosphine ligands (entries 6–8) were less effective catalysts than $PdCl_2(PPh_3)_2$.

The $PdCl_2(PPh_3)_2$-catalyzed hydrocarboxylation of **1b** in THF solution gave **10b** exclusively, in 73% yield (entry 2, Table V). Similarly, **10c** was produced exclusively, and in high yield, from **1c** (entry 3, Table V). Thus, when $PdCl_2(PPh_3)_2$ was the catalyst, both the hydroesterification and hydrocarboxylation of **1a–c** were highly β-regioselective.

The alkoxyvinylsilanes **1d** and **1e** and the fluorovinylsilanes **1f** and **1g** could not be hydrocarboxylated under the conditions described here. Resinous products were obtained in all cases. Presumably, the compounds (or species derived therefrom) were hydrolyzed to silanols, which then condensed to form siloxanes.

Attempts to hydrocarboxylate compounds **1a–g** in THF solution in the presence of $Co_2(CO)_8$ failed. However, propionic acid was isolated in low yield from the attempted hydrocarboxylation of **1a**.

A reasonable mechanism for the palladium(II) complex-catalyzed hydroesterification and hydrocarboxylation is shown in Scheme III. It can be assumed that the steric effect of the silyl substituent is such that the addition to the vinylsilane of the palladium hydride complex would yield **12a** in preference to **13a**.[17] Insertion of carbon monoxide into the carbon–palladium bond of **12a** and **13a** would yield acylpalladium species. Subsequent nucleophilic attack by ethanol or water would yield the final products.[18]

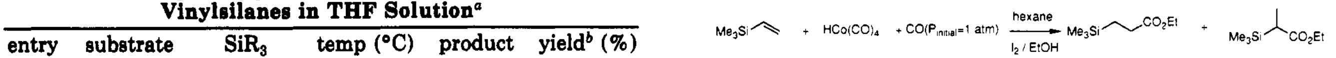


12 **13**

a; M = Pd

b; M = Co

Scheme IV



Temperature(°C)	Yield of 2a and 3a (%)			
0	22	85	:	15
25	33	85	:	15
33	14	54	:	46

Table VI. Effect of Temperature on the $Co_2(CO)_8$-Catalyzed Hydroesterification of Trimethylvinylsilane[a]

entry	temp (°C)	yield[b] (%) **2a** + **3a**	**2a**[b]:**3a**[b]
1	170	74	1:99
2	140	81	7:93
3	120	66	8:92
4[c]	110	26	40:60

[a] A stirred mixture of trimethylvinylsilane (10 mmol), EtOH (50 mmol), $Co_2(CO)_8$ (0.1 mmol), and MeCN (10 mL) was heated under CO ($P_{initial}$ = 70 kg cm^{-2}) for 7 h. [b] Determined by GLC. [c] $Co_2(CO)_8$ (0.5 mmol), reaction time = 24 h.

Because the $Co_2(CO)_8$-catalyzed hydroesterification probably involves the addition to vinylsilane of $HCo(CO)_4$ generated in situ, we decided to determine the regioselectivity of the addition to **1a** of $HCo(CO)_4$. Thus, the reaction of a *stoichiometric* amount of $HCo(CO)_4$ and **1a** in hexane solution in the presence of carbon monoxide and ethanol was examined (Scheme IV). Reaction both at 0 and 25 °C gave **2a** as the major product. However, elevating the reaction temperature to 50 °C led to an increase in the proportion of **3a** in the mixture of products. These observations suggested that the rate of isomerization of **12b** to **13b** increases with an increase in temperature. Thus, in the $Co_2(CO)_8$-catalyzed reaction, some **12b**, which would be formed initially, would, at the relatively high reaction temperatures employed, isomerize to **13b** before insertion of carbon monoxide could occur. The α-silyl ester **3** would be formed via the carbonylation of **13b**. As the results summarized in Table VI show, the **3a**:**2a** ratio did increase as the reaction temperature was increased. At 170 °C, a 99:1 mixture of **3a** and **2a** was produced. There is evidence that species analogous to **12b**, derived from simple 1- and 2-alkenes, are thermally isomerized more readily than are the corresponding analogues of **12a**.[20,21] Another factor to be considered is that **13b** would be stabilized by delocalization of the partial negative charge on the carbon adjacent to silicon by carbon–silicon via carbon–silicon ($p \rightarrow d$)π bonding.[22]

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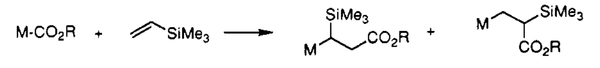
[18] A possible alternative mechanism involves the addition of M–CO_2R to the carbon–carbon double bond of the vinylsilane and demetalation by acid of the metalated esters (**14** and **15**) so formed (eq iii).[19]



(Eq. iii)

14 **15**

If such a mechanism were operative, when hydroesterification or hydrocarboxylation is carried out in nonacidic solvents, the rates of demetalation of **14** and **15** would be expected to be slow. However, because the reactions proceed smoothly and fairly rapidly in nonacidic solvents, it seem unlikely that species like M–CO_2R, **14** and **15**, are involved.

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Experimental Section

Materials. All reagents were dried and purified before use by the usual procedures. Carbon monoxide (>99.9%) was used as received without further purification. $PdCl_2(PhCN)_2$,[23] $PdCl_2(PPh_3)_2$,[24] and $PtCl_2(AsPh_3)_2$[25] were prepared by literature methods. $PdCl_2(dppe)$, $PdCl_2(dppb)$, $PdCl_2(dppf)$, $PdCl_2(AsPh_3)_2$, and $PdCl_2(PCy_3)_2$ were prepared by the reaction of $PdCl_2(PhCN)_2$ with the corresponding phosphine. $Co_2(CO)_8$ was recrystallized from *n*-pentane before use. Tri-*n*-butylvinylsilane was prepared by the reaction of trichlorovinylsilane and *n*-BuMgBr. Methyldiphenylvinylsilane was prepared by the reaction of dichloromethylvinylsilane and PhMgBr. Fluorodiphenylvinylsilane and diphenylfluorovinylsilane were prepared by a literature method from the corresponding chlorovinylsilane and copper fluoride.[26] (*E*)-1-Trimethylsilyl-1-hexene was prepared by a literature method.[27] α-(Trimethylsilyl)styrene was prepared by the reaction of α-styrylmagnesium bromide and Me_3SiCl. $HCo(CO)_4$ was also prepared by a literature method.[28]

General Methods. Boiling points and melting point are uncorrected. ^1H NMR spectra were recorded at 270 MHz and ^{13}C NMR spectra were recorded at 67.8 MHz in $CDCl_3$ solutions with Me_4Si as an internal standard. GC analyses were performed with 3-mm × 2-m glass columns packed with either 20% SE-30 on 60/80 mesh chromosorb W, AW-DMCS; 5% OV-17% on 60/80 mesh chromosorb W, AW-DMCS; or 5% FFAP on 60/80 mesh Flusin P. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

General Procedure for the Carbonylation of Vinylsilanes. A mixture of the solvent (10 mL), EtOH, or water (25 or 50 mmol), the vinylsilane (5 or 10 mmol), and the catalyst (Palladium(II) complex: 1–2 mol %, based on vinylsilane; $Co_2(CO)_8$: 2–4 mol %, based on vinylsilane) was placed in a 50-mL stainless steel autoclave (Yuasa Giken; SUS 316) equipped with a glass liner and a magnetic stirring bar. The reactor was sealed and was flushed with carbon monoxide, and then it was pressured with carbon monoxide to 60 kg cm^{-2} (Pd cases) or 70 kg cm^{-2} (Co cases). The stirred mixture was heated. Reaction temperature and reaction times are shown in the tables. The reaction was terminated by rapid cooling. The products were isolated by vacuum distillation.

Reaction of Trimethylvinylsilane with $HCo(CO)_4$. To a solution of $HCo(CO)_4$ (240 mg, 1.4 mmol) and hexane (5 mL) in a 50-mL two-necked flask connected to a rubber balloon filled with carbon monoxide was added neat trimethylvinylsilane (702 mg, 7.0 mmol). The mixture was stirred at the temperature indicated in Scheme IV for 3 h. A solution of I_2 (711 mg, 2.8 mmol) and EtOH (5 mL) was then added. After 30 min, the solution was diluted with Et_2O (10 mL) and was washed with saturated aqueous sodium thiosulfate (10 mL × 2). The Et_2O solution was analyzed by GLC to determine the yields of **2a** and **3a**.

Ethyl 3-(trimethylsilyl)propionate (2a): bp 68–69 °C (11 Torr); ^1H NMR δ 0.01 (s, 9 H, $Si(CH_3)_3$), 0.84 (m, 2 H, $SiCH_2$), 1.26 (t, 3 H, $J = 7.26$ Hz, OCH_2CH_3), 2.27 (m, 2 H, CH_2COOEt), 4.12 (q, 2 H, $J = 7.26$ Hz, OCH_2); ^{13}C NMR δ −2.2 ($Si(CH_3)_3$), 11.5 ($SiCH_2$), 14.0 (OCH_2CH_3), 28.7 (CH_2COOEt), 60.0 (OCH_2CH_3), 174.8 ($C{=}O$); IR 1740 cm^{-1}. Anal. Calcd for $C_8H_{18}SiO_2$: C, 55.12; H, 10.41; O, 18.36; Si, 16.11. Found: C, 55.20; H, 10.67.

Ethyl 2-(trimethylsilyl)propionate (3a): bp 53–54 °C (9 Torr); ^1H NMR δ 0.01 (s, 9 H, $Si(CH_3)_3$, 1.17 (d, 3 H, $J = 7.26$ Hz, $SiCHCH_3$), 1.24 (t, 3 H, $J = 7.26$ Hz, OCH_2CH_3), 2.04 (q, 1 H, $J = 7.26$ Hz, $CHCOOEt$), 4.02–4.19 (m, 2 H, OCH_2); ^{13}C NMR δ −3.0 ($Si(CH_3)_3$), 10.8 ($SiCH(CH_3)COOEt$), 14.4 (OCH_2CH_3), 30.1 ($CHCOOEt$), 59.5 (OCH_2CH_3), 176.1 ($C{=}O$); IR 1715 cm^{-1}. Anal. Calcd for $C_8H_{18}SiO_2$: C, 55.12; H, 10.41; O, 18.36; Si, 16.11. Found: C, 55.10; H, 10.64.

Ethyl 3-(tri-*n*-butylsilyl)propionate (2b): bp 142–144 °C (1 Torr); ^1H NMR δ 0.51 (t, 6 H, $J = 6.93$ Hz, $SiCH_2CH_2CH_2CH_3$), 0.86 (m, 2 H, $SiCH_2$), 0.88 (t, 9 H, $J = 7.26$ Hz, CH_2CH_3), 1.22–1.38 (m, 12 H, $SiCH_2CH_2CH_2CH_3$), 1.26 (t, 3 H, $J = 7.26$ Hz, OCH_2CH_3), 2.26 (m, 2 H, CH_2COOEt), 4.12 (q, 2 H, $J = 7.26$ Hz, OCH_2CH_3); ^{13}C NMR δ 7.6 ($SiCH_2CH_2COOEt$), 11.8 ($SiCH_2CH_2CH_2CH_3$), 13.7 (CH_2CH_3), 14.2 (OCH_2CH_3), 26.0 ($SiCH_2CH_2CH_2CH_3$), 26.8 ($SiCH_2CH_2CH_2CH_3$), 28.9 (CH_2COOEt), 60.3 (OCH_2CH_3), 175.2 ($C{=}O$); IR 1740 cm^{-1}. Anal. Calcd for $C_{17}H_{36}SiO_2$: C, 67.94; H, 12.07; Si, 9.34; O, 10.65. Found: C, 68.13; H, 12.32.

Ethyl 2-(tri-*n*-butylsilyl)propionate (3b): bp 123–125 °C (4 Torr); ^1H NMR δ 0.60 (t, 6 H, $J = 6.60$ Hz, $SiCH_2CH_2CH_2CH_3$), 0.89 (t, 9 H, $J = 6.93$ Hz, CH_2CH_3), 1.18 (d, 3 H, $J = 7.26$ Hz, $SiCH(CH_3)COOEt$), 1.24 (t, 3 H, $J = 7.26$ Hz, OCH_2CH_3), 1.31–1.41 (m, 12 H, $SiCH_2CH_2CH_2CH_3$), 2.12 (q, 1 H, $J = 7.26$ Hz, $CHCOOEt$), 4.09 (q, 2 H, $J = 7.26$ Hz, OCH_2CH_3); ^{13}C NMR δ 11.1 ($SiCH_2CH_2CH_2CH_3$), 11.2 ($SiCH(CH_3)COOCH_2CH_3$), 13.7 ($CHCH_3$), 14.3 (OCH_2CH_3), 25.7 ($SiCH_2CH_2CH_2CH_3$), 26.8 ($SiCH_2CH_2CH_2CH_3$), 27.5 ($CHCOOEt$), 59.7 (OCH_2CH_3), 176.6 ($C{=}O$); IR 1720 cm^{-1}. Anal. Calcd for $C_{17}H_{36}SiO_2$: C, 67.94; H, 12.07; Si, 9.34; O, 10.65. Found: C, 67.86; H, 12.37.

Ethyl 3-(methyldiphenylsilyl)propionate (2c): bp 167 °C (1 Torr); ^1H NMR δ 0.56 (s, 3 H, $SiCH_3$), 1.20 (t, 3 H, $J = 7.26$ Hz, OCH_3CH_3), 1.41 (m, 2 H, $SiCH_2$), 2.32 (m, 2 H, CH_2COOEt), 4.08 (q, 2 H, $J = 7.26$ Hz, OCH_2CH_3), 7.30–7.38 (m, 6 H, phenyl), 7.49–7.55 (m, 4 H, phenyl); ^{13}C NMR δ −4.7 ($SiCH_3$), 9.3 ($SiCH_2$), 14.1 (OCH_2CH_3), 28.8 (CH_2COOEt), 60.3 (OCH_2CH_3), 127.9 (phenyl), 129.3 (phenyl), 134.4 (phenyl), 136.0 (phenyl), 174.6 ($C{=}O$); IR 1730 cm^{-1}. Anal. Calcd for $C_{18}H_{22}SiO_2$: C, 72.44; H, 7.43; Si, 9.41; O, 10.72. Found: C, 72.24; H, 7.31.

Ethyl 2-(methyldiphenylsilyl)propionate (3c): bp 164 °C (4 Torr); ^1H NMR δ 0.66 (s, 3 H, $SiCH_3$), 0.95 (t, 3 H, $J = 7.26$ Hz, OCH_2CH_3), 1.25 (d, 3 H, $J = 7.26$ Hz, $SiCH(CH_3)COOEt$), 2.64 (q, 1 H, $J = 7.26$ Hz, $CHCOOEt$), 3.79–3.99 (m, 2 H, OCH_2CH_3), 7.30–7.39 (m, 6 H, phenyl), 7.50–7.61 (m, 4 H, phenyl); ^{13}C NMR δ −5.6 ($SiCH_3$), 11.9 ($SiCH(CH_3)COOEt$), 13.9 (OCH_2CH_3), 28.9 ($CHCOOEt$), 59.9 (OCH_2CH_3), 127.7 (phenyl), 127.9 (phenyl), 129.54 (phenyl), 129.60 (phenyl), 134.27 (phenyl), 134.29 (phenyl), 134.75 (phenyl), 134.79 (phenyl), 175.8 ($C{=}O$); IR 1710 cm^{-1}. Anal. Calcd for $C_{18}H_{22}SiO_2$: C, 72.44; H, 7.43; Si, 9.41; O, 10.72. Found: C, 72.37; H, 7.56.

Ethyl 3-(ethoxydimethylsilyl)propionate (2d): bp 87–88 °C (10 Torr); ^1H NMR δ 0.12 (s, 6 H, $Si(CH_3)_2$), 0.92 (m, 2 H, $SiCH_2$), 1.18 (t, 3 H, $J = 6.93$ Hz, $Si(OCH_2CH_3)$), 1.26 (t, 3 H, $J = 6.93$ Hz, $COOCH_2CH_3$), 2.33 (m, 2 H, CH_2COOEt), 3.67 (q, 2 H, $J = 6.93$ Hz, $Si(OCH_2CH_3)$), 4.12 (q, 2 H, $J = 6.93$ Hz, $COOCH_2CH_3$); ^{13}C NMR δ −2.4 ($SiCH_3$), 11.2 ($SiCH_2$), 14.0 ($COOCH_2CH_3$), 18.3 ($Si(OCH_2CH_3)$), 28.0 (CH_2COOEt), 58.1 ($Si(OCH_2CH_3)$), 60.1 ($COOCH_2CH_3$), 174.6 ($C{=}O$); IR 1730 cm^{-1}. Anal. Calcd for $C_9H_{20}SiO_3$: C, 52.90; H, 9.87; Si, 13.74; O, 23.49. Found: C, 52.77; H, 10.10.

Ethyl 2-(ethoxydimethylsilyl)propionate (3d): bp 83–84 °C (11 Torr); ^1H NMR δ 0.18 (s, 3 H, $Si(CH_3)_2$), 0.19 (s, 3 H, $Si(CH_3)_2$), 1.19 (t, 3 H, $J = 6.93$ Hz, $Si(OCH_2CH_3)$), 1.21 (d, 3 H, $J = 7.26$ Hz, $SiCH(CH_3)COOEt$), 1.25 (t, 3 H, $J = 6.93$ Hz, $COOCH_2CH_3$), 2.17 (q, 1 H, $J = 7.26$ Hz, $CHCOOEt$), 3.71 (qd, 2 H, $J = 6.93, 1.65$ Hz, $Si(OCH_2CH_3)$), 4.12 (qd, 2 H, $J = 6.93, 1.65$ Hz, $COOCH_2CH_3$); ^{13}C NMR δ −3.2 ($SiCH_3$), −3.6 ($SiCH_3$), 10.4 ($SiCH(CH_3)COOEt$), 14.3 ($COOCH_2CH_3$), 18.3 ($Si(OCH_2CH_3)$), 30.9 ($CHCOOEt$), 58.7 ($Si(OCH_2CH_3)$), 59.8 ($COOCH_2CH_3$), 175.5 ($C{=}O$); IR 1715 cm^{-1}. Anal. Calcd for $C_9H_{20}SiO_3$: C, 52.90; H, 9.87; Si, 13.74; O, 23.49. Found: C, 52.90; H, 9.92.

Methyl 3-(trimethoxysilyl)propionate (2e): bp 74–76 °C (4 Torr); ^1H NMR δ 0.97 (m, 2 H, $SiCH_2$), 2.40 (m, 2 H, CH_2COOMe), 3.57 (s, 9 H, $Si(OCH_3)_3$), 3.67 (s, 3 H, $COOCH_3$); ^{13}C NMR δ 4.2 ($SiCH_2$), 27.2 (CH_2COOMe), 50.4 ($Si(OCH_3)_3$), 51.5 ($COOCH_3$), 174.6 ($C{=}O$); IR 1730 cm^{-1}. Anal. Calcd for $C_7H_{16}SiO_5$: C, 40.37; H, 7.74; Si, 13.48; O, 38.41. Found: C, 40.21; H, 7.94.

Methyl 2-(trimethoxysilyl)propionate (3e): bp 66–68 °C (5 Torr); ^1H NMR δ 1.28 (d, 3 H, $J = 7.26$ Hz, $SiCH(CH_3)COOMe$), 2.26 (q, 1 H, $J = 7.26$ Hz, $CHCOOMe$), 3.60 (s, 9 H, $Si(OCH_3)_3$), 3.70 (s, 3 H, $COOCH_3$); ^{13}C NMR δ 10.5 ($SiCH(CH_3)COOMe$), 26.1 ($CHCOOMe$), 50.5 ($Si(OCH_3)_3$), 51.0 ($COOCH_3$), 174.9 ($C{=}O$); IR 1720 cm^{-1}; EIMS *m/e* (rel intensity) 180

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(M$^+$ – Si, 1), 177 (M$^+$ – OMe, 10), 153 (38), 121 (100), 91 (56), 90 (15).

Ethyl 3-(fluorodiphenylsilyl)propionate (2f): bp 168–172 °C (4 Torr); ^{1}H NMR δ 1.18 (t, 3 H, *J* = 6.93 Hz, $\mathrm{OCH_2C}H_3$), 1.56 (m, 2 H, $\mathrm{SiC}H_2$), 2.44 (m, 2 H, $\mathrm{C}H_2\mathrm{COOEt}$), 4.05 (q, 2 H, *J* = 6.93 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.30–7.48 (m, 6 H, phenyl), 7.57–7.62 (m, 4 H, phenyl); ^{13}C NMR δ 9.2 (d, $J_{\mathrm{C\text{-}F}}$ = 15.9 Hz, $\mathrm{Si}C\mathrm{H_2}$), 14.1 ($\mathrm{OCH_2}C\mathrm{H_3}$), 27.4 ($C\mathrm{H_2COOEt}$), 60.5 ($\mathrm{O}C\mathrm{H_2CH_3}$), 128.1 (phenyl), 130.7 (phenyl), 132.5 (d, $J_{\mathrm{C\text{-}F}}$ = 15.8 Hz, phenyl), 134.1 (d, $J_{\mathrm{C\text{-}F}}$ = 2.5 Hz, phenyl), 173.9 (C=O); IR 1740 cm^{-1}. Anal. Calcd for $\mathrm{C_{17}H_{19}FSiO_2}$: C, 67.52; H, 6.33; F, 6.28; Si, 9.29; O, 10.58. Found: C, 67.23; H, 6.36; F, 6.20.

Ethyl 3-(difluorophenylsilyl)propionate (2g): bp 124–127 °C (8 Torr); ^{1}H NMR δ 1.21 (t, 3 H, *J* = 7.26 Hz, $\mathrm{OCH_2C}H_3$), 1.36 (m, 2 H, $\mathrm{SiC}H_2$), 2.51 (m, 2 H, $\mathrm{C}H_2\mathrm{COOEt}$), 4.11 (q, 2 H, *J* = 7.26 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.24–7.55 (m, 3 H, phenyl), 7.62–7.71 (m, 2 H, phenyl); ^{13}C NMR δ 7.2 (t, $J_{\mathrm{C\text{-}F}}$ = 17.1 Hz, $\mathrm{Si}C\mathrm{H_2}$), 14.0 ($\mathrm{OCH_2}C\mathrm{H_3}$), 26.6 ($C\mathrm{H_2COOEt}$), 60.8 ($\mathrm{O}C\mathrm{H_2CH_3}$), 128.2 (phenyl), 128.6 (t, $J_{\mathrm{C\text{-}F}}$ = 19.5 Hz), 131.9 (phenyl), 133.7 (phenyl), 173.4 (C=O); IR 1730 cm^{-1}. Anal. Calcd for $\mathrm{C_{11}H_{14}F_2SiO_2}$: C, 54.08; H, 5.78; F, 15.55; Si, 11.50; O, 13.10. Found: C, 53.95; H, 5.90; F, 15.12.

Ethyl 3-(trimethylsilyl)hydrocinnamate (5): bp 110–112 °C (3 Torr); ^{1}H NMR δ –0.04 (s, 9 H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 1.07 (t, 3 H, *J* = 6.93 Hz, $\mathrm{OCH_2C}H_3$), 2.59–2.85 (m, 3 H, $\mathrm{PhC}H\mathrm{(SiMe_3)C}H_2$), 3.99 (qd, 2 H, *J* = 6.93, 2.64 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.02–7.14 (m, 2 H, phenyl), 7.15–7.31 (m, 3 H, phenyl); ^{13}C NMR δ –3.1 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 14.0 ($\mathrm{OCH_2}C\mathrm{H_3}$), 32.6 ($\mathrm{Ph}C\mathrm{H(SiMe_3)CH_2}$), 34.9 ($C\mathrm{H_2COOEt}$), 60.2 ($\mathrm{O}C\mathrm{H_2CH_3}$), 124.7 (phenyl), 127.3 (phenyl), 128.0 (phenyl), 142.4 (phenyl), 173.2 (C=O); IR 1740 cm^{-1}. Anal. Calcd for $\mathrm{C_{14}H_{22}SiO_2}$: C, 67.15; H, 8.86; Si, 11.22; O, 12.78. Found: C, 66.85; H, 8.76.

Ethyl 2-methyl-2-(trimethylsilyl)phenylacetate (6): bp 107–109 °C (3 Torr); ^{1}H NMR δ 0.04 (s, 9 H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 1.27 (t, 3 H, *J* = 7.26 Hz, $\mathrm{OCH_2C}H_3$), 1.61 (s, 3 H, $\mathrm{PhC(C}H_3\mathrm{)COOEt}$), 4.19 (q, 2 H, *J* = 7.26 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.02–7.12 (m, 2 H, phenyl), 7.18–7.29 (m, 3 H, phenyl); ^{13}C NMR δ –2.7 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 14.2 ($\mathrm{OCH_2}C\mathrm{H_3}$), 19.2 ($C\mathrm{H_3}$), 43.7 ($C\mathrm{COOEt}$), 60.5 ($\mathrm{O}C\mathrm{H_2CH_3}$), 125.3 (phenyl), 126.7 (phenyl), 127.9 (phenyl), 141.9 (phenyl), 176.0 (C=O); IR 1720 cm^{-1}.

Ethyl 2-[(trimethylsilyl)methyl]hexanoate (8): bp 85 °C (7 Torr); ^{1}H NMR δ –0.05 (s, 9 H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 0.64 (dd, 1 H, *J* = 14.85, 5.61 Hz, $\mathrm{SiC}H_2\mathrm{CHCOOEt}$), 0.83 (t, 3 H, *J* = 7.26 Hz, $\mathrm{CH_2CH_2C}H_3$), 0.90 (dd, 1 H, *J* = 14.85, 9.24 Hz, $\mathrm{SiC}H_2\mathrm{CHCOOEt}$), 1.16–1.28 (m, 4 H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 1.21 (t, 3 H, *J* = 7.26 Hz, $\mathrm{OCH_2C}H_3$), 1.30–1.44 (m, 1 H, $\mathrm{CH(C}H_2\mathrm{CH_2CH_2CH_3)COOEt}$), 1.51–1.65 (m, 1 H, $\mathrm{CH(C}H_2\mathrm{CH_2CH_2CH_3)COOEt}$), 2.40–2.29 (m, 1 H, $\mathrm{C}H\mathrm{(CH_2CH_2CH_2CH_3)COOEt}$), 4.06 (qd, 2 H, *J* = 7.26, 1.32 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$); ^{13}C NMR δ –1.3 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 13.9 ($\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$), 14.2 ($\mathrm{OCH_2}C\mathrm{H_3}$), 20.0 ($\mathrm{Si}C\mathrm{H_2CHCOOEt}$), 22.5 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 29.5 ($C\mathrm{H_2CH_2CH_3}$), 35.7 ($\mathrm{CH(COOEt)}C\mathrm{H_2CH_2CH_2CH_3}$), 41.3 ($C\mathrm{HCOOEt}$), 59.9 ($\mathrm{O}C\mathrm{H_2CH_3}$), 177.1 (C=O); IR 1730 cm^{-1}. Anal. Calcd for $\mathrm{C_{12}H_{26}SiO_2}$: C, 62.56; H, 11.38; Si, 12.15; O, 13.90. Found: C, 62.34; H, 11.64.

Ethyl 2-(trimethylsilyl)heptanoate (9): bp 58–62 °C (4 Torr); ^{1}H NMR δ 0.06 (s, 9 H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 0.87 (t, 3 H, *J* = 6.60 Hz, $\mathrm{CH_2CH_2C}H_3$), 1.24 (t, 3 H, *J* = 6.60 Hz, $\mathrm{OCH_2C}H_3$), 1.22–1.38 (m, 7 H, $\mathrm{CH_3C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CHCOOEt}$), 1.86–1.75 (m, 1 H, $\mathrm{C}H_2\mathrm{CH(SiMe_3)COOEt}$), 1.95 (dd, 1 H, *J* = 11.55, 1.98 Hz, $\mathrm{C}H\mathrm{(SiMe_3)COOEt}$), 4.11 (q, 2 H, *J* = 6.60 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$); ^{13}C NMR δ –2.7 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 14.0 ($C\mathrm{H_3CH_2CH_2}$), 14.4 ($\mathrm{OCH_2}C\mathrm{H_3}$), 22.4 ($\mathrm{CH_3}C\mathrm{H_2CH_2}$), 26.7 ($\mathrm{CH_3CH_2}C\mathrm{H_2}$), 30.1 ($\mathrm{CH_3CH_2CH_2}C\mathrm{H_2}$), 31.6 ($C\mathrm{H_2CH(SiMe_3)COOEt}$), 37.8 ($C\mathrm{HCOOEt}$), 59.5 ($\mathrm{O}C\mathrm{H_2CH_3}$), 175.4 (C=O); IR 1710 cm^{-1}.

3-(Trimethylsilyl)propionic acid (10a): bp 103–105 °C (9 Torr); ^{1}H NMR δ 0.02 (s, 9 H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 0.85 (m, 2 H, $\mathrm{SiC}H_2$), 2.33 (m, 2 H, $\mathrm{C}H_2\mathrm{COOH}$), 11.37 (br, $\mathrm{COO}H$); ^{13}C NMR δ –2.0 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 11.4 ($\mathrm{Si}C\mathrm{H_2}$), 28.8 ($C\mathrm{H_2COOH}$), 181.8 ($C\mathrm{OOH}$); IR 1710 cm^{-1}. Anal. Calcd for $\mathrm{C_6H_{14}SiO_2}$: C, 49.27; H, 9.65; Si, 19.20; O, 21.88. Found: C, 49.34; H, 9.84.

2-(Trimethylsilyl)propionic acid (11a): bp 103–105 °C (9 Torr); ^{1}H NMR δ 0.03 (s, 9 H, $\mathrm{Si(C}H_3\mathrm{)_3}$), 1.19 (d, 3 H, *J* = 6.93 Hz, $\mathrm{SiCH(C}H_3\mathrm{)}$), 2.09 (q, 1 H, *J* = 6.93 Hz, $\mathrm{C}H\mathrm{COOH}$), 11.38 (br, $\mathrm{COO}H$); ^{13}C NMR δ –3.1 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 10.6 ($\mathrm{SiCH}C\mathrm{H_3}$), 30.5 ($C\mathrm{H_2COOH}$), 183.2 ($C\mathrm{OOH}$).

3-(Tri-*n*-butylsilyl)propionic acid (10b): bp 171–173 °C (1 Torr); ^{1}H NMR δ 0.52 (t, 6 H, *J* = 7.26 Hz, $\mathrm{SiC}H_2\mathrm{CH_2CH_2CH_3}$), 0.87 (m, 2 H, $\mathrm{SiC}H_2$), 0.88 (t, 9 H, *J* = 6.93 Hz, $\mathrm{C}H_3\mathrm{CH_2}$), 1.19–1.37 (m, 12 H, $\mathrm{SiCH_2C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 2.31 (m, 2 H, $\mathrm{C}H_2\mathrm{COOH}$), 11.80 (br, $\mathrm{COO}H$); ^{13}C NMR δ 7.5 ($\mathrm{Si}C\mathrm{H_2CH_2COOH}$), 11.8 ($\mathrm{Si}C\mathrm{H_2CH_2CH_2CH_3}$), 13.7 ($\mathrm{SiCH_2CH_2CH_2}C\mathrm{H_3}$), 26.0 ($\mathrm{SiCH_2CH_2}C\mathrm{H_2CH_3}$), 26.8 ($\mathrm{SiCH_2}C\mathrm{H_2CH_2CH_3}$), 28.8 ($C\mathrm{H_2COOH}$), 182.0 ($C\mathrm{OOH}$); IR 1710 cm^{-1}. Anal. Calcd for $\mathrm{C_{15}H_{32}SiO_2}$: C, 66.11; H, 11.84; Si, 10.31; O, 11.74. Found: C, 66.09; H, 12.13.

3-(Methyldiphenylsilyl)propionic Acid (10c). The cooled reaction mixture was extracted with 20% aqueous NaOH (20 mL × 2). The extract was acidified with 10% aqueous HCl. The acidic mixture was, in turn, extracted with $\mathrm{Et_2O}$ (20 mL × 2). The $\mathrm{Et_2O}$ solution was dried with $\mathrm{MgSO_4}$ and concentrated. Pure **10c** was obtained by recrystallizing the residue from hexane at –20 °C. **10c**: mp 63–64 °C; ^{1}H NMR δ 0.56 (s, 3 H, $\mathrm{SiC}H_3$), 1.41 (m, 2 H, $\mathrm{SiC}H_2$), 2.36 (m, 2 H, $\mathrm{C}H_2\mathrm{COOH}$), 7.33–7.38 (m, 6 H, phenyl), 7.49–7.52 (m, 4 H, phenyl), 10.97 (br, $\mathrm{COO}H$); ^{13}C NMR δ –4.7 ($\mathrm{Si}C\mathrm{H_3}$), 9.2 ($\mathrm{Si}C\mathrm{H_2}$), 28.7 ($C\mathrm{H_2COOH}$), 128.0 (phenyl), 129.5 (phenyl), 134.4 (phenyl), 135.9 (phenyl), 181.1 ($C\mathrm{OOH}$); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $\mathrm{C_{16}H_{18}SiO_2}$: C, 71.07; H, 6.71; Si, 10.39; O, 11.83. Found: C, 70.99; H, 6.70.

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