4864 J. Org. Chem. 1987, 52, 4864-4868

The Catalyzed Reaction of α,β-Unsaturated Esters with Various Hydrosilanes

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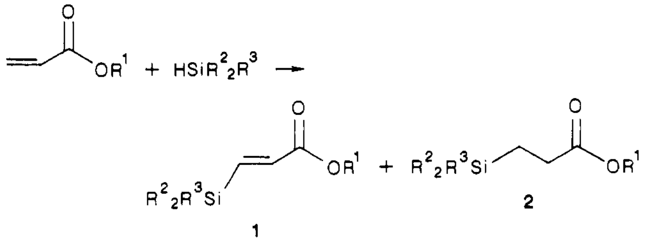
Received April 15, 1987

The $Co_2(CO)_8$-catalyzed reaction of acrylic acid esters (methyl acrylate, ethyl acrylate, and butyl acrylate) with $HSiEt_2Me$ gave the corresponding (*E*)-3-silylacrylate in high yields, along with only a small amount of β-adducts, when the esters were used in excess. Thus, the (*E*)-3-silylacrylates were obtained from $HSiMe_3$, $HSiEt_2Me$, $HSiMe_2Ph$, and $HSi(OEt)_3$. The ratio of (*E*)-3-silylacrylate to β-adduct decreased with an increase in the molar ratio of hydrosilane to methyl acrylate. The use of an excess of hydrosilane resulted in the formation of only the β-adduct. The reaction of methyl methacrylate and methyl crotonate gave an alkylsilane or a mixture of an alkylsilane and an allylsilane. Some rhodium and ruthenium complexes also yielded a mixture of (*E*)-3-silylacrylate and β-adduct, but the selectivity was lower than that from cobalt complexes. Extensive intermolecular deuterium exchange occurred in the reaction of methyl acrylate with $DSiEt_2Me$. The reaction of (*E*)-3-silylacrylate with a hydrosilane and $Co_2(CO)_8$ resulted in hydrogenation to give the corresponding β-adduct.

Hydrosilylation of α,β-unsaturated esters has been extensively studied and known to afford four types of addition products: α- and β-adducts from 1,2-addition to the C=C bond, a 1,2-adduct from the 1,2-addition to the C=O bond, and a 1,4-adduct.[2] Platinum catalysts have been shown to be effective in producing the α- and β-adducts.[2a-e] A nickel phosphine complex is known to be effective for the preparation of the β-adduct in the reaction of methyl acrylate with dichloromethylsilane.[2g] Ketene silyl acetals (1,4-adduct) have been obtained in the reaction catalyzed by chloroplatinic acid[2f] or $RhCl(PPh_3)_3$.[2h-j] Ojima and co-workers reported that only an α-adduct was obtained in the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of methyl acrylate with chlorodimethylsilane and the similar reaction with ethyldimethylsilane selectively yielded the β-adduct.[2j]

In a preliminary paper, we have reported that a new type of the addition product ((*E*)-3-silylacrylate) was obtained in the $Co_2(CO)_8$-catalyzed reaction of methyl acrylate with hydrosilanes.[3] This reaction was the first example of the direct formation of a vinylsilane from an olefin and hydrosilanes catalyzed by $Co_2(CO)_8$. The mechanism of the hydrosilylation of olefins using $Co_2(CO)_8$ as a catalyst was proposed by Chalk and Harrod,[4a] and it is commonly accepted; however, it does not apply to this new reaction. We describe here the full details of the scope and limitations of the $Co_2(CO)_8$-catalyzed reaction of α,β-unsaturated esters with hydrosilanes as well as the reaction mechanism.

Table I. Reaction of Acrylic Acid Esters with Hydrosilanes[a]



R^1	R^2	R^3	product	yield, %[b]
Me	Et	Me	**1a**	86
			2a	3
Me	Me	Me	**1b**	65
			2b	8
Me	Me	Ph	**1c**	69
			2c	8
Me	OEt	OEt	**1d**	43[c]
			2d	4[c]
Et	Et	Me	**1e**	76
			2e	2
n-C_4H_9	Et	Me	**1f**	86
			2f	3

[a] Ester (50 mmol), hydrosilane (10 mmol), $Co_2(CO)_8$ (0.4 mmol), benzene (10 mL), 25 °C, 3 h. [b] Determined by GLC. [c] Without benzene.

Results and Discussion

Reaction of Various α,β-Unsaturated Esters with Hydrosilanes. It is well-known that $Co_2(CO)_8$ is an effective catalyst for the hydrosilylation of olefins to produce alkylsilanes.[4] For example, the $Co_2(CO)_8$-catalyzed hydrosilylation of 1-olefins gives alkylsilanes in high yields.[4a] Chalk noted that the α-adduct was obtained in the hydrosilylation of acrylonitrile.[4c] The hydrosilylation of styrene, vinylsilane, and allylamine catalyzed by $Co_2(CO)_8$ have also been reported to give the corresponding alkylsilanes.[4d-i] On the other hand, $Co_2(CO)_8$-catalyzed hydrosilylation of α,β-unsaturated esters has received little attention.

In contrast to the above results, we have found that the reaction of an excess of methyl acrylate with $HSiEt_2Me$ in the presence of $Co_2(CO)_8$ at 25 °C gave mostly methyl (*E*)-3-(diethylmethylsilyl)propenoate (**1a**) in high yield, along with only a small amount of β-adduct (**2a**) (eq 1). Hydrogen did not evolved, but methyl propionate was

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(1) (a) Kagawa University. (b) Osaka University.

(2) (a) Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974. (b) Sommer, L. H.; Mackay, F. P.; Steward, O. W.; Campbell, P. G. *J. Am. Chem. Soc.* **1957**, *79*, 2764. (c) Goodman, L.; Silverstein, R. M.; Benitez, A. *J. Am. Chem. Soc.* **1957**, *79*, 3073. (d) Curry, J. W.; Harrison, G. W. *J. Org. Chem.* **1958**, *23*, 627. (e) Rijkens, F.; Janssen, M. J.; Drenth, W.; Van der Kerk *J. Organomet. Chem.* **1964**, *2*, 374. (f) Petrov, A. D.; Sadykh-Zade, S. I.; Filatova, E. I. *Zh. Obshch. Khim.* **1959**, *29*, 2963. (g) Kiso, Y.; Kumada, M.; Tamao, K.; Utimoto, M. *J. Organomet. Chem.* **1973**, *50*, 297. (h) Yoshii, E.; Kobayashi, Y.; Koizumi, T.; Oribe, T. *Chem. Pharm. Bull.* **1974**, *22*, 2767. (i) Yoshii, E.; Koizumi, T.; Kawazoe, T. *Chem. Pharm. Bull.* **1976**, *24*, 1957. (j) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1976**, *43*, 111.

(3) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1193.

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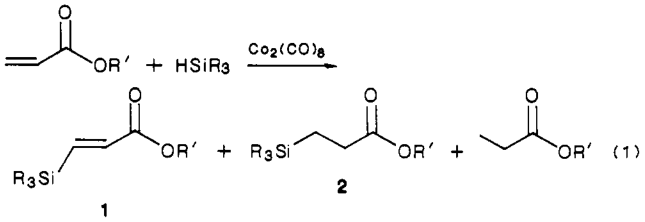
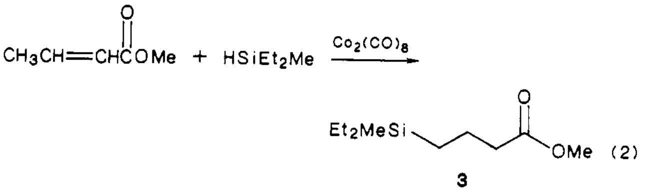


a, R₃Si = Et₂MeSi, R' = Me
b, R₃Si = Me₃Si, R' = Me
c, R₃Si = Me₂PhSi, R' = Me
d, R₃Si = (EtO)₃Si, R' = Me
e, R₃Si = Et₂MeSi, R' = Et
f, R₃Si = Et₂MeSi, R' = Bu

obtained in high yield. The results obtained for the reaction of various α,β-unsaturated esters with hydrosilanes are summarized in Table I. A similar reaction of ethyl acrylate and butyl acrylate gave predominantly **1e** and **1f** in high yields, respectively. Trialkylsilanes such as $HSiEt_2Me$, $HSiMe_3$, and $HSiMe_2Ph$ reacted smoothly to give **1a**–**c** in high yields. In the case of $HSiMe_3$ and $HSiMe_2Ph$, the yield of the β-adduct (**2b** and **2c**) slightly increased. The reactivity of $HSi(OEt)_3$ was lower than that of trialkylsilanes. The reaction with trichlorosilane was unsuccessful (no reaction).

The effect of the reaction conditions on the yields of **1a** and **2a** are shown in Table II. With a 10-fold excess of methyl acrylate, the vinylsilane (**1a**) was obtained mostly high selectively and in high yield. Interestingly, the ratio of the β-adduct (**2a**) to **1a** increased with an increase in the molar ratio of $HSiEt_2Me$ to methyl acrylate. When a 2-fold excess of $HSiEt_2Me$ was used, only **2a** was obtained in 37% yield. Although the reaction at 0 °C instead of 25 °C also yielded **1a** in 69% yield, the ratio of **2a** increased slightly.

The reactivity of α,β-unsaturated esters having a substituent at the carbon–carbon double bond is generally lower than that of acrylic acid esters. The reaction of an excess of methyl crotonate (50 mmol) with $HSiEt_2Me$ (10 mmol) in the presence of $Co_2(CO)_8$ (0.4 mmol) for 3 h at 25 °C gave methyl 4-(diethylmethylsilyl)butanoate (**3**) in 19% yield, along with some oligomers of methyl crotonate. With a 3-fold excess of $HSiEt_2Me$ under similar reaction conditions, almost no reaction took place after 3 h, but after 48 h, only **3** was obtained in 32% yield without formation of the oligomers (eq 2). The reaction path is assumed as follows. Initially methyl crotonate would isomerize to methyl 3-butenoate, and then it would react with $HSiEt_2Me$ to give **3**. The reaction of a 5-fold excess of methyl methacrylate with $HSiEt_2Me$ gave a mixture of an alkylsilane (**4**) and an allylsilane (**5**) in 16% and 17% yields, respectively (eq 3). On the other hand, with a 3-fold excess of $HSiEt_2Me$ over methyl methacrylate, **4** and **5** were obtained in 21% and 3% yields, respectively. The ratio of **4** to **5** increased with an increase in the ratio of a hydrosilane to methyl methacrylate. Ketene silyl acetals (1,4-adducts) have been obtained in the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of methyl crotonate or methyl methacrylate.[2j] However, under the present reactions, ketene silyl acetals were not detected. A similar reaction of methyl cinnamate did not yield the corresponding adduct. Only the α,β-unsaturated esters having no substituent at the β-position of the carbon–carbon double bond can give the vinylsilane or the allylsilane. Thus, a steric factor at the β-position influences the reaction process.



$$CH_3CH{=}CH\overset{O}{\overset{\|}{C}}OMe + HSiEt_2Me \xrightarrow{Co_2(CO)_8} Et_2MeSi\text{-}CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OMe \quad (2)$$

3

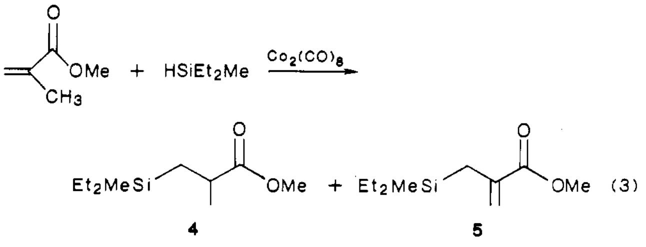


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Table II. Effect of the Reaction Conditions[a]

methyl acrylate, mmol	$HSiEt_2Me$, mmol	**1a** + **2a** yield, %[b]	**1a**/**2a**, %[b]	
			1a	**2a**
100	10	83	98	2
50	10	89	97	3
25	10	99	95	5
10	10	45	67	23
10	20	37	0	100
10	30	58	0	100
50	10	84[c]	82	18

[a] $Co_2(CO)_8$ (0.4 mmol), benzene (10 mL), 25 °C, 3 h unless otherwise noted. [b] Determined by GLC. [c] 0 °C.

Table III. Catalytic Activity of Various Metal Complexes[a]

catalyst	**1a** + **2a** yield, %[b]	**1a**/**2a**, %[b]	
		1a	**2a**
$RhCl(PPh_3)_3$	86	70	30
$RhCl(CO)(PPh_3)_2$	99	67	33
$Ru_3(CO)_{12}$	10	67	33
$RuCl_2(PPh_3)_3$	7	76	24
$IrCl(CO)(PPh_3)_2$	22	73	27
$Fe_2(CO)_9$	0		
$Co_2(CO)_8$	18	92	8
$Co_2(CO)_8$	88[c]	94	6
$Et_2MeSiCo(CO)_4$	100[d]	96	4

[a] Methyl acrylate (50 mmol), $HSiEt_2Me$ (10 mmol), catalyst (0.05 mmol), benzene (10 mL), 80 °C, 3 h unless otherwise noted. [b] Determined by GLC. [c] 0.1 mmol. [d] 0.8 mmol.

Catalytic Activity of Various Metal Complexes. As mentioned before, several complexes are known to be effective catalysts in the hydrosilylation of methyl acrylate.[2] However, the catalytic activity of these complexes under conditions using a large excess of methyl acrylate has not been examined. We examined the activity of some rhodium, ruthenium, iridium, and cobalt complexes. The results obtained are shown in Table III. Although the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of methyl acrylate has been reported to give a mixture of the β-adduct and the disilylated product without the formation of the vinylsilane,[2j] a similar reaction using an excess of methyl acrylate gave a mixture of **1a** and **2a** in high yield without the production of the disilylated product. The selectivity of **1a** was 70%. The reaction of $RhCl(CO)(PPh_3)_2$ gave a similar result compared to $RhCl(PPh_3)_3$. It has been reported that $Ru_3(CO)_{12}$ is an effective catalyst to give vinylsilanes from olefins and hydrosilanes.[5] However, the activity of $Ru_3(CO)_{12}$ in the reaction of methyl acrylate was very low. The results of $RuCl_2(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$ were similar to that of $Ru_3(CO)_{12}$. In the hydrosilylation of methyl acrylate, rhodium complexes were more reactive than ruthenium and iridium complexes. Some iron complexes have also been known to be effective to

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[5] Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 3890.

Table IV. Distribution of Deuteriated Products from $Co_2(CO)_8$-Catalyzed Reaction of $DSiEt_2Me$ and Methyl Acrylate

product	relative abundance, %[a]		
	d_0	d_1	d_2
1a	82	16	2
methyl propionate	52	38	10
methyl acrylate	65	28	7

[a] Determined by mass spectra.

Table V. Distribution of Protons in Deuteriated Products

products	number of protons[a]
1a	SiCH=C, 0.86; SiC=CH, 0.86; OCH_3, 3
methyl propionate	CH_3CCO, 2.6; CCH_2CO, 1.8; OCH_3, 3
methyl acrylate	CH_2=CHCO, 2.6; OCH_3, 3

[a] Determined by ^{1}H-NMR.

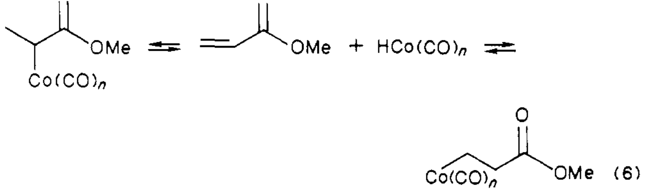
produce vinylsilanes from olefins and hydrosilanes.[6] However, $Fe_2(CO)_9$ was not effective in the present reaction. With 0.05 mmol of $Co_2(CO)_8$, the combined yield was only 18%, but the ratio of **1a** was 92:8. When more than 0.1 mmol of $Co_2(CO)_8$ was employed, both the yield and the selectivity were very high. Thus, $Co_2(CO)_8$ was the best catalyst for the preparation of the vinylsilane from methyl acrylate and hydrosilanes. When 0.8 mmol of $Et_2MeSiCo(CO)_4$,[7] the suspected key catalyst, was used, **1a** was obtained in 96% yield, along with **2a** (4% yield).

Mechanistic Aspects of the Catalyzed Reaction of α,β-Unsaturated Esters with Hydrosilanes. The reaction of methyl acrylate with $DSiEt_2Me$ was carried out in order to identify the fate of the hydrogen of $HSiEt_2Me$. A solution of methyl acrylate (15 mmol), $DSiEt_2Me$ (6 mmol), $Co_2(CO)_8$ (0.24 mmol), and toluene (10 mL) was heated at 25 °C for 3 h. GLC analysis showed that the reaction mixture contained the vinylsilane **1a** (5.5 mmol), the β-adduct **2a** (0.4 mmol), methyl acrylate (3.5 mmol), and methyl propionate (5.5 mmol). Methyl acrylate also behaved as a hydrogen acceptor. This implies that an excess of methyl acrylate is necessary in order to obtain **1** in high yield. The deuterium content in the products and starting materials were calculated from NMR and mass spectra. The starting material, methyl acrylate, and the products (**1a** and methyl propionate) were deuteriated. These results are shown in Tables IV and V. Their analysis clearly showed that extensive deuterium scrambling had occurred both in the starting material and in the products.

It is known that $Co_2(CO)_8$ reacts with $HSiR_3$ to give a mixture of $HCo(CO)_n$ and $R_3SiCo(CO)_4$. $HCo(CO)_n$ (n = 3 or 4) further reacts with $HSiR_3$ to give $R_3SiCo(CO)_4$ and hydrogen (eq 4 and 5).[4a,b] Hydrocobalt–carbonyl ($HCo(CO)_n$) is known to smoothly react with olefins to form an alkylcobalt complex.[8] The extensive intermolecular deuterium exchange clearly shows that the conversion to an alkylcobalt complex from methyl acrylate and $HCo(CO)_n$ is rapidly reversible by a β-elimination process (eq 6).

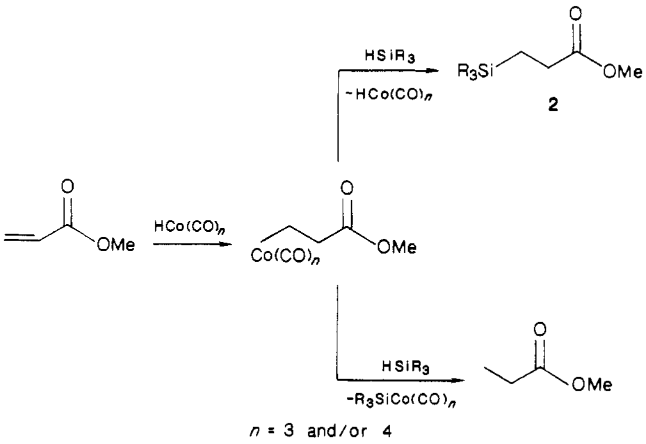
$$Co_2(CO)_8 + HSiR_3 \xrightarrow[(-CO)]{} HCo(CO)_n + R_3SiCo(CO)_4 \quad (4)$$

$$HCo(CO)_n + HSiR_3 \xrightarrow{(CO)} R_3SiCo(CO)_4 + H_2 \quad (5)$$



(6)

Scheme I



Two reaction paths are envisioned in the reaction of the alkylcobalt complex with $HSiR_3$. One of them gives a β-adduct and $HCo(CO)_n$. The other involves hydrogenation of methyl acrylate to produce methyl propionate and $R_3SiCo(CO)_n$ (Scheme I). The former was proposed by Chalk and Harrod and is commonly accepted as the mechanism of $Co_2(CO)_8$-catalyzed hydrosilylation of olefins.[4a] However, the formation of **1a** cannot be accounted for via these alkylcobalt complexes.

In order to ascertain whether **1a** and **2a** are independently produced, the yields of **1a** and **2a** were measured as a function of time. When the reaction of methyl acrylate (10 mmol) with an excess of $HSiEt_2Me$ (30 mmol) in the presence of $Co_2(CO)_8$ (0.4 mmol) was run at 25 °C for 10 min, **1a** and **2a** were obtained in 3% and 22% yields, respectively. After 20 min, only **2a** was observed in 50% yield and **1a** disappeared. In this reaction, the corresponding disiloxane, $(Et_2MeSi)_2O$, was also obtained in 10% yield based on methyl acrylate. The reaction using an excess of methyl acrylate gave little disiloxane. Next, the reaction of $Co_2(CO)_8$ (0.4 mmol) with $HSiEt_2Me$ (10 mmol) in benzene (10 mL) for 2 h at 25 °C was run to give the silylcobalt–carbonyl adduct. After the evolution of molecular hydrogen had completely subsided, methyl acrylate (5 mmol) was added at 25 °C to the solution. In spite of the use of an excess of a hydrosilane, the vinylsilane **1a** was obtained after 1 h (29% yield), along with **2a** in 33% yield. However, after 48 h, **1a** disappeared, and only **2a** was obtained in 35% yield. These results suggest that the silylcobalt–carbonyl can react with methyl acrylate to give **1a**, which subsequently reacts with the hydrosilane in the presence of $Co_2(CO)_8$. Thus, when a solution of **1a** (4.8 mmol), $HSiEt_2Me$ (5 mmol), $Co_2(CO)_8$ (0.2 mmol), and benzene (5 mL) was stirred at 20 °C for 3 h, only 0.3 mmol of **1a** remained in the solution, and **2a** was obtained in 25% yield based on the starting **1a**. The fate of 69% of the starting **1a** was uncertain. Disiloxane also formed in 20% yield based on $HSiEt_2Me$. From these experiments, it is

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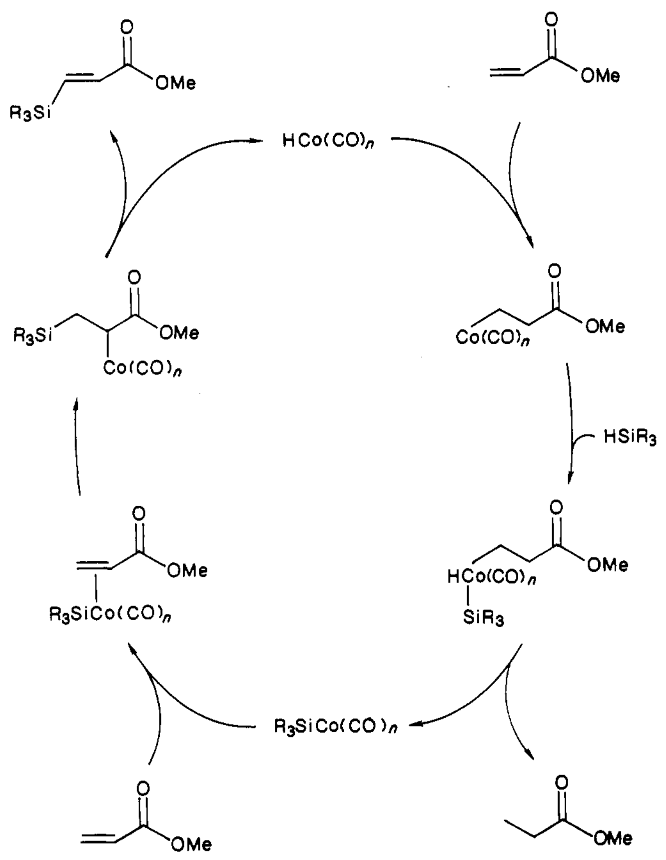
(6) (a) Nesmeyanov, A. N.; Freidlina, R. Kh.; Chukovskaya, E. C.; Petrova, R. G.; Belyavsky, A. B. *Tetrahedron* **1962**, *17*, 61. (b) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (c) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *No. 168*, 189.

(7) Prepared by the reaction of $Co_2(CO)_8$ with $HSiEt_2Me$, bp 71–73 °C (10 mmHg).

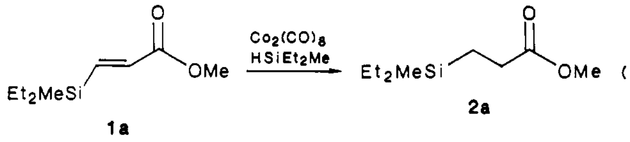
(8) (a) Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980. (b) Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259.

Scheme II



$n = 3$ and/or 4

clear that **1a** is hydrogenated with $HSiEt_2Me$ in the presence of $Co_2(CO)_8$ to give **2a** (eq 7). The conversion



1a **2a** (7)

of the vinylsilane to the alkylsilane with a hydrosilane and $Co_2(CO)_8$ leads us to suggest the possibility of a new mechanism of $Co_2(CO)_8$-catalyzed hydrosilylation that involves a separate hydrogenation step (eq 7).

Recently, it has been reported that the reaction of olefins with hydrosilanes in the presence of metal complexes directly yields the corresponding vinylsilanes and that the mechanism involves olefin insertion into a M–Si bond.[9] Wrighton and co-workers have reported that the irradiation of $Et_3SiCo(CO)_4$ in the presence of 1-pentene leads to the formation of pentenylsilanes.[10] Although the mechanism of the formation of **1a** from acrylic acid esters and hydrosilanes is not clear at the present stage, it is attractive to consider the insertion of an olefin into the Si–Co bond of the silylcobalt–carbonyl (Scheme II).

It should be noted that **1** is known as a useful building block in organic synthesis. It has been reported by Cunico and co-workers that (*E*)-3-silylacrylate **1** can be prepared in a six-step reaction sequence starting from pro-2-yn-1-ol.[11] Fleming and co-workers also prepared **1** using a similar reaction sequence and showed **1** to be an important intermediate in the synthesis of silyl-substituted 1,3-diene.[12] Therefore, the present reaction offers an extremely convenient method for the preparation of (*E*)-3-silylacrylate **1**.

It has been shown that silylcobalt–carbonyl is the key catalyst species in the new $Co_2(CO)_8$-catalyzed reaction of various oxygenated compounds with $HSiR_3$ and CO.[13] It has also been reported that the stoichiometric reaction of $Me_3SiCo(CO)_4$ with some oxygenated compounds afforded a new entry to π-allylcobalt–tricarbonyls.[14] Likewise, the study of the direct transfer of the R_3Si moiety of $R_3SiCo(CO)_4$ to the C=C bond should result in the development of new chemistry, although this has received little attention to date.

Work is in progress to further examine the chemical reactivity of the silylcobalt–carbonyl intermediate.

Experimental Section

General Comments. All temperatures are uncorrected. IR spectra were recorded with a Shimazu IR-400. The ^1H NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer or a Varian EM-360 spectrometer with Me_4Si as an internal standard. Mass spectra were recorded on a Hitachi mass spectrometer Model RMU-6E. Analytical gas chromatography (GLC) was carried out on a Shimazu GC-3BF or Shimazu GC-4CM with flame ionization detectors. The GLC columns used were a 6 m × 3 mm stainless steel or a 3 m × 3 mm glass containing 5% Silicon OV-1 supported on 60–80 mesh Uniport KS. Preparative GLC was carried out with a Hitachi GC-164. Unsaturated esters and hydrosilanes were commercially available and were purified by distillation. Benzene was dried over sodium–lead alloy. $Co_2(CO)_8$, $RhCl(PPh_3)_3$, $RhCl(CO)\ (PPh_3)_2$, $IrCl(CO)\ (PPh_3)_2$, and $Fe_2(CO)_9$ were commercially available. $RuCl_2(PPh_3)_3$[15] and $Et_2MeSiCo(CO)_4$[4a] were prepared according to the literature.

Reaction of α,β-Unsaturated Esters with Hydrosilanes in the Presence of $Co_2(CO)_8$. A general procedure is given by the preparation of methyl (*E*)-3-(diethylmethylsilyl)propenoate (**1a**). A 20-mL two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stir bar was dried with free flame under a stream of nitrogen and then was charged with 50 mmol of methyl acrylate, 10 mmol of $HSiEt_2Me$, 0.4 mmol of $Co_2(CO)_8$, and 10 mL of benzene. The flask was evacuated and refilled to atmospheric pressure with pure nitrogen. This procedure was repeated three times. The solution was heated at 25 °C for 3 h with stirring. Analysis of the reaction mixture by GLC (100 °C, *n*-tridecane as an internal standard) showed **1a** and **2a** in 86% and 3% yields, respectively. Distillation (102–105 °C (20 mmHg)) of the reaction mixture and preparative GLC afforded the analytical sample.

For **1a**: IR (neat) 1730 (C=O), 1600 cm^{-1} (C=C); NMR (CCl_4) δ 0.09 (s, 3 H), 1.45–1.75 (m, 4 H), 0.84–1.08 (m, 6 H), 3.66 (s, 3 H), 6.15 (d, J = 19 Hz, 1 H), 7.11 (d, J = 19 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 171 (4), 157 (97), 129 (100), 75 (26).

Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.01; H, 9.74. Found: C, 57.90; H, 9.78.

The retention time and the spectral data of **2a** agreed with that of the authentic sample independently prepared.[2j]

Methyl (*E*)-3-(trimethylsilyl)propenoate (1b): yield 65%; bp 95–98 °C (60 mmHg); IR (neat) 1730 (C=O), 1600 cm^{-1} (C=C); NMr (CCl_4) δ 0.14 (s, 9 H), 3.69 (s, 3 H), 6.12 (d, J = 19 Hz, 1 H), 7.14 (s, 1 H); mass spectrum, *m/e* (relative intensity) 158 (3),

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143 (100), 127 (13), 89 (69), 73 (25).

Anal. Calcd for $C_7H_{14}O_2Si$: C, 53.12; H, 8.92. Found: C, 53.09; H, 9.20.

Methyl (*E*)-3-(dimethylphenylsilyl)propenoate (1c): yield 69%; bp 160–168 °C (30 mmHg); IR (neat) 1730 (C=C), 1600 cm^{-1} (C=C); NMR (CCl_4) δ 0.39 (s, 6 H), 3.66 (s, 3 H), 6.18 (d, *J* = 19 Hz, 1 H), 7.17–7.50 (c, 6 H); mass spectrum, *m/e* (relative intensity) 220 (44), 219 (48), 205 (77), 189 (23), 177 (24), 151 (23), 145 (31), 135 (48), 121 (47), 89 (100).

Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.42; H, 7.53.

Methyl (*E*)-3-(triethoxysilyl)propenoate (1d): yield 47%; bp 130–138 °C (50 mmHg); IR (neat) 1730 (C=O), 1605 cm^{-1} (C=C); NMR (CCl_4) δ 1.27 (t, *J* = 7 Hz, 9 H), 3.73 (s, 3 H), 3.83 (t, *J* = 7 Hz, 6 H), 6.32 (d, *J* = 19 Hz, 1 H), 6.87 (d, *J* = 19 Hz, 1 H).

Ethyl (*E*)-3-(diethylmethylsilyl)propenoate (1e): yield 76%; bp 116–118 °C (20 mmHg); IR (neat) 1730 (C=O), 1605 cm^{-1} (C=C); NMR (CCl_4) δ 0.09 (s, 3 H), 0.45–0.75 (m, 4 H), 0.84–1.08 (m, 6 H), 1.26 (t, *J* = 8 Hz, 3 H), 4.14 (q, *J* = 8 Hz, 2 H), 6.15 (d, *J* = 19 Hz, 1 H), 7.11 (d, *J* = 19 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 185 (3), 171 (95), 143 (100), 115 (9), 113 (11).

Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.82; H, 10.32.

Butyl (*E*)-3-(diethylmethylsilyl)propenoate (1f): yield 86%; bp 145–150 °C (20 mmHg); IR (neat) 1730 (C=O), 1600 cm^{-1} (C=C); NMR (CCl_4) δ 0.09 (s, 3 H), 0.45–0.75 (m, 4 H), 0.81–1.08 (m, 9 H), 1.20–1.71 (c, 4 H), 4.05 (t, *J* = 7 Hz, 2 H), 6.12 (d, *J* = 19 Hz, 1 H), 7.07 (d, *J* = 19 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 213 (2), 199 (100), 185 (4), 171 (73), 143 (37), 115 (15).

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 62.74; H, 10.79.

Methyl 4-(diethylmethylsilyl)butanoate (3): bp 125–135 °C (10 mmHg); IR (neat) 1740 cm^{-1} (C=O); NMR (CCl_4) δ 0.07 (s, 3 H), 0.40–0.80 (m, 6 H), 0.80–1.17 (m, 6 H), 1.47–1.94 (c, 2 H), 2.37 (t, *J* = 7 Hz, 2 H), 3.74 (s, 3 H); mass spectrum, *m/e* (relative intensity) 187 (5), 174 (95), 117 (8), 113 (14), 103 (100), 75 (30), 73 (30).

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.43; H, 10.87.

Methyl 3-(diethylmethylsilyl)-2-methylpropanoate (4): bp 90–100 °C (10 mmHg); IR (neat) 1740 cm^{-1} (C=O); NMR (CCl_4) δ -0.07 (s, 3 H), 0.43–0.77 (m, 6 H), 0.77–1.07 (m, 6 H), 1.20 (d, *J* = 7 Hz, 3 H), 2.33–2.77 (m, 1 H), 3.70 (s, 3 H); mass spectrum, *m/e* (relative intensity) 187 (11), 173 (97), 117 (11), 103 (100), 75 (50), 73 (33).

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.23; H, 10.89.

Methyl 2-[(diethylmethylsilyl)methyl]propenoate (5): IR (neat) 1720 (C=O), 1620 cm^{-1} (C=C); NMR (CCl_4) δ 0.08 (s, 3 H), 0.57–0.93 (m, 4 H), 0.93–1.27 (m, 6 H), 1.90 (s, 2 H), 3.77 (s, 3 H), 5.33 (br s, 1 H), 5.97 (d, *J* = 2 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 200 (10), 185 (37), 171 (70), 157 (7), 117 (10), 103 (70), 101 (33), 75 (40), 73 (100).

Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.69; H, 10.20.

Reaction of Methyl Acrylate with $DSiEt_2Me$ in the Presence of $Co_2(CO)_8$. A solution of 15 mmol methyl acrylate, 6 mmol of $DSiEt_2Me$, 0.24 mmol of $Co_2(CO)_8$, and 10 mL of toluene was heated at 25 °C for 3 h with stirring. Analysis of the reaction mixture by GLC (90 °C, *n*-heptane as an internal standard) showed it to contain 3.5 mmol of methyl acrylate and 5.5 mmol of methyl propionate. $DSiEt_2Me$ was completely consumed. Analysis of the reaction mixture (110 °C, *n*-tridecane as an internal standard) showed **1a** and **2a** in 92% and 6% yields, respectively. Distillation of the reaction mixture and preparative GLC afforded analytical samples of methyl acrylate, methyl propionate, and **1a**. The deuterium content in the products (**1a** and methyl propionate) and the starting material (methyl acrylate) were calculated from NMR and mass spectra as shown in Table IV and V.

Registry No. **1a**, 88761-81-3; **1b**, 42201-68-3; **1c**, 88761-82-4; **1d**, 110434-16-7; **1e**, 110434-17-8; **1f**, 110434-19-0; **2a**, 110434-15-6; **2b**, 18296-04-3; **2c**, 59344-04-6; **2d**, 104564-46-7; **2e**, 110434-18-9; **2f**, 110434-20-3; **3**, 110434-21-4; **4**, 17962-96-8; **5**, 110434-22-5; $Co_2(CO)_8$, 15226-74-1; $RhCl(PPh_3)_3$, 14694-95-2; $RhCl(CO)(PPh_3)_2$, 13938-94-8; $IrCl(CO)(PPH_3)_2$, 14871-41-1; $Et_2MeSiCo(CO)_4$, 69897-17-2; $CH_3CH{=}CHCOOMe$, 18707-60-3; $HSiEt_2Me$, 760-32-7; $CH_2{=}CHCOOMe$, 96-33-3; $CH_2{=}CHCOOEt$, 140-88-5; $CH_2{=}CHCOO\text{-}n\text{-}C_4H_9$, 141-32-2; $HSiMe_3$, 993-07-7; $HSiMe_2Ph$, 766-77-8; $HSi(OEt)_3$, 998-30-1; $CH_2{=}C(CH_3)COOMe$, 80-62-6.

Formation and Reactions of Olefins with Vicinal Silyl and Stannyl Substituents

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Received March 27, 1987

The silicon–tin bond in Me_3SiSnR_3 (R = Me, *n*-Bu) adds regio- and stereospecifically to 1-alkynes and also to a limited number of nonterminal alkynes when $Pd(PPh_3)_4$ is added as a catalyst. The use of the (*Z*)-silylstannylalkenes thus formed in synthesis either via organolithiums or via palladium-catalyzed carbon–carbon bond formation has been investigated. Halodestannylation using halogens is nonstereospecific, while that using *N*-bromosuccinimide is stereospecific except in the styryl system. Halodemethylation at tin occurs readily and leads to allene formation when a hydroxy group is present β to the tin moiety.

Introduction

Following our discovery[2] that hexamethylditin adds stereospecifically cis to 1-alkynes (and also to allenes[3]) under the influence of $Pd(PPh_3)_4$ as catalyst, we were able to show that this compound also catalyzes the stereo- and regiospecific addition of (trimethylsilyl)trimethylstannane to 1-alkynes and that it also adds regiospecifically to 1,1-dimethylallene.[4] After our preliminary communication[4] had appeared, Chenard et al. reported[5] on the addition of $t\text{-}BuMe_2SnSiMe_3$ to 1-alkynes: they have since shown[6]

[†] In part.

[1] The work reported here is taken mainly from the Dissertation of R. Wickenamp (Univ. Dortmund, 1987).

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