Hydroformylation of alkenes having organosilicon substituents

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Abstract

The hydroformylation of vinyltrimethylsilane catalyzed by transition metal complexes has been studied. Rh catalysts showed high activity with low regioselectivity. Addition of large excess of triphenylphosphine improved the regioselectivity to normal aldehyde. In contrast, a Co and a Pt catalyst gave exclusively n-aldehyde. Vinyltrimethoxysilane is also hydroformylated by transition metal catalysts. The factors for regioselectivity are discussed.
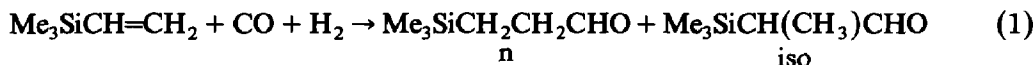
Introduction

Hydroformylation has gained much importance in the synthesis of aldehyde compounds. The scope and mechanism of hydroformylation have been studied in detail [1,2]. A variety of alkenes having substituents such as carboalkoxy [3], cyano [4], hydroxy [5] and alkoxy [6] have been successfully hydroformylated to bifunctional compounds containing the formyl group. However, little was known about the hydroformylation of alkenes having an organosilicon substituent [7]. The hydroformylation of vinyltrimethylsilane catalyzed by $Rh_4(CO)_{12}$ results in the nonregioselective (normal/iso ratio = 56/44%) formation of isomeric aldehydes in 45% yield [7b]. These products, organosilicon aldehydes, are potential building blocks for organic synthesis, but their syntheses by traditional methods are all complicated [8]. A simpler and more straightforward synthesis was desired. The regioselective hydroformylation of unsaturated organosilicon compounds was proposed so as to provide the most convenient method. In order to develop the hydroformylation of alkenes, having an organosilicon substituent, in high yields and with high regioselectivities, we studied the dependence of the regioselectivity on the reaction variables and the metal species. We describe here the details of our research on the hydroformylation of alkenes, having organosilicon substituents, catalyzed by transition metal complexes.

Results

Rh-catalyzed hydroformylation of vinyltrimethylsilane

The hydroformylation of vinyltrimethylsilane proceeds in the presence of a rhodium catalyst to give 3-trimethylsilylpropanal and 2-trimethylsilylpropanal (the normal- and iso-aldehydes) (eq. 1). The activities of several rhodium catalyst

$$Me_3SiCH=CH_2 + CO + H_2 \rightarrow Me_3SiCH_2CH_2CHO + Me_3SiCH(CH_3)CHO \qquad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad n \qquad\qquad\qquad\qquad iso$$

precursors were examined; the results are listed in Table 1. Regardless of the nature of the rhodium catalysts examined, these hydroformylations afforded the isomeric aldehydes nonregioselectively in excellent yields. The regioselectivity observed is similar to that for simple alkenes [9]. 1-Trimethylsiloxypropene, which is the isomerization product of the iso-aldehyde via a 1, 3 silicon shift from carbon to oxygen [10], was not detected under our reaction conditions.

The addition of a phosphorus ligand significantly improved the selectivity to the n-aldehyde (Table 2). In the presence of an 80-fold excess of triphenylphosphine over the Rh complex, a selectivity to n-aldehyde of almost 95% was achieved (Run 11). Tri-n-butyl-phosphine and triphenylphosphite showed a product distribution similar to that obtained with triphenylphosphine (Runs 7 and 8). Bidentate phosphorus ligands effectively in improved the selectivity to the n-aldehyde at P/Rh = 20 (Runs 13 and 16). The most regiospecific formation of n-aldehyde was observed at a P/Rh ratio of 30, but the yield was low (Run 14). The selectivity dropped to 60% when 1,3-bis(diphenylphosphino)propane was used (Run 15). This low regioselectivity is probably caused by the instability of the chelate formed, owing to the strong steric repulsion of 1,3-diaxial phenyl groups of the six-membered chelate ring, which is made up by the coordination of two phosphorus atoms to the rhodium center. The same tendency was observed in the hydroformylation of methyl crotonate catalyzed by the $[Rh(CO)_2Cl]_2$–diphosphine system [3e]. The catalytic activity of $Rh_6(CO)_{16}$ was greatly enhanced by the addition of triphenylphosphine (Runs 17 and 18). At P/Rh = 50, n-aldehyde was obtained exclusively in excellent yield (Run 22). Tri-n-butylphosphine and triphenylphosphite were also effective (Runs 19 and 20).

The ratio of n-/iso-aldihydes strongly depends on the catalyst concentration (Fig. 1). As the catalyst concentration was increased to 2.5 mM, the selectivity to n-aldehyde rose to 99%.

Table 1

Rh-catalyzed hydroformylation of vinyltrimethylsilane [a]

Run	Catalyst	Alkene/catalyst [b]	Temp/°C	Time/h	Yield/% [c]	n/iso [d]
1	$RhH(CO)(PPh_3)_3$	2000	80	3	98	54 46
2	$RhH(PPh_3)_4$	2000	80	2	99	52 48
3	$Rh_6(CO)_{16}$	1000	100	8	85 [e]	51 49
4	$[Rh(CO)_2Cl]_2$	1000	100	3	86	50 50
5	$RhCl(PPh_3)_3$	2000	100	5	93 [f]	56 44

[a] Vinyltrimethylsilane (10 mmol), benzene (10 ml), CO (40 kg cm^{-2}), H$_2$ (40 kg cm^{-2}). [b] In mol vinyltrimethylsilane/mol metal. [c] Determined by GLC based on vinyltrimethylsilane charged. [d] Determined by GLC. [e] Conversion 96%; EtSiMe$_3$ 1%. [f] Conversion 99%; EtSiMe$_3$ 1%.

Table 2

Effects of phosphorus ligands [a]

Run	Catalyst [b]	Ligand	P/Rh [c]	Yield [d]	n/i [e]	
6	RhH(CO)(PPh$_3$)$_3$	PPh$_3$	10	95	65	35
7		PBu$_3$	10	98	61	39
8		P(OPh)$_3$	10	95	72	28
9		PPh$_3$	30	100	80	20
10		PPh$_3$	50	100	80	20
11		PPh$_3$	80	88	95	5
12		Ph$_2$P(CH$_2$)$_2$PPh$_2$	10	97	57	43
13		Ph$_2$P(CH$_2$)$_2$PPh$_2$	20	93	80	20
14		Ph$_2$P(CH$_2$)$_2$PPh$_2$	30	33	96	4
15		Ph$_2$P(CH$_2$)$_3$PPh$_2$	20	94	60	40
16		Ph$_2$P(CH$_2$)$_4$PPh$_2$	20	97	81	19
17	Rh$_6$(CO)$_{16}$	PPh$_3$	2	17	80	20
18		PPh$_3$	10	89	78	22
19		PBu$_3$	10	94	76	24
20		P(OPh)$_3$	10	96	70	30
21		PPh$_3$	30	100	81	19
22		PPh$_3$	50	85	100	0
23		Ph$_2$P(CH$_2$)$_2$PPh$_2$	10	100	60	40

[a] Vinyltrimethylsilane (10 mmol), benzene (10 ml), CO (40 kg cm^{-2}), H$_2$ (40 kg cm^{-2}) at 80°C for 4 h.
[b] RhH(CO)(PPh$_3$)$_3$; alkene/Rh = 2000, Rh$_6$(CO)$_{16}$; alkene/Rh = 1000. [c] In mol phosphorus/mol metal.
[d] Determined by GLC based on vinyltrimethylsilane charged. [e] Determined by GLC.

An increase in the concentration of free triphenylphosphine at a higher catalyst concentration probably induces an associative mechanism, as suggested by Wilkinson [11]. RhH(CO)$_2$(PPh$_3$)$_2$, which is an active species in this mechanism, may lead
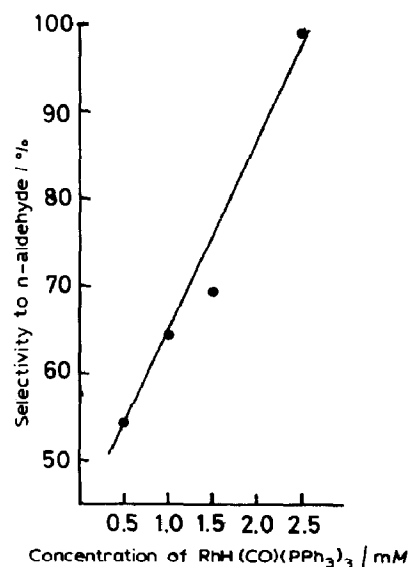

Fig. 1. Effect of the catalyst concentration on the regioselectivity in the hydroformylation of vinyltrimethylsilane; vinyltrimethylsilane (10 mmol), benzene (10 ml) at 80°C for 3 h under CO (40 kg cm^{-2}) and H$_2$ (40 kg cm^{-2}).

Table 3

Hydroformylation of vinyltrimethylsilane catalyzed by group 8, 9 and 10 transition-metal complexes [a]

Run	Catalyst	Alkene /catalyst [b]	Pressure /kg cm^{-2}	Temp /°C	Time /h	Yield [c] /%	n/iso [d]		Yield of e EtSiMe$_3$/%
24	Co$_2$(CO)$_8$	50	120	120	8	73	100	0	1
25 [e]	PtCl$_2$(PPh)$_2$	200	120	100	6	73	100	0	2
26	Ru$_3$(CO)$_{12}$	50	100	110	6	73	86	14	4

[a] Vinyltrimethylsilane (10 mmol), benzene (10 ml), CO/H$_2$ =1/1. [b] In mol vinyltrimethylsilane/mol metal. [c] Determined by GLC based on vinyltrimethylsilane charged. [d] Determined by GLC. [e] SnCl$_2$· 2H$_2$O, Sn/Pt = 5, acetone (10 ml).

to the preferred formation of a linear alkyl rhodium complex because of the large steric interaction of the incoming alkene with bulky PPh$_3$ groups. The same tendency was observed in the hydroformylation of 1-hexene [1].

Hydroformylation of vinyltrimethylsilane by some group 8, 9 or 10 transition-metal catalysts

Hydroformylation of vinyltrimethylsilane catalyzed by other transition metal complexes, which are used as typical hydroformylation catalysts, were investigated. The results are listed in Table 3. The catalysts hydroformylate vinyltrimethylsilane under more rigorous conditions than do the rhodium complexes. In sharp contrast to the rhodium-catalyzed reaction, the cobalt- and platinum-catalyzed reaction proceeds regiospecifically to give n-aldehyde (Runs 24 and 25). The ruthenium catalyst favors the formation of n-aldehyde (Run 26). The hydrogenation of vinyltrimethylsilane was not a serious problem with these catalysts. The product of the rearrangement of the iso-aldehyde was not detected.

Hydroformylation of vinyltrimethoxysilane

Vinyltrimethoxysilane was also hydroformylated to give a mixture of isomeric aldehydes, 3-trimethoxysilylpropanal and 2-trimethoxysilylpropanal, in good yields (eq. 2). Results are summarized in Table 4. Rhodium was a superior catalyst to
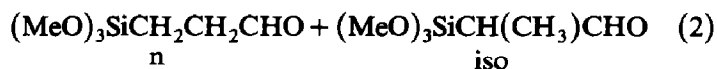
$$(MeO)_3SiCH{=}CH_2 + CO + H_2 \rightarrow$$

$$\underset{n}{(MeO)_3SiCH_2CH_2CHO} + \underset{iso}{(MeO)_3SiCH(CH_3)CHO} \quad (2)$$

Table 4

Hydroformylation of vinyltrimethoxysilane [a]

Run	Catalyst	Alkene /catalyst [b]	Pressure /kg cm^{-2}	Temp /°C	Time /h	Yield [c] /%	n/iso [d]
27	RhH(CO)(PPh$_3$)$_3$	2000	80	80	6	83	52 48
28 [e]	PtCl$_2$(PPh$_3$)$_2$	200	120	100	7	0	–
29	Co$_2$(CO)$_8$	50	100	120	6	63	62 38

[a] Vinyltrimethoxysilane (10 mmol), benzene (10 ml), CO/H$_2$ =1/1. [b] In mol vinyltrimethoxysilane/mol metal. [c] Determined by GLC based on vinyltrimethoxysilane charged. [d] Determined by GLC. [e] SnCl$_2$· 2H$_2$O, Sn/Pt = 5, acetone (10 ml).

cobalt and platinum (Run 27). The platinum catalyst gave no hydroformylated products (Run 28). Unlike the outcome for vinyltrimethylsilane, the methoxyvinylsilane in the presence of the cobalt catalyst gave the two isomeric aldehydes (Run 29). These reactions also gave no rearranged product.

Discussion

In the hydroformylation of alkenes, the equilibrium between the n-alkyl and the iso-alkyl metal complexes is suggested to be the initial step (Scheme 1) [12], and is also important factor in determining the product distribution and which of the complexes is preferably formed. The reaction was much less regioselective in the presence of rhodium.

$$CH_3-\underset{\underset{(iso)}{MLn}}{\overset{\beta}{CH}}-SiMe_3 \rightleftharpoons CH_2-\underset{H-MLn}{\overset{\alpha}{CH}}-SiMe_3 \rightleftharpoons CH_2-\underset{\underset{(normal)}{MLn}}{CH_2}-SiMe_3$$
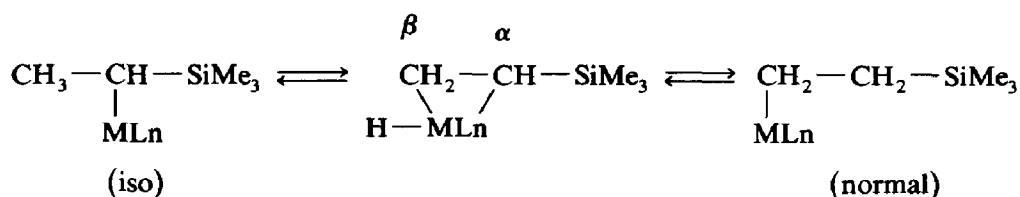
Scheme 1

In order to determine which of the complexes forms initially, we investigated the effects of temperature and carbon monoxide pressure on the regioselectivity of the reaction catalyzed by $RhH(CO)(PPh_3)_3$. The results are shown in Figs. 2 and 3. Although the n-aldehyde was obtained in 75% selectivity at 50°C, increasing the temperature resulted in a fall in the selectivity to the n-aldehyde. The fall in selectivity at elevated temperature is rationalized in terms of the ease with which the isomerization between the n-alkyl and the isoalkyl metal complexes occurs. The selectivity to the n-aldehyde was increased from 51% to 64% when the carbon monoxide pressure was increased from 10 to 80 kg cm^{-2}. The elevated carbon
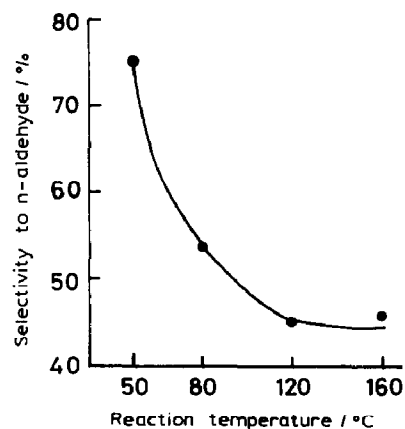

Fig. 2. Effect of the reaction temperature on the regioselectivity in the hydroformylation of vinyltrimethylsilane; vinyltrimethylsilane (10 mmol), $RhH(CO)(PPh_3)_3$ (0.005 mmol), benzene (10 ml) for 3 h under CO (40 kg cm^{-2}) and H_2 (40 kg cm^{-2}).
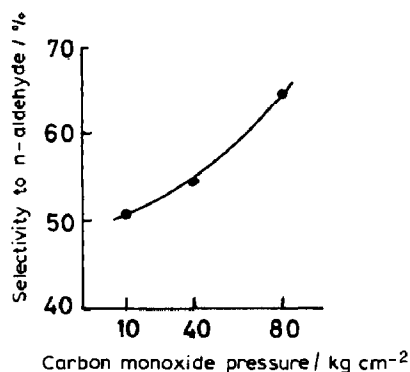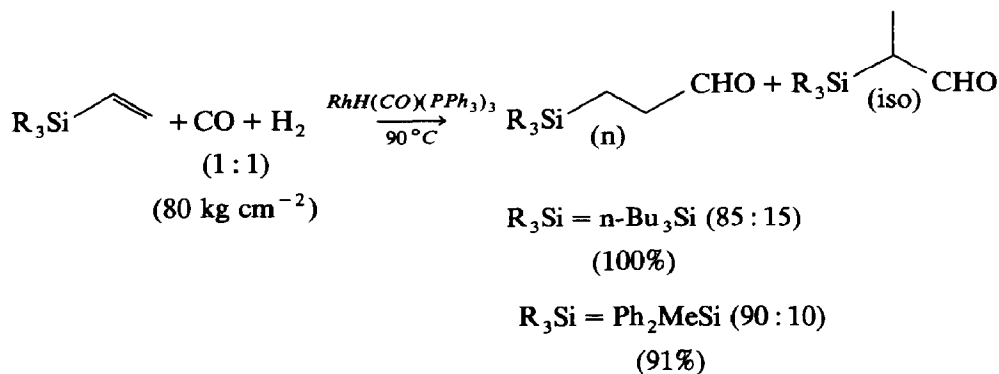
Fig. 3. Effect of the carbon monoxide pressure on the regioselectivity in the hydroformylation of vinyltrimethylsilane; vinyltrimethylsilane (10 mmol), $RhH(CO)(PPh_3)_3$ (0.005 mmol), benzene (10 ml) at $80\,^\circ C$ for 3 h under H_2 (40 kg cm^{-2}).
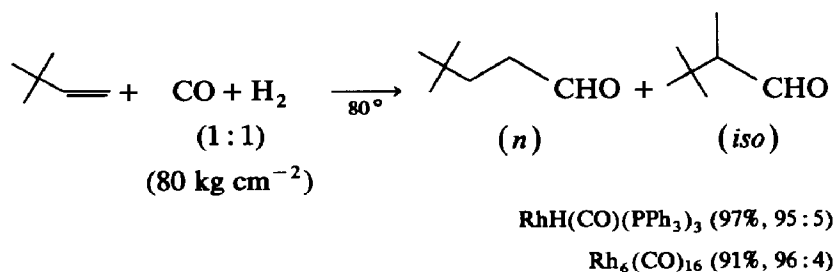
monoxide pressure inhibits isomerization and enhances the insertion of carbon monoxide [3f]. Thus, it is apparent that the normal alkyl rhodium complex is formed as the initial intermediate. Then it isomerizes to the isoalkyl rhodium complex. We have asked ourselves why rhodium prefers the normal alkyl complex: It is well known that trimethylsilyl group stabilizes the β positive charge (β-silicon effect) [13]. Owing to the β-silicon effect 1 is more stable than 2. Therefore, in the

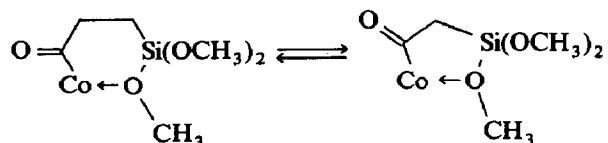$$^+CH_2CHSiMe_3 \qquad\qquad CH_2CH^+SiMe_3$$
$$| \qquad\qquad\qquad\qquad |$$
$$HMLn \qquad\qquad\qquad HMLn$$

$$(1) \qquad\qquad\qquad (2)$$
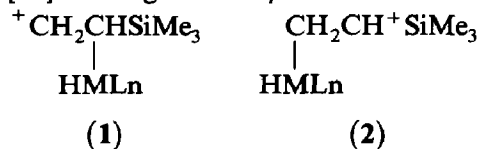
η^2-alkene rhodium complex, the formation of the C_α–Rh bond might be favored over that of the C_β–Rh bond (Scheme 1). If electronic effects predominate, the isoalkyl rhodium complex should form initially. From steric effects, the sterically less hindered normal alkyl rhodium complex is favored. Since the normal alkyl rhodium complex was formed initially, it is apparent that steric effects are more important than the electronic effects. In order to obtain further evidence for this proposed mechanism, we hydroformylated tri-n-butylvinylsilane and diphenylmethylvinylsilane which are more sterically hindered alkenes (Scheme 2). If the above hypothesis is correct, the n-aldehyde will be formed predominantly owing to the

$$R_3Si\diagup\!\!\!\!\diagdown + CO + H_2 \xrightarrow[90\,^\circ C]{RhH(CO)(PPh_3)_3} R_3Si\diagup\!\!\diagdown\!\!\diagup CHO + R_3Si\diagup\!\!\diagdown CHO$$

$$(1:1)$$

$$(80 \text{ kg cm}^{-2})$$

$$R_3Si = n\text{-}Bu_3Si \ (85:15)$$

$$(100\%)$$

$$R_3Si = Ph_2MeSi \ (90:10)$$

$$(91\%)$$

Scheme 2

$$\text{(1:1)} \quad \xrightarrow[80°]{} \quad \text{CHO} \quad (n) \quad + \quad \text{CHO} \quad (iso)$$

(Scheme 1, reaction)

$$\text{alkene} + CO + H_2 \quad (1:1)$$
$$(80 \text{ kg cm}^{-2})$$

$RhH(CO)(PPh_3)_3$ (97%, 95:5)

$Rh_6(CO)_{16}$ (91%, 96:4)

Scheme 3

Scheme 4

greater steric hindrance than the SiMe3-stabilized alkene, As we expected, the n-aldehyde was obtained predominantly in both cases.

The cobalt-catalyzed reaction proceeded regiospecifically to give the n-aldehyde at 80 and 120 °C. This results seems to indicate that the initial intermediate in the cobalt-catalyzed reaction is the normal alkyl cobalt complex. Cobalt is much more sensitive to the steric hindrance in the hydroformylation than rhodium because of its atomic size is smaller than that of rhodium [14]. Consequently, the formation of the less sterically hindered normal alkyl metal complex is much more favorable in the cobalt case. In the platinum-catalyzed reaction, $PtH(SnCl_3)(CO)(PPh_3)$ is the putative active species [15]. The relatively large bulk of the $SnCl_3^-$ ligand should favor addition to give the sterically less hindered normal alkyl platinum complex. The platinum catalyst showed an extremely high regioselectivity even in the case of 1-heptene [15].

For comparison with the outcome of the reaction of vinyltrimethylsilane, we attempted the hydroformylation of 3,3-dimethyl-1-butene (Scheme 3). Surprisingly, even in the presence of rhodium catalyst, a regioselectivity of almost 95% was achieved. This result is explained as follows. The length of the $Si–C_{sp^2}$ bond (1.84 Å) is much longer than the $C_{sp^3}–C_{sp^2}$ bond (1.46 Å) [16]. Thus, the steric hindrance by the t-Bu group to rhodium should be greater than that by the SiMe3 group.

The hydroformylation of vinyltrimethoxysilane in the presence of the cobalt catalyst gave the iso aldehyde with 38% selectivity. The fall in the selectivity to n-aldehyde was confirmed by the ready isomerization of the six-membered cobalt acyl complex, initially formed, to a five-membered one (Scheme 4). Such isomerization of cobalt acyl complexes is well known [17]. Thus the iso-aldehyde was obtained in the case of the cobalt catalyst.

Experimental section

General methods. Boiling points are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM FX-90Q spectrometer with Me4Si as the internal

standard. The IR spectra were recorded on a JASCO IR-810 spectrometer. The mass spectra were recorded on a Hitachi M-70 spectrometer. The GC-MS spectra were recorded on a Shimadzu QP-2000 spectrometer. The gas chromatographic analysis was carried out with a Hitachi 163 with a Shimadzu CR-6A integrator in columns packed with SP-2300 (5% on Chromosorb W AWDMCS 80–100 mesh, 3 mm $\times$ 2 m), DEGA (15% on Chromosorb W AWDMCS 60–80 mesh, 3 mm $\times$ 3 m) or SE-30 (20% on Chromosorb W AWDMCS 60–80 mesh, 3 mm $\times$ 3 m). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. The reagents were purified by distillation under argon before use. Carbon monoxide ($> 99.9\%$) and hydrogen ($> 99.9\%$) were used without further purification. $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ were purchased from Strem Chemicals. $Co_2(CO)_8$ was recrystallized from pentane before use. $Rh_6(CO)_{16}$ was purchased from Aldrich Chemicals. $RhH(CO)(PPh_3)_3$ [18], $RhH(PPh_3)_4$ [19]. $RhCl(PPh_3)_3$ [20], $[Rh(CO)_2Cl]_2$ [21] were prepared by published procedures. Tri-n-butylvinylsilane was prepared from vinyltrichlorosilane and n-butylmagnesium bromide. Diphenylmethylvinylsilane was prepared from dichloromethylvinylsilane and phenylmagnesium bromide.

General procedure for hydroformylation

A mixture of benzene (10 ml), akenylsilane (10 mmol) and catalyst (0.005 mmol) was placed in a 50-ml stainless steel autoclave (Yuasa Giken; SUS 316) equipped with a glass liner and a magnetic stirrer bar. The vessel was pressurized to 80 kg cm^{-2} ($CO/H_2 = 1/1$) and heated at 80°C for 3 h. The products were isolated by distillation and separated by preparative GLC.

Study of the effect of temperature on regioselectivity

The procedures were similar to those described above. In order to initiate each reaction exactly at the recorded temperature, only carbon monoxide was introduced to the reaction mixture. The autoclave was heated to the reaction temperature and kept at that temperature for 15 min, then hydrogen introduced.

3-Trimethylsilylpropanal. Colorless oil. bp. 57–58°C/30 Torr. ^{13}C NMR (CDCl$_3$): δ − 2.1 (q, Si(CH$_3$)$_3$), 8.0 (t, SiCH$_2$), 38.2 (t, CH$_2$CHO), 202.8 (d, CHO). ^{1}H NMR (CDCl$_3$): δ 0.13 (s, 9H, Si(CH$_3$)$_3$), 0.87 (t, 2H, $J = 8.4$ Hz, SiCH$_2$), 2.49 (td, 2H, $J = 8.4$ Hz, 2.2 Hz, CH$_2$CHO), 9.85 (t, 1H, $J = 2.2$ Hz, CHO). IR(neat): ν(C=O) 1730 cm^{-1}. MS(m/e): 130 (M^+), 115 ($M^+ -$ CH$_3$), 101 (M^+–CHO). Anal. Found: C, 55.05; H, 10.99. C$_6$H$_{14}$SiO calcd.: C, 55.32; H, 10.83%.

2-Trimethylsilylpropanal. Colorless oil. ^{13}C NMR (CDCl$_3$): δ − 2.9 (q, Si(CH$_3$)$_3$), 7.8 (q, SiCH(CH$_3$)CHO), 43.4 (d, SiCH(CH$_3$)CHO), 203.5(d, CHO). ^{1}H NMR (CDCl$_3$); δ 0.13 (s, 9H, Si(CH$_3$)$_3$), 1.17 (d, 3H, $J = 6.6$ Hz, SiCH(CH$_3$)-CHO), 2.43 (qd, 1H, $J = 6.6$ Hz, 2.2 Hz, SiCH(CH$_3$)CHO), 9.70 (d, 1H, $J = 2.2$ Hz, CHO). IR(neat): ν(C=O) 1700 cm^{-1}. MS(m/e): 130 (M^+), 115 (M^+–CH$_3$).

3-Tri-n-butylsilylpropanal. Colorless oil. 98–101°C/2 Torr. ^{13}C NMR (CDCl$_3$): δ 4.1 (t, SiCH$_2$CH$_2$CHO), 11.9 (t, Si(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$), 13.6 (q, CH$_3$), 26.0 (t, Si(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$), 26.7 (t, Si(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$), 38.4 (t, SiCH$_2$CH$_2$CH-O), 202.9 (d, CHO). ^{1}H NMR (CDCl$_3$): δ 0.44–1.37 (m, 29H, (n-Bu)$_3$SiCH$_2$), 2.37 (td, 2H, $J = 8.8$ Hz, 1.8 Hz, CH$_2$CHO). 9.74 (t, 1H, $J = 1.8$ Hz, CHO). IR(neat): ν(C=O) 1725 cm^{-1}. MS(m/e): 256(M^+), 227 ($M^+ -$ CHO), 199($M^+ -$ n-Bu).

2-Tri-n-butylsilylpropanal. Colorless oil. ^{13}C NMR (CDCl$_3$): δ 8.2(q, SiCH(CH$_3$)CHO), 11.9 (t, Si(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$), 13.6 (q, CH$_3$), 26.0 (t, Si(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$), 26.7 (t, Si(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$), 41.3 (d, SiCH(CH$_3$)CHO), 203.2 (d, CHO). IR(neat): ν (C=O) 1700 cm^{-1}.

3-Diphenylmethylsilylpropanal. Colorless oil. 139–142°C/2 Torr. ^{13}C NMR (CDCl$_3$): δ −4.7 (q, SiCH$_3$), 5.7 (t, SiCH$_2$), 38.10 (t, CH$_2$CHO), 127.8 (d, phenyl), 129.3 (d, phenyl), 134.2 (d, phenyl), 135.8 (s, phenyl), 202.0 (d, CHO). ^{1}H NMR (CDCl$_3$): δ 0.54 (s, 3H, SiCH$_3$), 1.30 (t, 2H, J = 8.4 Hz, SiCH$_2$), 2.38 (td, 2H, J = 8.4 Hz, 1.3 Hz, CH$_2$CHO), 7.27–7.55 (m, 10H, phenyl), 9.63 (t, 1H, J = 1.3 Hz, CHO). IR(neat): ν(C=O) 1725 cm^{-1}. MS(m/e): 254 (M$^+$), 239 (M$^+$ − CH$_3$), 225 (M$^+$ − CHO).

2-Diphenylmethylsilylpropanal. Colorless oil. ^{13}C NMR (CDCl$_3$): δ −4.7 (q, SiCH$_3$), 8.4 (q, SiCH(CH$_3$)CHO), 41.4 (d, SiCH(CH$_3$)CHO), 127.8 (d, phenyl), 129.3 (d, phenyl), 134.2 (d, phenyl), 135.8 (s, phenyl), 202.9 (d, CHO). IR (neat): ν(C=O) 1700 cm^{-1}.

3-Trimethoxysilylpropanal. Colorless oil. 83–85°C/14 Torr. ^{13}C NMR (CDCl$_3$): δ 0.5 (t, SiCH$_2$), 36.6 (t, SiCH$_2$CH$_2$), 50.0 (q, Si(OCH$_3$)$_3$), 201.4 (d, CHO). ^{1}H NMR (CDCl$_3$): δ0.90 (t, 2H, J = 7.9 Hz, SiCH$_2$), 2.54 (td, 2H, J = 7.9 Hz, 1.3 Hz, CH$_2$CHO), 3.58 (s, 9H, Si(OCH$_3$)$_3$), 9.77 (d, 1H, J = 1.3 Hz, CHO). IR(neat): ν(C=O) 1720 cm^{-1}.

2-Trimethoxysilylpropanal. Colorless oil. ^{13}C NMR (CDCl$_3$): δ 6.5 (q, SiCH(CH$_3$)CHO), 38.7 (d, SiCH(CH$_3$)CHO), 50.5 (q, Si(OCH$_3$)$_3$), 200.8 (d, SiCH(CH$_3$)CHO). IR(neat): ν(C=O) 1700 cm^{-1}.

4,4-Dimethylpentanal. Colorless oil. 64–65°C/55 Torr. ^{13}C NMR (CDCl$_3$): δ 28.8 (q, (CH$_3$)$_3$C), 29.7 (s, (CH$_3$)$_3$C), 35.2 (t, CH$_2$CH$_2$CHO), 39.5 (t, CH$_2$CHO), 202.4 (d, CHO). ^{1}H NMR (CDCl$_3$): δ 0.91 (s, 9H, (CH$_3$)$_3$C), 1.52 (t, 2H, J = 7.9 Hz, (CH$_3$)$_3$CCH$_2$), 2.41 (td, 2H, J = 7.9 Hz, 1.8 Hz, CH$_2$CHO), 9.78 (t, 1H, J = 1.8 Hz, CHO). IR (neat): ν(C=O) 1730 cm^{-1}. MS(m/e): 99 (M$^+$ − CH$_3$), 85 (M$^+$ − CHO). Anal. Found: C, 72.80; H, 12.41; O, 14.64. C$_7$H$_{14}$O calcd.: C, 73.63; H, 12.36; O, 14.01%.

The minor product (4%) of the hydroformylation of 3,3-dimethyl-1-butene could not be separated by the preparative GLC so the identification was performed by GC-MS.

2-Methyl-3,3-dimethylbutanal. MS(m/e): 99 (M$^+$ − CH$_3$), 85 (M$^+$ − CHO).

References

1 P. Pino, F. Pianceti, and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyl, Vol. 2, Wiley-Interscience, New York, 1977, P. 43.
2 B. Cornils, in J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer Verlag, Berlin, 1980, p. 1.
3 (a) Y. Takegami, C. Yokokawa and Y. Watanabe, Bull. Chem. Soc. Jpn., 39 (1966) 2430; (b) Y. Takegami, Y. Watanabe and H. Masada, ibid, 40 (1967) 1459; (c) J. Falbe and N. Huppes, Brennstoff-Chem, 48 (1967) 46; (d) V.B. Fell and M. Barl, J. Mol. Cat., 2 (1977) 301; (e) M. Tanaka, T. Hayashi and I. Ogata, Bull. Chem. Soc. Jpn., 50 (1977) 2351; (f) C.U. Pittman, Jr., W.D. Honnick

and J.J. Yang, J. Org. Chem., 45 (1980) 684; (g) M. Matsumoto and M. Tamura, J. Mol. Cat., 16 (1982) 195.

4 Y. Sato, Y. Ono, M. Takesada and H. Wakamatsu, J. Chem. Soc., Chem. Commun., (1970) 1255.

5 (a) J. Falbe, H.J. Schulze-Steiner and F. Korte, Chem. Ber., 98 (1965) 886; (b) C.U. Pittman, Jr., and W.D. Honnick, J. Org. Chem., 45 (1980) 2132.

6 (a) H. Adkins and G. Kresek, J. Am. Chem. Soc., 71 (1949) 3051; (b) R. Lazzaroni, S. Pucci, S. Bertozzi and D. Pini, J. Organomet. Chem., 247 (1983) C56.

7 (a) M.M. Doyle, W.R. Jackson and P. Perlmutter. Tetrahedron. Lett., 30 (1989) 233; (b) L.V. Morozova, G.K.-I. Magomedov and V.D. Scheludyakov, Zh. Obshch. Khim., 47 (1977) 1519; (c) C.A. Burkhurd and T. Hurd, J. Org. Chem., 17 (1952) 1107.

8 (a) K. Frisch and P. Schroff, J. Am. Chem. Soc., 75 (1953) 1249; (b) G.V. Golodnikov and A.A, Khalyutina, Zh. Obshch. Khim. 32 (1962) 2303; (c) J.W. Wilt, O. Kolewe and J.F.K. Kraemer, J. Am. Chem. Soc., 91 (1969) 2624; (d) T. Sato, T. Abe and I. Kuwajima, Tetrahedron. Lett., (1978) 259; (e) P.F. Hudrlik, A.M. Hudrlik, R.N. Misra, D. Peterson, G.P. Withers and A.K. Kulkarni, J. Org. Chem., 45 (1980) 4444; (f) J.M. Muchowski, R. Naef, and M.L. Maddox, Tetrahedron. Lett., 26 (1985) 5375.

9 (a) B.L. Booth, M.J. Else, R. Fields and R.N. Haszeldine, J. Organomet. Chem., 27 (1971) 119; (b) H. Wakamatsu, Nippon Kagaku Zasshi, 85 (1964) 227; Chem. Abstr., 61 (1964) 13173.

10 (a) A.G. Brook, D.M. MacRae and W.W. Limburg, J. Am. Chem. Soc., 89 (1967) 5493; (b) A.G. Brook, D.M. MacRae and A.R. Bassindale, J. Organomet. Chem., 86 (1975) 185.

11 C.K. Brown and G. Wilkinson, J. Chem. Soc. (A), (1970) 2753.

12 See Ref. 2, p. 7.

13 M.R. Ibrahim and W.L. Jorgensen, J. Am. Chem. Soc., 111 (1989) 819.

14 See Ref. 2, p. 38.

15 I. Schwager and J.F. Knifton, J. Catal., 45 (1976) 256.

16 J. Hine, Structural Effects on Equilibria in Organic Chemistry, Wiley-Interscience, New York, 1975, p. 8.

17 (a) Y. Takegami, C. Yokokawa, Y. Watanabe and Y. Okuda, Bull. Chem. Soc. Jpn., 37 (1964) 181. (b) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, ibid, 37 (1964) 1190.

18 N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth., 15 (1974) 59.

19 N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth., 15 (1974) 58.

20 J.A. Osborn and G. Wilkinson, Inorg. Synth., 10 (1967) 68.

21 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.