Journal of Organometallic Chemistry, 403 (1991) 73–84
Elsevier Sequoia S.A., Lausanne
JOM 21310

Reaction of terminal olefins with a hydrosilane and with carbon monoxide catalyzed by complexes of cobalt, ruthenium, and rhodium

Yoshio Seki * and Kazuaki Kawamoto

Faculty of Economics, Kagawa University, Takamatsu, Kagawa 760 (Japan)

Naoto Chatani, Akihiko Hidaka, Noboru Sonoda, Kouichi Ohe, Yoshikane Kawasaki and Shinji Murai *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565 (Japan)

(Received July 27th, 1990)

Abstract

The $Co_2(CO)_8$-catalyzed reaction of 1-hexene with diethylmethylsilane and carbon monoxide gave high total yields of four isomers of enol silyl ethers (regio- and stereoisomers) as the results of CO incorporation. The effects of changes in reaction conditions (CO pressure, molar ratio of the reactants, and temperature) on the isomer composition were studied. The catalytic activity of various transition metal complexes was examined and $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and $RhCl(PPh_3)_3$ shown to be effective. The catalyzed reaction of methyl acrylate also gave the corresponding enol silyl ethers. The $Co_2(CO)_8$-catalyzed reaction of 1,5-hexadiene with a hydrosilane and carbon monoxide afforded a cyclic compound in addition to straight-chain enol silyl ethers.

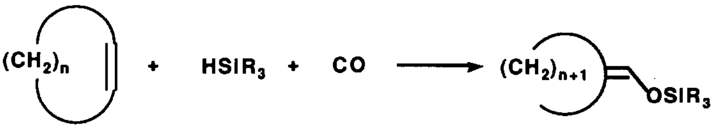
Introduction

The hydroformylation, which affords carbonyl compounds from olefins, carbon monoxide, and hydrogen, is one of the most important carbonylation reaction in industry, and has been extensively investigated [1]. The idea of replacing molecular hydrogen in the reactants with a hydrosilane has led us to the discovery of a new catalytic reaction of olefins with a hydrosilane and carbon monoxide [2,3]. Subsequently the new catalytic system has been extended not only to olefins [4,5] but also to the reactions of various oxygen-containing compounds [5,6].

In this paper, we wish to describe detailed study of the catalytic reaction of olefins including 1-hexene, methyl acrylate, and 1,5-hexadiene with a hydrosilane and carbon monoxide using $Co_2(CO)_8$ as a catalyst. Comparison with hydroformylation reactions will be made with respect to the reaction conditions and the catalysts.

Results and discussion

The $Co_2(CO)_8$-catalyzed reaction of cycloalkanes with a hydrosilane and carbon monoxide has been shown to give an enol silyl ether in high yields as shown in eq. 1 [4]. A cycloalkene, a hydrosilane, and carbon monoxide are incorporated into the enol silyl ether. Although straightforward formal analogy with hydroformylation would suggest that an acylsilane or a β-silyl aldehyde might be the product [7], neither compound was detected. Information about the distinction between the new catalyzed reaction and conventional hydroformylation will be of value for better understanding of the basic features of the new catalyzed reaction using a hydrosilane.

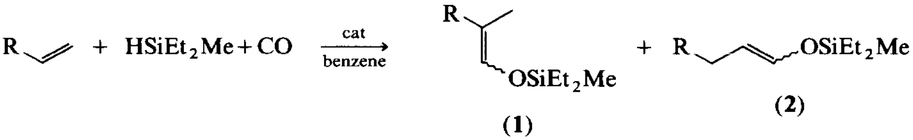


(1)

Hydroformylation of terminal olefins has been known to give straight- and branched-chain aldehydes and numerous studies have been made dealing on the relation between the ratio of these isomers and the reaction conditions [1b]. In comparing this mode of regioselectivity with that of the reaction of olefins with a hydrosilane and carbon monoxide, the new catalyzed reaction of a cycloalkene affords only limited information about the relationships between product distributions and reaction conditions, since it gives only one product, an enol silyl ether (eq. 1). Therefore, the catalyzed reaction of terminal alkenes with a hydrosilane and carbon monoxide is studied in detail especially with respect to the dependence of the product distribution on the reaction conditions.

$Co_2(CO)_8$-catalyzed reaction of 1-hexene with $HSiEt_2Me$ and CO

Since two reaction sites are available in a terminal olefin, four isomers of enol silyl ethers (regio- and stereoisomers) are expected in this case. The reaction of 1-hexene (200 mmol) with $HSiEt_2Me$ (10 mmol) and carbon monoxide (50 kg/cm^2) in the presence of $Co_2(CO)_8$ (0.4 mmol) at 140 °C for 20 h (there are the optimized reaction conditions) gave four isomers, *Z*- and *E*-isomers of **1a** and *Z*- and *E*-isomers of **2a** in 13, 13, 34, and 20% yields, respectively, as shown in eq. 2 [8]. The regioisomers **1a** and **2a** are branched- and straight-chain isomers of enol silyl ethers, respectively, and may correspond to branched- and straight-chain isomers of the aldehyde obtained by hydroformylation of 1-hexene. We use the term S/B



(2)

(**1a**, **2a**: R = n-C_4H_9;
1b, **2b**: R = CO_2CH_3)

Table 1

Effect of CO pressure in the reaction of 1-hexene [a]

CO [b] (kg/cm^2)	Total yield and ratio of (*Z*)-**1a**/(*E*)-**1a**/(*Z*)-**2a**/(*E*)-**2a**(%) [c]	S/B [c,d]
20	52 (15/17/41/27)	2.0
30	51 (15/17/44/24)	2.2
50	65 (16/18/41/25) [e]	1.9
80	68 (15/17/43/25)	2.1
150	67 (17/17/42/24)	1.8

[a] Reaction conditions; 1-hexene (50 mmol), $HSiEt_2Me$ (10 mmol), $Co_2(CO)_8$ (0.4 mmol), 140 °C, 20 h in benzene (20 ml). [b] Initial pressure at 25 °C. [c] Determined by GLC. [d] S/B = ratio of **2a**/**1a**. [e] Accompanied by probably the double bond isomers of **2a** (only by GC-MS analysis) (4% yield).

throughout to indicate the ratio of straight- to branched-chain enol silyl ethers (**2** to **1**).

The effects of changes in reaction conditions have been examined for the $Co_2(CO)_8$ catalyzed reaction of 1-hexene with $HSiEt_2Me$ and CO. The standard reaction conditions were the same as the optimized conditions described above except for the amount of 1-hexene used, i.e., 50 mmol and gave **1a** and **2a** in a combined yield of 65% with S/B of 1.9–2.0. The variation of other factors from this standard condition gave the results described below.

The use of smaller amounts of catalyst gave lower yields, while the use of a large amount of catalyst (1 mmol) resulted in the formation of a hydrosilylation product (n-$C_6H_{13}SiEt_2Me$) at the expense of **1a** and **2a**. The catalytic reaction was therefore carried out employing the molar ratio of a catalyst : $HSiEt_2Me = 1:25$ with 0.4 mmol of $Co_2(CO)_8$.

The increase in CO pressure in the range between 20 and 150 kg/cm^2 (initial pressure at 25 °C) had little effect on the S/B ratio, although the combined yield of **1a** and **2a** increased moderately, as shown in Table 1.

The molar ratio of a hydrosilane to an olefin can not be directly compared with the partial pressure of hydrogen in hydroformylation, since molecular hydrogen is a gas substance at room temperature, and hydrosilanes are liquid.

Table 2

Effect of molar ratio of 1-hexene to $HSiEt_2Me$ [a]

1-Hexene (mmol)	Total yield and ratio of (*Z*)-**1a**/(*E*)-**1a**/(*Z*)-**2a**/(*E*)-**2a**(%) [b]	S/B [b,c]
10	7 (16/16/37/31)	2.1
20	12 (13/13/32/42)	2.9
25	22 (14/15/52/19)	2.3
30	57 (16/16/43/25) [d]	2.1
50	65 (16/18/41/25) [d]	1.9
100	71 (13/14/48/25) [d]	1.8
200	80 (14/14/50/22)	2.1

[a] Reaction conditions; $HSiEt_2Me$ (10 mmol), $Co_2(CO)_8$ (0.4 mmol), CO (50 kg/cm^2), 140 °C, 20 h in benzene (20 ml). [b] Determined by GLC. [c] S/B = ratio of **2a**/**1a**. [d] Accompanied by probably the double bond isomers of **2a** (only by GCMS analysis) (4% yield).

Table 3

Effect of reaction temperature [a]

Temp. (°C)	Total yield and ratio of (*Z*)-**1a**/(*E*)-**1a**/(*Z*)-**2a**/(*E*)-**2a**(%) [b]	S/B [b,c]	Other product(%) [b,d]
90	2 (30/30/20/20)	0.7	tr
107	38 (14/18/45/23)	2.1	2
125	46 (14/17/45/24)	2.3	3
140	65 (16/18/41/25)	1.9	4
180	41 (19/18/46/17)	1.7	11
210	45 (23/26/32/19)	1.1	12

[a] Reaction conditions; 1-hexene (50 mmol), $HSiEt_2Me$ (10 mmol), $Co_2(CO)_8$ (0.4 mmol), CO (50 kg/cm^2), 20 h in benzene (20 ml). [b] Determined by GLC. [c] S/B = ratio of **2a**/**1a**. [d] Probably the double bond isomers of **2a** (only by GCMS analysis).

Importantly, however, the combined yield (**1a** and **2a**) was increased markedly by the use of a higher molar ratio of 1-hexene to hydrosilane. The results are shown in Table 2.

The total yields were 7, 57, and 80% at the olefin/hydrosilane ratios of 1 : 1, 3 : 1, and 20 : 1, respectively. The yields rapidly increased as the ratio increased from 2 : 1 to 3 : 1, but the S/B values were almost unchanged.

A good result was obtained at a reaction temperature of 140 °C as shown in Table 3. The yields of **1a** and **2a** decreased with decreasing temperature, and no reaction took place below 80 °C. The ratio S/B also decreased with decreasing temperature from 140 to 90 °C. This result is similar to that of propylene hydroformylation [9]. The S/B ratio also decreased at 180 and 210 °C, but this decrease was due to formation of isomers probably by the migration of the double bond in the product (**2a**) as suggested by GC-MS analysis.

The catalytic activity of various transition metal complexes was examined for the reaction of 1-hexene with $HSiEt_2Me$ and CO. The following complexes show little or no catalytic activity: CuCl, $CuCl_2$, $W(CO)_6$, $Mn_3(CO)_{10}$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe(CO)_4PPh_3$, $RuCl_2(PPh_3)_3$, Rh_2O_3, $IrCl(CO)(PPh_3)_2$, $Ni(CO)_4$, $Ni(CO)_2(PPh_3)_2$, $Ni(acac)_2$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, Pd-black, H_2PtCl_6, Pt-black. The effective complexes found are listed in Table 4. Although Rh_2O_3 and $IrCl(CO)PPh_3)_3$ have

Table 4

Effective catalysts for the reaction of 1-hexene with $HSiEt_2Me$ and CO [a]

Catalyst (mmol)	Total yield and ratio of (*Z*)-**1a**/(*E*)-**1a**/(*Z*)-**2a**/(*E*)-**2a**(%) [b]	S/B [b,c]
$Co_2(CO)_8$ (0.4)	57 (16/16/43/25)	2.1
$Ru_3(CO)_{12}$ (0.4)	40 (4/7/44/45)	8.1
$RhCl(PPh_3)_3$ (0.4)	41 (9/9/58/24)	4.6
$Co_2(CO)_8$ (0.4) + $n\text{-}Bu_3P$ (1.0)	18 (2/6/70/22)	12
$Co_2(CO)_8$ (0.4) + Ph_3P (1.0)	77 (7/10/59/24)	4.9
$RhCl(PPh_3)_3$ (0.4) + Et_3N (1.0)	88 (8/13/56/23)	3.8

[a] Reaction conditions; 1-hexene (50 mmol), $HSiEt_2Me$ (10 mmol), $Co_2(CO)_8$ (0.4 mmol), 140 °C, 20 h in benzene (20 ml). [b] Determined by GLC. [c] S/B = ratio of **2a**/**1a**.

Table 5

Effect of PR_3 in hydroformylation of 1-hexene and $Co_2(CO)_8$-catalyzed reaction of 1-hexene with $HSiEt_2Me$ and CO

Catalyst	Straight-chain isomer (S/S + B)(%) [a]	
	present reaction	hydroformylation
$Co_2(CO)_8$	68	55
$Co_2(CO)_8$—Ph_3P	83	62
$Co_2(CO)_8$—n-Bu_3P	92	90

[a] S/S + B = ratio of **2a**/(**1a** + **2a**).

been known to be active in hydroformylation [1], their activity in hydrosilylation has been scarcely known. The activity of $PdCl_2(PPh_3)_2$ and H_2PtCl_6 in hydrosilylation has been well known [10], but hydroformylation using these complexes has not been reported. It has already been reported that $Co_2(CO)_8$ [1], $Ru_3(CO)_{12}$ [11], and $RhCl(PPh_3)_3$ [12] are effective for hydroformylation of olefins. Although hydrosilylation using $Co_2(CO)_8$ [13] and $RhCl(PPh_3)_3$ [14] as the catalyst has been studied in great detail, hydrosilylation using $Ru_3(CO)_{12}$ has received little attention so far. Recently, we have found that $Ru_3(CO)_{12}$ is an effective catalyst for the dehydrogenative silylation of olefins with hydrosilanes to give vinylsilanes [15]. It is interesting to note from these results of metal-screening that the effective catalysts for the new catalytic reaction using a hydrosilane and carbon monoxide seem to be limited to those complexes which are active for both hydroformylation and hydrosilylation.

In hydroformylation of 1-hexene using $Co_2(CO)_8/PPh_3$ and $Co_2(CO)_8$/n-Bu_3P as a catalyst, the ratio of the straight-chain isomer has been reported to be 62 and 90%, respectively [16]. Similarly, the ratio of straight-chain isomers (**2a**) in the present reaction increased by using $Co_2(CO)_8$/n-Bu_3P as a catalyst, as shown in Table 5. It is noteworthy that the change in regioselectivity is similar to that observed in hydroformylation when using $Co_2(CO)_8/PR_3$ as a catalyst.

$Co_2(CO)_8$-catalyzed reaction of methyl acrylate with $HSiEt_2Me$ and CO

The similar catalytic reaction of methyl acrylate, a terminal olefin having an electron withdrawing group, also gave four isomers of enol silyl ethers (*Z*- and

Table 6

$Co_2(CO)_8$-catalyzed reaction of methyl acrylate with $HSiEt_2Me$ and CO [a]

Methyl acrylate (mmol)	$HSiEt_2Me$ (mmol)	CO [b] (kg/cm^2)	Temp. (°C)	Total yield and ratio of (*Z*)-**1b**/(*E*)-**1b**/(*Z*)-**2b**/(*E*)-**2b**(%) [c]	S/B [c,d]
30	10	80	140	49 (0/12/59/29)	7.3
30	10	50	140	50 (0/16/58/26)	5.3
30	10	30	140	49 (0/12/61/27)	7.3
30	10	30	70	29 (8/55/30/7)	0.6
10	10	80	140	44 (0/9/68/23)	10
10	30	80	140	6 (0/5/72/23)	19

[a] Reaction conditions; $Co_2(CO)_8$ (0.2 mmol), 20 h in benzene (20 ml). [b] Initial pressure at 25°C. [c] Determined by GLC. [d] S/B = ratio of **2b**/**1b**.

E-isomers of **1b** and *Z*- and *E*-isomers of **2b**). The yields and product distributions with change in reaction conditions are shown in Table 6. The combined yield increased with increase in the ratio of methyl acrylate to $HSiEt_2Me$. Branched-chain isomers (**1b**) were major products at 70 °C, but straight-chain isomers (**2b**) were mainly obtained at 140 °C. It has already been reported that branched aldehyde similarly increased at lower temperature in hydroformylation of ethyl acrylate catalyzed by $Co_2(CO)_8$ [17]. The influence of the CO pressure on the yields and S/B was small. The effect of molar ratio of methyl acrylate to $HSiEt_2Me$ and that of temperature on the yield and S/B were similar to those observed in the reaction of 1-hexene. No reaction took place with acrylonitrile. The reaction with styrene gave a number of products and no was made to analyze these products.

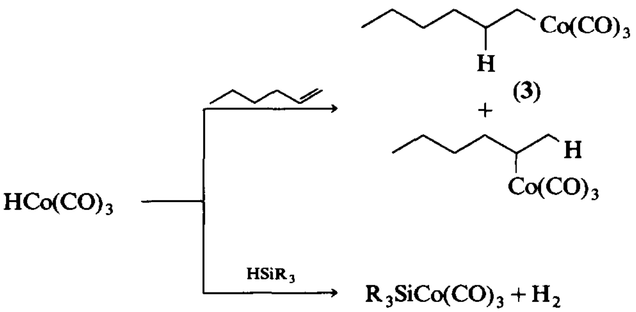
Importance of hydrocobalt carbonyl as the catalyst species

The reaction of trialkylsilanes with $Co_2(CO)_8$ has been known to give $HCo(CO)_n$ ($n = 3$ or 4) and $R_3SiCo(CO)_4$ as shown in eq. 3 [18]. It has been well-established that hydrocobalt carbonyl is the active catalyst in hydroformylation of olefins [1].

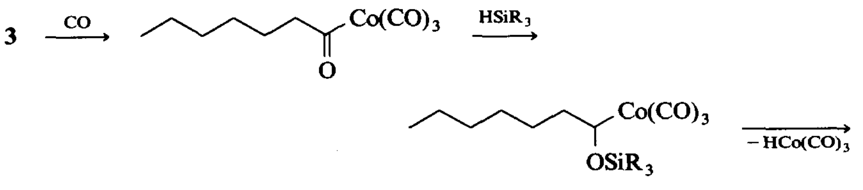
$$Co_2(CO)_8 \xrightarrow{HSiR_3} HCo(CO)_n + R_3SiCo(CO)_4 \qquad (3)$$

The similarity in regioselectivity between the present reaction and hydroformylation especially for the cases using $Co_2(CO)_8/PR_3$ and also the similarity in the relationships between the product ratio and reaction conditions strongly suggest that the interaction of a terminal olefin with $HCo(CO)_3$ is important as the initial step in the reaction using a hydrosilane and carbon monoxide.

The hydrocobalt carbonyl can also react with a hydrosilane to give $R_3SiCo(CO)_4$ (eq. 4) [18] which has no catalytic activity for the present reaction [19]. In the competitive reactions shown in eq. 4, only the reaction of hydrocobalt carbonyl with 1-hexene leads to the products via acylcobalt complexes (eq. 5). The observed facts that the yield decreased with the decrease in molar ratio of a terminal olefin to $HSiEt_2Me$ suggest the importance of the competitive processes of eq. 4.



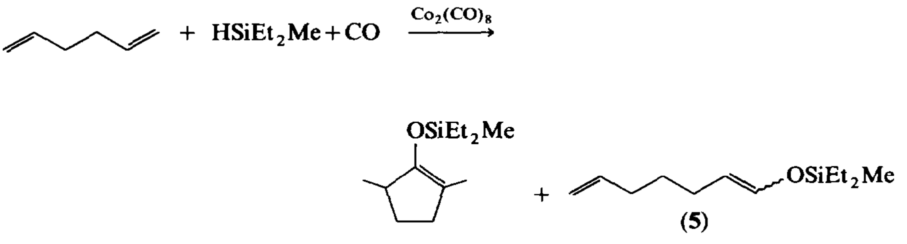
(4)



2a (5)

Catalyzed reaction of 1,5-hexadiene with diethylmethylsilane and CO

The reaction of 1,5-hexadiene (50 mmol) with $HSiEt_2Me$ (10 mmol) and CO (50 kg/cm^2) in the presence of $Co_2(CO)_8$ (0.4 mmol) gave 1-diethylmethylsiloxy-2,5-dimethylcyclopentene (**4**) in 44% yield together with linear enol silyl ethers (**5**) (31% yield) as shown in eq. 6. Branched-chain isomer was not obtained.

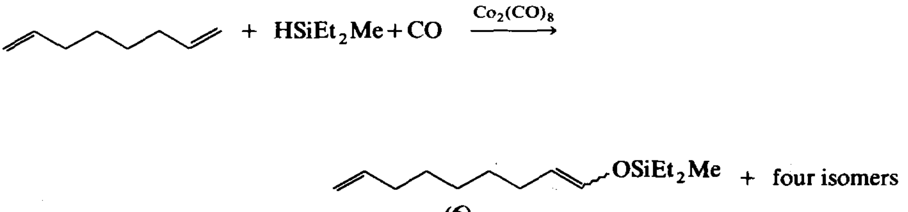


(**4**) (**5**) (6)

Effect of the reaction conditions are shown in Table 7. The combined yield of **4** and **5** increased with increases in carbon monoxide pressure, reaction temperature, and the molar ratio of 1,5-hexadiene to the silane. The use of an excess amount of $HSiEt_2Me$ resulted in a very low yield. These effects in the reaction of 1,5-hexadiene were similar to those observed for 1-hexene and methyl acrylate.

Catalytic activities of various complexes were examined. Although $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$ were effective catalysts for the reaction of 1-hexene, these two complexes were not good catalysts for the cyclization product (**4**) as shown in Table 8. In these cases, many unidentified compounds which may be the regioisomers of **5** were present in the reaction mixture. The reaction using $RhCl(PPh_3)_3/Et_3N$ also gave **4** in only 1% yield. The addition of $n-Bu_3P$ and Ph_3P in the $Co_2(CO)_8$-catalyzed reaction of 1,5-hexadiene decreased the combined yields.

The reaction of 1,7-octadiene with $HSiEt_2Me$ and CO gave *Z*- and *E*-isomers of the corresponding straight-chain enol silyl ethers **6** in 24 and 12% yields, respectively, together with four isomers (combined yields 15%) as shown in eq. 7.



(**6**) (7)

The analysis of four isomers by GC-mass spectrometry showed that these isomers have the same molecular weight as **6**, but it is not clear whether one of those four isomers is the corresponding cyclization product. No further efforts was made to establish the structure of those products.

Intramolecular interception of an acylcobalt carbonyl intermediate by a double bond has been reported [20]. For example, $Co_2(CO)_8$-catalyzed reaction of 1,5-hexadiene with carbon monoxide and water has been reported to give 2,5-dimethylcyclopentanone [21]. Cyclization of the acyl cobalt complex in which the intramolecular C=C bond coordinates to the cobalt metal has been demonstrated by Heck [22].

Table 7

$Co_2(CO)_8$-catalyzed reaction of 1,5-hexadiene with $HSiEt_2Me$ and CO [a]

Diene (mmol)	$HSiEt_2Me$ (mmol)	CO (kg/cm^2)	Temp. (°C)	Total yield(%) [b]	Product ratio(%) [b]	
					4	5(Z:E)
50	10	10	140	38	59	41(75:25)
50	10	50	140	75	58	42(74:26)
50	10	50	70	18	52	48(44:56)
30	10	50	140	58	60	40(65:35)
10	10	50	140	21	67	33(71:29)
10	30	50	140	3	56	44(71:29)

[a] Reaction conditions: $Co_2(CO)_8$ (0.4 mmol), 20 h in benzene (20 ml). [b] Determined by GLC.

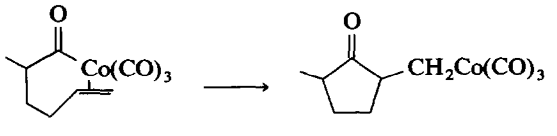
Table 8

Effective catalysts for the reaction of 1,5-hexadiene with $HSiEt_2Me$ and CO [a]

Catalyst (mmol)	Total yield(%) [b]	Product ratio(%) [b]	
		4	5(Z:E)
$Co_2(CO)_8$ (0.4)	58	60	40(65:35)
$Ru_3(CO)_{12}$ (0.4)	13	8	92(67:33)
$RhCl(PPh_3)_3$ (0.4)	15	5	95(75:25)
$Co_2(CO)_8$ (0.4) + n-Bu_3P (1.0)	8	51	44(69:31)
$Co_2(CO)_8$ (0.4) + Ph_3P (1.0)	45	60	40(67:33)
$RhCl(PPh_3)_3$ (0.4) + Et_3N (1.0)	21	4	96(70:30)

[a] Reaction conditions: 1-hexene (50 mmol), $HSiEt_2Me$ (10 mmol), $Co_2(CO)_8$ (0.4 mmol), 140 °C, 20 h in benzene (20 ml). [b] Determined by GLC.

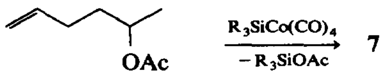
Thus, it is likely that intermediate **7** has afforded the cyclized product as shown in eq. 8.



(8)

(7)

$Co_2(CO)_8$-catalyzed reaction of 5-acetoxy-1-hexene with an excess amount of $HSiEt_2Me$ and CO has been shown also to give a cyclized produced (**4**) [23]. In this case, silyl cobalt carbonyl would be responsible to give the same acyl cobalt intermediate **7** as shown in eq. **9**. That a common intermediate **7** can be accessed from different routes is interesting and may be useful.



(9)

In conclution, terminal olefins can be converted to enol silyl ethers with one additional carbon chain arising from carbon monoxide when the olefins are subjected to the catalytic system of $HSiEt_2Me$, CO, and $Co_2(CO)_8$. The initial step is suggested to be the reaction of olefins with $HCo(CO)_3$. Intramolecular trapping of an acylcobalt carbonyl intermediate has been demmonstrated in the reaction of 1,5-hexadiene.

Experimental

General comments

All temperatures are uncorrected. IR spectra were recorded with a Hitachi IR-270-50. The ^{1}H NMR spectra were measured on a Varian EM-360 spectrometer, JEOL JNM-PS-100 or a JEOL JNM-GSX27S with Me_4Si as an internal standard. Mass spectra were recorded on a Hitachi RMU-6E or a JEOL JMS-DX303HF mass spectrometer. Analytical gas chromatography (GLC) was carried out by use of Shimazu GC-3BF with flame ionization detectors. Preparative GLC was carried out by use of a Hitachi GC-164. A hydrosilane, olefins, diolefins, and transition metal complexes were commercial products. Benzene was dried over sodium–lead alloy.

Reaction of 1-hexene with a diethylmethylsilane and carbon monoxide in the presence of a catalytic amount of $Co_2(CO)_8$

A solution of 3.7 ml (30 mmol) of 1-hexene, 1.02 g (10 mmol) of diethylmethylsilane, and 0.136 g (0.4 mmol) of $Co_2(CO)_8$ in 20 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed with N_2 (50 kg/cm^2) and CO (50 kg/cm^2), then charged with CO to 50 kg/cm^2 and heated at 140 °C with stirring. After 20 h, the autoclave was cooled and depressurised. Analysis of the reaction mixture by GLC (Silicon OV-1, 5%, on Uniport KS, 6m, 115 °C) with an internal standard (n-tetradecane, RRT = 1, RRT stands for relative retention time in GLC) showed it to contain enol silyl ethers ((*Z*)-**1a**; RRT 0.36, (*E*)-**1a**; RRT 0.39, (*Z*)-**2a**; RRT 0.45, (*E*)-**2a**; RRT 0.60) and $(Et_2MeSi)_2O$ in 57% (total) and 5% yields, respectively. Analytical samples were obtained by fractional distilation (B.p. 105–115 °C (12 Torr)) followed by repeating preparative GLC.

For (*Z*)-**1a**, IR (neat): 1670 cm^{-1} (C=C); NMR (CCl_4): δ 0.08 (s, 3H), 0.62 (m, 4H), 0.70–1.14 (m, 9H), 1.14–1.50 (c, 4H) overlaped with 1.48 (d, 3H), 2.00 (m, 2H), 5.90 (s, 1H); mass spectrum *m/e* (rel. intensity): 214 (35), 199 (6), 185 (28), 171 (50), 101 (100). An exact mass determination gave *m/e* 214.1747 ($C_{12}H_{26}OSi$ calcd.: 214.1751).

For (*E*)-**1a**, IR (neat): 1670 cm^{-1} (C=C); NMR 9CCl_4): δ 0.08 (s, 3H), 0.60 (m, 4H), 0.84–1.12 (m, 9H), 1.12–1.50 (m, 4H) overlaped with 1.50 (d 3H), 1.83 (m, 2H), 5.92 (m, 1H).

For (*Z*)-**2a**, IR (neat): 1660 cm^{-1} (C=C); NMR (CCl_4): δ 0.10 (s, 3H), 0.60 (m, 4H), 0.80–1.15 (m, 9H), 1.15–1.40 (c, 6H), 1.96 (m, 2H), 4.30 (dt, $J = 6$ and 8 Hz, 1H), 6.02 (d, $J = 6$ Hz, 1H); mass spectrum *m/e* (rel. intensity): 214 (4), 185 (76), 157 (38), 101 (85), 89 (100). An exact mass determination gave *m/e* 214.1728 ($C_{12}H_{26}OSi$ calcd.: 214.1751).

For (*E*)-**2a**, IR (neat): 1660 cm^{-1} (C=C); NMR (CCl_4): δ 0.10 (s, 3H), 0.60 (m, 4H), 0.80–1.14 (m, 9H), 1.14–1.48 (c, 6H), 1.80 (m, 2H), 4.80 (dt, $J = 12$ and 6 Hz, 1H), 6.08 (d, $J = 12$ Hz, 1H); mass spectrum *m/e* (rel. intensity): 214 (3), 185 (54), 157 (36), 101 (66), 89 (100). An exact mass determination gave *m/e* 185.1346 ($C_{10}H_{21}OSi$ (P–Et) calcd.: 185.1359).

$Co_2(CO)_8$-catalyzed reaction of methyl acrylate with diethylmethylsilane with carbon monoxide

A solution of 2.7 ml (30 mmol) of methyl acrylate, 1.02 g (10 mmol) of $HSiEt_2Me$, and 0.068 g (0.2 mmol) of $Co_2(CO)_8$ in 20 ml of benzene was placed in a 100 ml stainless steel autoclave. The autoclave was flushed two times with CO (50 kg/cm^2), then charged with CO to 80 kg/cm^2 and heated at 140 °C with stirring. After 20 h, the autoclave was cooled and depressurised. Analysis of the reaction mixture by GLC (Silicon OV-1, 5%, on Uniport KS, 3 m, 120 °C) with an internal standard (n-tetradecane, RRT = 1) showed it to contain (*Z*)- and (*E*)-1-diethylmethylsiloxy-2-carbomethoxyprop-1-ene (**1b**) and (*Z*)- and (*E*)-1-diethylmethylsiloxy-3-carbomethoxyprop-1-ene (**2b**) in 49% combined yields. Analytical samples were obtained by fractional distillation (b.p. 130–160 °C (17 Torr)) followed by preparative GLC.

For (*Z*)-**1b**, RRT = 0.633; IR (neat): 2950, 2860, 1725, 1700, 1640, 1300, 1260, 1190, 1130, 820, 770 cm^{-1}; NMR (CCl_4): δ 0.17 (s, 3H), 0.68 (m, 4H), 1.00 (m, 6H), 1.69 (s, 3H), 3.65 (s, 3H), 6.53 (s, 1H); mass spectrum *m/e* (rel. intensity) 216 (2), 201 (6), 187 (100), 159 (23), 103 (90), 91 (35), 89 (35), 75 (52). An exact mass determination gave *m/e* 187.0804 ($C_8H_{15}O_3Si$ (P–Et) calcd.: 187.0789).

For (*E*)-**1b**, RRT = 0.744; IR (neat): 2920, 1720, 1640, 1300, 12220, 1120, 820, 760 cm^{-1}; NMR 9CCl$_4$): δ 0.22 (s, 3H), 0.74 (m, 4H), 1.00 (m, 6H), 1.70 (d, $J = 2$ Hz, 3H), 3.64 (s, 3H), 7.35 (q, $J = 2$ Hz, 1H); mass spectrum *m/e* (rel. intensity) 216 (2), 201 (7), 187 (100), 103 (95), 75 (87). An exact mass determination gave *m/e* 187.0821 ($C_8H_{15}O_3Si$ (P–Et) ca.cd.: 187.0789).

For (*Z*)-**2b**; RRT = 0.625. IR (neat): 2950, 2870, 1740, 1660, 1330, 1260, 1160, 1120, 1040, 1010, 840, 750 cm^{-1}; NMR (CCl_4): δ 0.15 (s, 3H), 0.66 (m, 4H), 1.00 (m, 6H), 3.03 (d, $J = 8$ Hz, 2H), 3.60 (s, 3H), 4.59 (dt, $J = 8$ Hz and 8 Hz, 1H), 6.15 (d, $J = 8$ Hz, 1H); mass spectrum *m/e* (rel. intensity): 216 (3), 187 (86), 157 (20), 103 (100), 101 (43), 75 (48), 73 941). An exact mass determination gave *m/e* 187.0802 ($C_8H_{15}O_3Si$ (P–Et) calcd.: 187.0789).

For (*E*)-**2b**, RRT = 0.706; The identification of (*E*)-**2b** was carried out from the NMR spectrum of a mixture of (*Z*)- and (*E*)-**2b**. NMR (CCl_4): δ 0.14 (s), 0.51–0.81 (m), 2.79 (d, $J = 8$ Hz), 3.58 (s), 4.89 (dt, $J = 12$ Hz and 8 Hz), 6.15 (d, $J = 12$ Hz).

Reaction of 1,5-hexadiene with diethylmethylsilane and carbon monoxide in the presence of metal complexes

A 100 ml stainless steel autoclave was charged with 5.9 ml (50 mmol) of 1,5-hexadiene, 1.02 g (10 mmol) of diethylmethylsilane, 0.136 g (0.4 mmol) of $Co_2(CO)_8$ and 20 ml of benzene. The autoclave was flushed with N_2 (50 kg/cm^2) and CO (50 kg/cm^2), then charged with CO to 50 kg/cm^2. The reaction vessel was then heated with magnetic stirring in an oil bath. The temperature was maintained at 140 °C for 5 h. Analysis of the reaction mixture by GLC (a 6 m × 3 mm glass column containing 15% DEGS supported on 60–80 mesh chromosorb W) with an internal standard (n-tridecane) showed it to contain **4** and **5**. Distillation (b.p. 120–125 °C (30 Torr)) of the reaction mixture and preparative GLC afforded the analytical samples.

For **4**, IR (neat): 1690 cm^{-1} (C=C); NMR (CCl_4): δ 0.10 (s, 3H), 0.50–0.80 (m, 4H), 0.80–1.10 (c, 9H), 1.43–1.53 (m, 3H), 1.97–2.25 (c, 4H), 2.26–2.67 (c, 1H); mass spectrum *m/e* (rel. intensity): 212 (52), 197 (22), 183 (46), 171 (28), 101 (84), 89 (100), 73 (82). An exact mass determination gave *m/e* 212.1597 ($C_{12}H_{24}OSi$ calcd.: 212.1597). Anal. Found: C, 67.62; H, 11.62. $C_{12}H_{24}OSi$ calcd.: C, 67.85; H, 11.38%.

For Z-isomer of **5**, IR (neat): 1660 cm^{-1} (C=C); NMR ($CDCl_3$): δ 0.12 (s, 3H), 0.58–0.67 (m, 4H), 0.94–1.03 (m, 6H), 1.43 (quintet, $J = 7.5$ Hz, 2H), 2.05–2.14 (m, 4H), 4.45 (dt, $J = 6$ and 7 Hz, 1H), 4.90–5.04 (c, 2H), 5.78–5.88 (m, 1H), 6.18 (dt, $J = 6$ and 1.5 Hz, 1H).

For E-isomer of **5**, IR (neat): 1670 cm^{-1} (C=C); NMR ($CDCl_3$): δ 0.12 (s, 3H), 0.59–0.68 (m, 4H), 0.94–1.00 (m, 6H), 1.41 (q, $J = 7$ Hz, 2H), 1.90 (dd, $J = 3.5$ and 1.2 Hz, 2H), 2.05 (t, $J = 7$ Hz, 2H), 4.91–5.03 (c, 3H), 5.74–5.84 (m, 1H), 6.21 (dt, $J = 12$ and 1.2 Hz, 1H); mass spectrum m/e (rel. intensity): 212 (0.2), 183 (28), 170 (10), 157 (37), 155 (40), 144 (22), 129 (19), 115 (46), 101 (100), 89 (100), 73 (94). An exact mass determination gave m/e 183.1208 ($C_{10}H_{19}OSi$ (P–Et) calcd.: 183.1205).

$Co_2(CO)_8$-catalyzed reaction of 1,7-octadiene with diethylmethylsilane and carbon monoxide

A 100 ml stainless steel autoclave was charged with 7.5 ml (50 mmol) of 1,7-octadiene, 1.02 g (10 mmol) of diethylmethylsilane, 0.136 g (0.4 mmol) of $Co_2(CO)_8$ and 20 ml of benzene. The autoclave was flushed with N_2 (50 kg/cm^2) and CO (50 kg/cm^2), then charged with CO to 50 kg/cm^2. The temperature was maintained at 140 °C for 20 h. Analysis of the reaction mixture by GLC (a 6 m × 3 mm glass column containing 5% Silicon OV-1 supported on Uniport KS) with an internal standard (n-tridecane) showed it to contain **6** and unidentified four isomers. Distillation (B.p. 115–118 °C (5 Torr)) of the reaction mixture and preparative GLC afforded the analytical samples.

For Z-isomer of **6**, IR (neat): 1660 cm^{-1} (C=C); NMR ($CDCl_3$): δ 0.12 (s, 3H), 0.58–0.68 (m, 4H), 0.95–1.00 (m, 6H), 1.32–1.42 (c, 6H), 2.00–2.09 (c, 4H), 4.45 (dt, $J = 6$ and 7 Hz, 1H), 4.90–5.03 (c, 2H), 5.74–5.87 (m, 1H), 6.17 9dt, $J = 6$ and 1.5 Hz, 1H).

E-isomer of **6**, IR (neat): 1668 cm^{-1} (C=C), NMR ($CDCl_3$): δ 0.12 (s, 3H), 0.64 (q, $J = 7.8$ Hz, 4H), 0.97 (t, $J = 7.8$ Hz, 6H), 1.25–1.40 (c, 6H), 1.88 (m, 2H), 2.06 (m, 2H), 4.89–5.04 (c, 3H), 5.73–5.88 (m, 1H), 6.21 (d, $J = 12$ Hz, 1H); mass spectrum m/e (rel. intensity): 240 (2), 211 (34), 283 (12), 157 (44), 129 (18), 115 (14), 101 (81), 89 (100), 73 (62). An exact mass determination gave m/e 240.1912 ($C_{14}H_{28}OSi$ calcd.: 240.1910).

Acknowledgement

This work was supported in part by a Grant-in Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

References

1 (a) P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley, New York, 1977, p. 43; (b) B. Cornils, in J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer-Verlag, Heidelberg, New York, 1980, p. 1.

2 Y. Seki, A. Hidaka, S. Murai and N. Sonoda, Angew. Chem., Int. Ed. Engl., 16 (1977) 174.

3 (a) Y. Colleuille, Holl. Pat.-Appl. 6513584 (1966); Chem. Abstr., 65 (1966) 8959; (b) G. Süss-Fink, Angew. Chem., Int. Ed. Engl., 21 (1982) 73.

4 Y. Seki, A. Hidaka, S. Makino, S. Murai and N. Sonoda, J. Organomet. Chem., 140 (1977) 361.

5 S. Murai and N. Sonoda, Angew. Chem., Int. Ed. Engl., 16 (1979) 837.

6 (a) S. Murai and Y. Seki, J. Mol. Catal., 41 (1987) 197; (b) T. Murai, E. Yasui, S. Kato, Y. Hatayama, S. Suzuki, Y. Yamasaki, N. Sonoda, H. Kurosawa, Y. Kawasaki and S. Murai, J. Am. Chem. Soc., 111 (1989) 7938;

7 I. Matsuda, A. Ogiso, S. Sato and Y. Izumi, J. Am. Chem. Soc., 111 (1989) 2332.

8 Y. Seki, S. Murai, A. Hidaka and N. Sonoda, Angew. Chem., Int. Ed. Engl., 16 (1977) 881.

9 P. Pino, F. Piacenti, M. Bianchi and R. Lazzaroni, Chim. Ind. (Mian), 50 (1968) 106.

10 E. Lukevics, Z.V. Belyakova, M.G. Pomerantseva and M.G. Voronkov, J. Organomet. Chem. Libr., 5 (1977) 1.

11 L. Marko, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Vol. 2, D. Reidel Publishing Company, Dordrecht and Boston, 1974, p. 3.

12 P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley, New York, 1977, p. 136.

13 (a) A.J. Chalk and J.F. Harrod, J. Am. Chem. Soc., 89 (1967) 1640; (b) J.F. Harrod and A.J. Chalk, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley, New York, 1977, p. 673.

14 A. Millan, M.J. Fernandez, P. Bentz and P.M. Maitlis, J. Mol. Catal., 26 (1984) 89.

15 For reviews, see: Y. Seki, K. Takeshita, K. Kawamoto, S. Murai and N. Sonoda, J. Org. Chem., 51 (1986) 3890.

16 E.R. Tucci, Ind. Eng. Chem. Prod. Res. Dev., 9 (1970) 516.

17 Y. Takegami, C. Yokokawa and Y. Watanabe, Bull. Chem. Soc. Jpn., 39 (1966) 2430.

18 Y.L. Baay and A.G. MacDiarmid, Inorg. Chem., 8 (1969) 986; A. Sisak, F. Ungvary and L. Marko, Organometallics, 5 (1986) 1019.

19 Unpublished result.

20 (a) P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley, New York, 1977, p. 215; (b) A. Mullen, in J. Falbe (Ed.), New Synthesis with Carbon Monoxide, Springer-verlag, New York, 1980, p. 414.

21 P.P. Klemchuk, U.S. Patent 2995607; Chem. Abstr., 56 (1962) 1363.

22 R.F. Heck, J. Am. Chem. Soc., 85 (1963) 3116.

23 N. Chatani, S. Fujii, Y. Yamasaki, S. Murai and N. Sonoda, J. Am. Chem. Soc., 108 (1986) 7361.