

$\text{Co}_2(\text{CO})_8$ -Catalyzed reaction of aromatic aldehydes with hydrosilanes under carbon monoxide as 1 atm: Incorporation of CO into the carbonyl carbon atom of aldehydes [☆]

Naoto Chatani, Hideo Tokuhisa, Ichiro Kokubu, Satoru Fujii, Shinji Murai ^{*}

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

Received 11 January 1995; in revised form 15 February 1995

Abstract

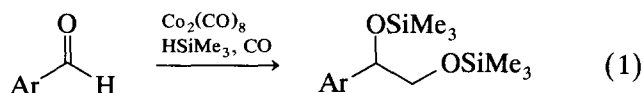
$\text{Co}_2(\text{CO})_8$ -catalyzed reaction of aromatic aldehydes with hydrosilanes under CO as 1 atm results in incorporation of CO into the carbonyl carbon atom of aldehydes to give aryloethane-1,2-diol disilyl ethers as the main product. The reaction of aliphatic aldehydes gives similar products, only with low yields.

Keywords: Cobalt; Silicon; Hydrosilane; Aldehyde; Carbon monoxide; Oxymethylation

1. Introduction

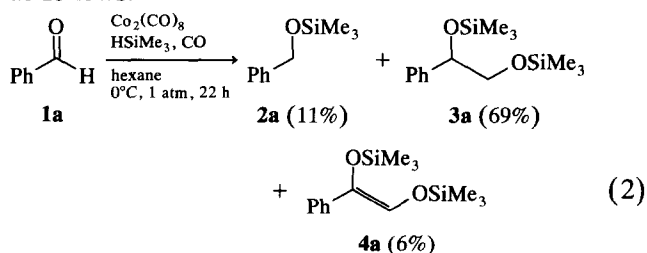
In a series of our studies on the $\text{Co}_2(\text{CO})_8$ -catalyzed reaction of oxygen-containing compounds with hydrosilanes and carbon monoxide at ambient reaction temperature under CO as 1 atm, new methods for the introduction of a siloxymethyl group with concomitant cleavage of a carbon–oxygen bond in various substrates such as cyclic ethers [1], sugars [2], benzylic esters [3] and cyclic ortho esters [4] have been reported. It is interesting to note that there is no report, to the best of our knowledge, describing the catalytic incorporation of CO into carbonyl compounds at ambient temperature and under CO as 1 atm [5,6], although many examples of carbonylation of various compounds under CO as 1 atm have been reported [7]. The carbonylation of a carbonyl carbon atom is not an easy task since generally a transition metal will bind preferably to the oxygen atom of carbonyl group rather than carbon atom, and this will lead to *O*-carbonylation rather than the desirable *C*-carbonylation of carbonyl group [8]. We now report that $\text{Co}_2(\text{CO})_8$ can catalyze the reaction of aromatic aldehydes

with hydrosilanes under CO as 1 atm with CO incorporation. The new catalytic reaction gives aryloethane-1,2-diol disilyl ethers as the main product with good yields:



2. Results and discussion

The reaction of benzaldehyde (**1a**) with HSiMe_3 (five equivalents) in the presence of $\text{Co}_2(\text{CO})_8$ (4 mol.%) is as follows:



Three kinds of product were obtained: benzyl trimethylsilyl ether (**2a**), phenylethane-1,2-diol bis(trimethylsilyl) ether (**3a**) and phenylethene-1,2-diol bis(trimethylsilyl) ether (**4a**). One molecule of CO and two molecules of HSiMe_3 were incorporated to give the

[☆] Dedicated to Professor Hideki Sakurai on his retirement from Tohoku University and in honor of his contribution to organometallic chemistry.

^{*} Corresponding author.

Table 1

Co₂(CO)₈-catalyzed reaction of benzaldehyde with HSiMe₃ and CO^a

Run	Solvent	Temperature (°C)	Time (h)	Yield ^b (%)		
				2a	3a	4a
1	Hexane	0	22	11	69	6
2		15	9	18	60	15
3	Benzene	0	37	17	50	7
4		15	10	23	47	19
5	CH ₂ Cl ₂	0	72	4	0	0
6		15	16	40	39	16

^a Reaction conditions: benzaldehyde, 2.5 mmol, 265 mg; HSiMe₃, 12.5 mmol, 1.5 ml; Co₂(CO)₈, 0.1 mmol, 34 mg; solvent, 5 ml.^b Gas-liquid chromatography (GLC) yields.

main product **3a** with a new carbon–carbon bond formation between the carbonyl carbon atom of **1a** and the carbon atom of CO. This reaction represents the first example, to our knowledge, of the carbonylation of carbonyl carbon atom using CO as 1 atm. The benzyl ether **2a** is a hydrosilylation product which is also obtainable by the catalytic reaction in the absence of CO. The formation of **4a** will be described later.

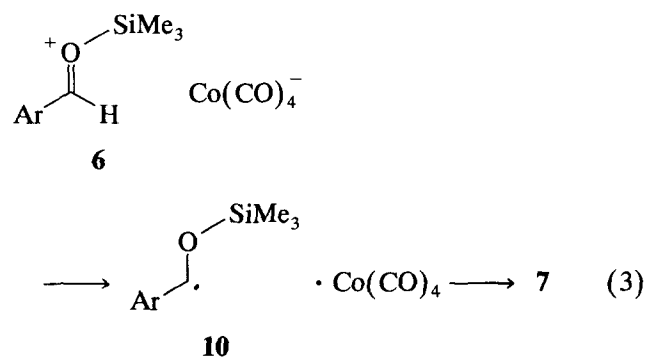
The results of changing the reaction conditions such as reaction temperatures and solvents are given in Table 1. Raising the temperature of the reaction in hexane resulted in a faster reaction rate and a poor product selectivity (run 2). The yields of both byproducts **2a** and **4a** were increased. A similar tendency was also observed in the reaction in benzene (runs 3 and 4). It was interesting to note that the reaction in CH₂Cl₂, a polar solvent, became very slow and the main course of the reaction was simple hydrosilylation, leading to **2a** (runs 5 and 6).

The results of the reaction of various aromatic aldehydes in benzene are summarized in Table 2. No distinct substitution effect both on product distribution and

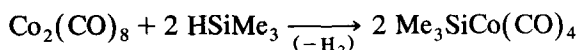
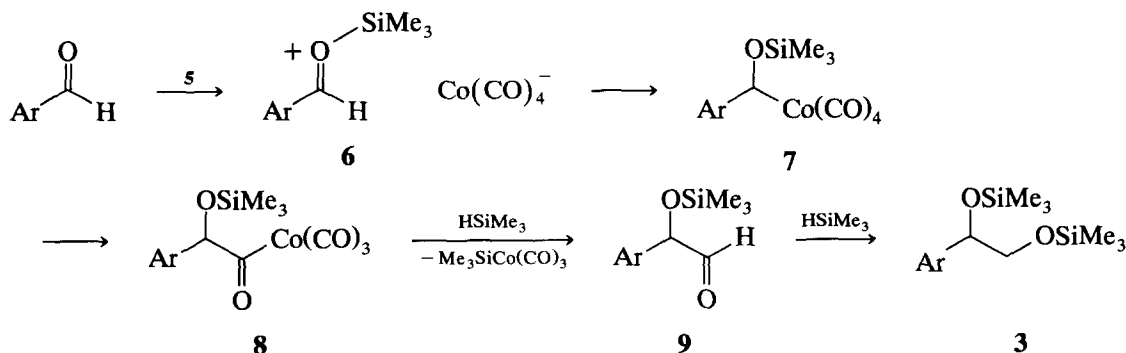
on reaction time was observed. *o*-Substituted benzaldehydes reacted slightly more rapidly than *p*-substituted benzaldehydes, do. The reason for these differences is not clear at the present time.

The proposed mechanism is shown in Scheme 1. The important catalytic species would be Me₃SiCo(CO)₄ (**5**) which is known to be formed by the reaction of Co₂(CO)₈ with HSiMe₃ [9]. The interaction of **5** with an aldehyde gives a silyloxonium ion intermediate **6**, to which the attack of Co(CO)₄[−] gives an α-siloxyalkylcobalt complex **7** [10]. Migratory insertion of CO into the carbon–cobalt bond in the alkylcobalt complex **7** gives an acylcobalt complex **8** [11]. Oxidative addition of HSiMe₃ to **8** followed by reductive elimination affords an aldehyde **9** [12], which is hydrosilylated to give the main product **3**. Me₃SiCo(CO)₃ reacts with CO to regenerate **5**. Byproduct **4** would be obtained by dehydrogenative silylation of **9** [13].

There are many alternative possibilities for the mechanism. The silyloxonium ion **6** could undergo a one-electron transfer process to give a free-radical pair **10** first and then couple to **7** [14]:



Oxidative addition of a hydrosilane to **8** followed by a 1,3-silicon shift would give a cobalt–carbene complex

**5**

Scheme 1.

Table 2
Cobalt-catalyzed reaction of arylaldehydes with HSiMe₃ and CO^a

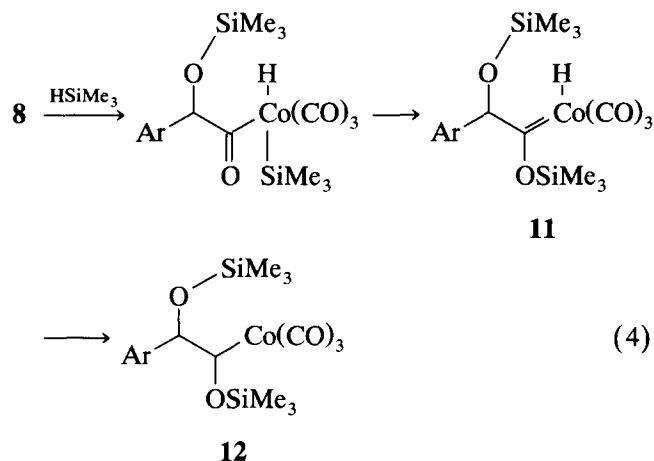
Substrate	Time (h)	Yield ^b (%)		
		2	3	4
C ₆ H ₅ CHO (1a)	37	17	50	7
<i>p</i> -MeOC ₆ H ₄ CHO (1b)	48 ^c	20	0	0
<i>p</i> -ClC ₆ H ₄ CHO (1c)	35	17	55	8
<i>p</i> -FC ₆ H ₄ CHO (1d)	34	7	66	9
<i>o</i> -MeOC ₆ H ₄ CHO (1e)	26	39	62	2
<i>o</i> -ClC ₆ H ₄ CHO (1f)	9	21	59	3
<i>o</i> -MeC ₆ H ₄ CHO (1g)	27	20	63	4

^a Reaction conditions: arylaldehyde, 2.5 mmol; HSiMe₃, 12.5 mmol, 1.5 ml; Co₂(CO)₈, 0.1 mmol, 34 mg; C₆H₆, 5 ml; 0°C.

^b GLC yields.

^c Incomplete reaction. When the reaction was run at 15°C, **2b** (41% yield), **3b** (28%) and **4c** (6%) were obtained after 39 h.

11, which then give an alkylcobalt **12** by a 1,2-hydrogen shift:



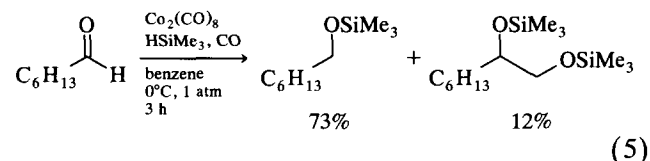
Further oxidative addition of a hydrosilane to **12** followed by reductive elimination should give the product **3**. The β -hydride elimination from **12** would account for the formation of the byproduct **4**.

The catalytic reaction was faster in hexane or in benzene than in dichloromethane. The faster rate in a non-polar solvent implies that the charge decreases in the transition state. This may suggest that the reaction of **6** with Co(CO)₄⁻ giving directly **7** (Scheme 1) or alternatively a one-electron transfer process affording a benzylic free radical **10** (Eq. (3)) is the rate-determining step of the catalytic reaction.

The proper explanation of the product distributions is not possible at present since the mechanism of the hydrosilylation leading to **2** is not known. The two important possibilities for the process to **2** are (1) direct hydrogen atom transfer to the silyloxonium ion from HSiMe₃ [15] and (2) reaction of **7**, after loss of CO, with HSiMe₃ followed by reductive elimination. These processes may compete with various steps in Scheme 1 and/or in Eqs. (3) and (4) so that the product distribu-

tions in Tables 1 and 2 are not straightforward to rationalize.

In contrast with aromatic aldehydes, aliphatic aldehydes reacted with HSiMe₃ under CO as 1 atm gave only a small amount of CO-incorporated product. For example, the reaction of heptanal, using the same molar ratio of reactants as in Table 1, afforded heptanol trimethylsilyl ether as the major product:



In conclusion, the present reaction provides the first example of CO incorporation into the aldehyde carbonyl carbon atom under CO as 1 atm at ambient temperature. The results suggest new possibilities of designing or exploiting a new catalytic carbonylation reaction.

3. Experimental section

3.1. General comments

Bulb-to-bulb distillations were done on a Sibata glass tube oven GTO-250R; boiling points refer to air bath temperature and are uncorrected. ¹H NMR and ¹³C NMR were recorded on a JEOL JMN-270 spectrometer in CDCl₃ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift δ , multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; c, complex), coupling constant, integration and interpretation. IR spectra were obtained on a Hitachi IR-270-50 spectrometer; absorptions are reported in reciprocal centimeters. Mass spectra were obtained on a Shimadzu GCMS-QP 1000 with an ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analyses Section of Osaka University. Analytical GLC was carried out on a Shimadzu GC-14A gas chromatograph, equipped with a flame ionization detector. Preparative GLC was carried out on a Hitachi 164 gas chromatograph.

3.2. General procedure for the Co₂(CO)₈-catalyzed reaction of aldehydes with HSiMe₃ and CO

In a 10 ml reaction flask with an efficient condenser (dry-ice-CH₃OH) was placed Co₂(CO)₈ (0.1 mmol, 34 mg), after the flask was flashed with CO (1 atm from a stock balloon); HSiMe₃ (12.5 mmol, 1.5 ml) was added via a pressure syringe [16] at 25°C. After 5 min, solvent (5 ml), arylaldehyde (**1**) (2.5 mmol) and appropriate hydrocarbons (C_nH_{2n+2}) calibrated against purified products for GLC yields were added and the mixture was stirred at 0°C under CO (1 atm). Solvent was

evaporated in vacuo and Kugelrohr distillation followed by preparative gas chromatography (Silicone OV-1) gave pure 3.

3.3. Phenylethanediole bis(trimethylsilyl) ether (3a)

^1H NMR (CDCl_3): δ – 0.02 (s, 9H, Me_3Si), 0.01 (s, 9H, Me_3Si), 3.52 (dd, $J = 10.3$ and 5.1 Hz, 1H, CH_2O), 3.56 (dd, $J = 10.3$ and 6.8 Hz, 1H, CH_2O), 4.63 (dd, $J = 6.8$ and 5.1 Hz, 1H, CHO), 7.15–7.29 (m, 5H, Ph) ppm. IR (neat): ν 3036w, 2964m, 2916w, 1498w, 1456w, 1252s, 1200w, 1150s, 1098m, 1028w, 968m, 842s, 752m, 698m cm^{-1} . Mass spectroscopy (MS): m/z (relative intensity) 282 (M^+ , 0), 179 ($\text{M}^+ - \text{CH}_2\text{OSiMe}_3$, 100), 147 (23), 73 (100). Anal. Found: C, 59.63; H, 9.43. $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}_2$ Calc.: C, 59.52; H, 9.28%.

3.4. 4-(Methoxyphenyl)ethanediole bis(trimethylsilyl) ether (3b)

^1H NMR (CDCl_3): δ 0.06 (s, 9H, Me_3Si), 0.07 (s, 9H, Me_3Si), 3.54 (dd, $J = 10.5$ and 4.8 Hz, 1H, CH_2O), 3.60 (dd, $J = 10.5$ and 7.1 Hz, 1H, CH_2O), 3.80 (s, 3H, CH_3O), 4.65 (dd, $J = 7.1$ and 5.3 Hz, 1H, CHO), 6.84 (d, $J = 6.7$ Hz, 2H, Ar), 7.25 (d, $J = 6.7$ Hz, 2H, Ar) ppm. ^{13}C NMR (CDCl_3): δ – 0.50 (Me_3Si), 0.17 (Me_3Si), 55.20 (CH_3O), 69.09 (CH_2OSi), 75.30 (CHOSi), 113.38, 127.42, 134.45, 158.85 (Ar) ppm. IR (neat): ν 2960m, 2912m, 2866w, 1616m, 1588w, 1516s, 1467w, 1367w, 1301w, 1249s, 1199m, 1171s, 1128m, 1091s, 1067m, 1038m, 969m, 889m, 841s, 749m, 686w cm^{-1} . MS: m/z (relative intensity) 312 (M^+ , 0), 297 ($\text{M}^+ - \text{Me}$, 1), 210 (18), 209 ($\text{M}^+ - \text{CH}_2\text{OSiMe}_3$, 100), 147 (21), 73 (60). Anal. Found: C, 57.29; H, 9.19. $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}_2$ Calc.: C, 57.64; H, 9.03%.

3.5. 4-(Chlorophenyl)ethanediole bis(trimethylsilyl) ether (3c)

^1H NMR (CDCl_3): δ 0.03 (s, 9H, Me_3Si), 0.05 (s, 9H, Me_3Si), 3.50 (dd, $J = 10.5$ and 5.1 Hz, 1H, CH_2O), 3.58 (dd, $J = 10.5$ and 7.0 Hz, 1H, CH_2O), 4.64 (dd, $J = 7.0$ and 5.1 Hz, 1H, CHO), 7.24–7.29 (m, 4H, Ar) ppm. ^{13}C NMR (CDCl_3): δ – 0.55 (Me_3Si), 0.11 (Me_3Si), 68.83 (CH_2OSi), 75.00 (CHOSi), 127.73, 128.13, 132.94, 140.93 (Ar) ppm. IR (neat): ν 2968m, 1496m, 1252s, 1132s, 1092s, 1016w, 968m, 844s, 756w, 688w cm^{-1} . MS: m/z (relative intensity) 316 (M^+ for ^{35}Cl , 0), 215 (26), 214 (12), 213 ($\text{M}^+ - \text{CH}_2\text{OSiMe}_3$, 71), 147 (33), 75 (10), 73 (100). Anal. Found: C, 53.08; H, 8.05. $\text{C}_{14}\text{H}_{25}\text{ClO}_2\text{Si}_2$ Calc.: C, 53.05; H, 7.95%.

3.6. 4-(Fluorophenyl)ethanediole bis(trimethylsilyl) ether (3d)

^1H NMR (CDCl_3): δ 0.04 (s, 9H, Me_3Si), 0.07 (s, 9H, Me_3Si), 3.52 (dd, $J = 10.5$ and 5.1 Hz, 1H, CH_2O),

3.60 (dd, $J = 10.5$ and 7.0 Hz, 1H, CH_2O), 4.67 (dd, $J = 7.0$ and 5.1 Hz, 1H, CHO), 6.96–7.03 (m, 2H, Ar), 7.26–7.32 (m, 2H, Ar) ppm. ^{13}C NMR (CDCl_3): δ – 0.56 (Me_3Si), 0.11 (Me_3Si), 68.92 (CH_2OSi), 74.98 (CHOSi), 114.77 ($J_{\text{C-F}} = 11$ Hz), 127.87 ($J_{\text{C-F}} = 7$ Hz), 138.10 ($J_{\text{C-F}} = 3$ Hz), 163.61 ($J_{\text{C-F}} = 245$ Hz) ppm. IR (neat): ν 2964m, 2868m, 1610m, 1514m, 1418w, 1368w, 1252s, 1224m, 1198m, 1130m, 1016w, 968m, 842s, 750m, 690w ppm. MS: m/z (relative intensity) 300 (M^+ for ^{19}F , 0), 198 (15), 197 ($\text{M}^+ - \text{CH}_2\text{OSiMe}_3$, 92), 147 (31), 73 (100). Anal. Found: C, 55.47; H, 8.30. $\text{C}_{14}\text{H}_{25}\text{FO}_2\text{Si}_2$ Calc.: C, 55.95; H, 8.39%.

3.7. 2-(Methoxyphenyl)ethanediole bis(trimethylsilyl) ether (3e)

^1H NMR (CDCl_3): δ 0.09 (s, 9H, Me_3Si), 0.11 (s, 9H, Me_3Si), 3.45 (dd, $J = 10.3$ and 7.8 Hz, 1H, CH_2O), 3.70 (dd, $J = 10.3$ and 3.0 Hz, 1H, CH_2O), 3.83 (s, 3H, CH_3O), 5.13 (dd, $J = 7.8$ and 3.0 Hz, 1H, CHO), 6.83 (d, $J = 8.3$ Hz, 1H, Ar), 6.96 (t, $J = 8.3$ Hz, 1H, Ar), 7.23 (td, $J = 8.3$ and 2.0 Hz, 1H, Ar), 7.49 (dd, $J = 2.0$ and 8.3 Hz, 1H, Ar) ppm. ^{13}C NMR (CDCl_3): δ – 0.41 (Me_3Si), 0.16 (Me_3Si), 55.14 (CH_3O), 67.80 (CH_2OSi), 70.29 (CHOSi), 109.78, 120.44, 127.38, 128.02, 130.28, 155.80 (Ar) ppm. IR (neat): ν 2962m, 2842w, 1604m, 1592m, 1494s, 1469m, 1442m, 1369m, 1280m, 1249s, 1191m, 1173m, 1131s, 1085s, 1030m, 969s, 889s, 841s, 754s, 687w cm^{-1} . MS: m/z (relative intensity) 312 (M^+ , 0), 210 (19), 209 ($\text{M}^+ - \text{CH}_2\text{OSiMe}_3$, 100), 147 (17), 73 (70).

3.8. 2-(Chlorophenyl)ethanediole bis(trimethylsilyl) ether (3f)

^1H NMR (CDCl_3): δ 0.09 (s, 18H, Me_3Si), 3.50 (dd, $J = 10.8$ and 7.3 Hz, 1H, CH_2O), 3.70 (dd, $J = 10.8$ and 3.5 Hz, 1H, CH_2O), 5.14 (dd, $J = 7.3$ and 3.5 Hz, 1H, CHO), 7.15–7.31 (m, 3H, Ar), 7.57 (dd, $J = 7.8$ and 1.9 Hz, 1H, Ar) ppm. ^{13}C NMR (CDCl_3): δ – 0.45 (Me_3Si), 0.07 (Me_3Si), 67.40 (CH_2OSi), 72.43 (CHOSi), 126.72, 128.39, 128.52, 128.94, 131.73, 139.56 (Ar) ppm. IR (neat): ν 3072m, 2964s, 1628w, 1600w, 1578w, 1476m, 1444m, 1410w, 1382w, 1252s, 1198m, 1128s, 1098s, 1072s, 1048m, 1036m, 968s, 888s, 842s, 754s, 696m cm^{-1} . MS: m/z (relative intensity) 316 (M^+ for ^{35}Cl , 0), 215 (35), 214 (15), 213 ($\text{M}^+ - \text{CH}_2\text{OSiMe}_3$, 93), 147 (44), 73 (100). Anal. Found: C, 52.75; H, 8.06, Cl, 11.43. $\text{C}_{14}\text{H}_{25}\text{ClO}_2\text{Si}_2$ Calc.: C, 53.05; H, 7.95, Cl, 11.19%.

3.9. 2-(Methylphenyl)ethanediole bis(trimethylsilyl) ether (3g)

^1H NMR (CDCl_3): δ 0.06 (s, 18H, Me_3Si), 2.34 (s, 3H, CH_3), 3.53 (dd, $J = 10.0$ and 4.9 Hz, 1H, CH_2O),

3.58 (dd, $J = 10.0$ and 6.8 Hz, 1H , CH_2O), 4.93 (dd, $J = 6.8$ and 4.9 Hz, 1H , CHO), 7.08–7.19 (m, 3H , Ar), 7.46–7.49 (m, 1H , Ar) ppm. ^{13}C NMR (CDCl_3): δ –0.50 (Me_3Si), 0.14 (Me_3Si), 19.24 (CH_3), 68.25 (CH_2OSi), 72.54 (CHOSi), 125.88, 126.63, 127.01, 129.87, 140.40 (Ar) ppm. IR (neat): ν 3032w, 2964m, 2868w, 1492w, 1464w, 1378w, 1252s, 1216w, 1180w, 1130s, 1086s, 1062m, 968m, 842s, 754m, 724w, 688w cm^{-1} . MS: m/z (relative intensity) 296 (M^+ , 0), 194 (17), 193 ($\text{M}^+ - \text{CH}_2\text{OSiMe}_3$, 100), 147 (25), 75 (10), 73 (84). Anal. Found: C, 60.74; H, 9.53. $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}_2$ Calc.: C, 60.75; H, 9.52%.

References

- [1] (a) S. Murai, Y. Hatayama, S. Murai and N. Sonoda, *Organometallics*, **2** (1983) 1883; (b) T. Murai, S. Kato, S. Murai, T. Toki, S. Suzuki and N. Sonoda, *J. Am. Chem. Soc.*, **106** (1984) 6093; (c) T. Murai, K. Furuta, S. Kato, S. Murai and N. Sonoda, *J. Organomet. Chem.*, **302** (1986) 248; (d) T. Murai, E. Yasui, S. Kato, Y. Hatayama, S. Suzuki, Y. Yamasaki, S. Murai and N. Sonoda, *J. Am. Chem. Soc.*, **111** (1989) 7938.
- [2] N. Chatani, T. Ikeda, T. Sano, N. Sonoda, H. Kurosawa, Y. Kawasaki and S. Murai, *J. Org. Chem.*, **53** (1988) 3387.
- [3] N. Chatani, T. Sano, K. Ohe, Y. Kawasaki and S. Murai, *J. Org. Chem.*, **55** (1990) 5923.
- [4] N. Chatani, Y. Kajikawa, Nishimura and S. Murai, *Organometallics*, **10** (1991) 21.
- [5] Previously we succeeded in incorporation of CO into aldehydes and cyclobutanones but under a high pressure at a high temperature; see Y. Seki, S. Murai and N. Sonoda, *Angew. Chem., Int. Edn. Engl.*, **17** (1978) 199; S. Murai, T. Kato, N. Sonoda, Y. Seki and K. Kawamoto, *Angew. Chem., Int. Edn. Engl.*, **18** (1979) 393; N. Chatani, H. Furukawa, T. Kato, S. Murai and N. Sonoda, *J. Am. Chem. Soc.*, **106** (1984) 430. Recently, C-carbonylation of aldehydes by Rh-catalyzed reaction of aldehydes with hydrosilanes and CO was reported by M.E. Wright and B.B. Cochran, *J. Am. Chem. Soc.*, **115** (1993) 2059.
- [6] L. Marko, *Transition Met. Chem.*, **17** (1992) 474.
- [7] For reviews on transition-metal-catalyzed carbonylation reactions, see I. Wender and P. Pino, *Organic Syntheses via Metal Carbonyls*, Vol. II, Wiley, New York, 1977; J. Falbe, *New Syntheses with Carbon Monoxide*, Springer, New York, 1980; I. Tkatchenko, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon, Oxford, 1982; Y.V. Gulevich, N.A. Bumagin and I.P. Beletskaya, *Russ. Chem. Rev.*, **57** (1988) 299; H.M. Colquhoun, D.J. Thompson and M.V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum, New York, 1991.
- [8] R.W. Goetz and M. Orchin, *J. Org. Chem.*, **27** (1962) 3698.
- [9] A.J. Chalk and J.F. Harrod, *J. Am. Chem. Soc.*, **89** (1967) 1640; Y.L. Baay and A.G. MacDiarmid, *Inorg. Chem.*, **8** (1969) 986.
- [10] For a paper on the α -alkoxyalkyl cobalt complex from the reaction of HCHO with $\text{Me}_3\text{SiCo}(\text{CO})_4$, see V. Galanb, L. Németh, F. Ungváry and G. Pályi, *Organometallics*, **8** (1989) 109.
- [11] The stoichiometric reaction of $\text{Me}_3\text{SiMn}(\text{CO})_5$ with aldehydes under CO as $150\text{--}350\text{ lb in}^{-2}$ gives α -siloxyacetylmanganese carbonyl complexes; see K.C. Brinkman and J.A. Gladysz, *Organometallics*, **3** (1984) 147.
- [12] The reaction of acetylcobalt complex with HSiEt_3 was reported to give acetaldehyde by R.W. Wegman, *Organometallics*, **5** (1986) 707.
- [13] Dehydrogenative silylation of ketones to enol silyl ethers catalyzed by $\text{Co}_2(\text{CO})_8$ was reported by H. Sakurai, K. Miyoshi and Y. Nakadaira, *Tetrahedron Lett.*, (1977) 2671.
- [14] We found that the reaction of benzaldehyde (10 mmol) with HSiEt_2Me (30 mmol) and CO (50 atm) in the presence of $\text{Co}_2(\text{CO})_8$ (0.2 mmol) and PPh_3 (0.2 mmol) at 140°C in C_6H_6 (20 ml) gave **1a** with a 37% yield along with 1,2-diphenylethane-1,2-diol disilyl ether with a 26% yield (dl/*meso*, 1/1). This result implies the intermediacy of a benzyl radical such as **10** in the reaction.
- [15] For a review on ionic hydrogenation by HSiR_3 , see W.P. Weber, *Silicon Reagents for Organic Synthesis*, Springer, Berlin, 1993, pp. 273–287.
- [16] We have designed a special apparatus for the handling of HSiMe_3 , which has a low boiling point [1d].