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$Co_2(CO)_8$-Catalyzed Ring-Opening Carbonylation of Cyclic Ethers Using *N*-Silylamines

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Synopsis. $Co_2(CO)_8$-catalyzed ring-opening carbonylation of oxiranes and oxetane smoothly proceeds with high regioselectivity under 1 atm of carbon monoxide at room temperature to give the corresponding β- and γ-siloxy amides in high yields, respectively. $[(R_3Si)_2NR^1R^2]^+[Co(CO)_4]^-$ is thought to be an active catalyst species and directs the high regioselectivity of the carbonylation.

Silicon–nitrogen bonds are readily formed by various methods[1,2] and the resulting *N*-silylamines are thought to represent a class of potential reactants or intermediates for organic synthesis. Recently, we have been bending our energies on developing the effective utilization of *N*-silylamines for the synthesis of nitrogen compounds.[3,4] Among the various possible reactions using *N*-silylamines, we focus our attention on the carbonylation of cyclic ethers, especially oxiranes,[3,5] since they reported until now were not attractive as a synthetic method because of their lack of regiochemical control for incorporation of carbon monoxide. Here, we will report $Co_2(CO)_8$-catalyzed effective and regioselective carbonylation of oxiranes and oxetane using *N*-silylamines under extremely mild reaction conditions; i.e., under 1 atm of carbon monoxide at room temperature.

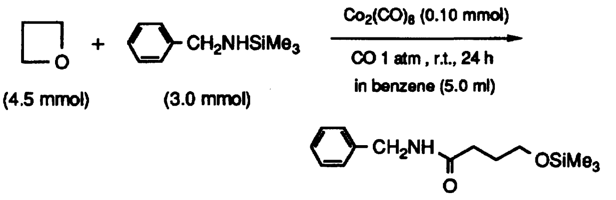
Firstly, we examined the effects of carbon monoxide pressure as well as reaction temperature on the regioselectivity of the carbonylation of propylene oxide using *N*-(trimethylsilyl)benzylamine (Scheme 1).

As can be readily seen from Scheme 1, both high pressure of carbon monoxide and high reaction temperature lead to poor regioselectivity. Consequently, under 1 atm of carbon monoxide at room temperature, only single regioisomer of the β-siloxy amide was obtained in 84% yield.

Various oxiranes were regioselectively carbonylated at the less hindered carbon atom under the present reaction conditions using *N*-silylamines, affording the corresponding β-siloxy amides in high yields (Table 1). Compared with our previous results, the yields of β-siloxy amide as well as selectivity increased considerably, since isomerization and/or polymerization of oxiranes were also suppressed under the present reaction conditions. As for *N*-silylamines, *N*-silylamines derived from either primary or secondary amines can be employed in the present carbonylation, whereas sterically hindered *N*-(*t*-butyldimethylsilyl)benzylamine[6] and low basic aromatic *N*-silylamines such as *N*-(trimethylsilyl)aniline did not react at all. Further, the importance of the N-SiR_3 functionality was explicitly demonstrated by the use of benzylamine in place of *N*-(trimethylsilyl)benzylamine. Under the same reaction conditions (under 1 atm of carbon monoxide at room temperature), no carbonylation of propylene oxide proceeded and benzylamine was recovered quantitatively.

The present carbonylation is characteristic of $Co_2(CO)_8$ catalyst. Other cobalt complexes such as $CoCl_2$, $CoCl_2(PPh_3)_2$, and $[PPN]Co(CO)_4$ ($[PPN]=$ bis(triphenylphosphoranylidene)ammonium) and transition-metal carbonyls such as $Ru_3(CO)_{12}$, $Rh_6(CO)_{16}$, $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Pt(CO)_2(PPh_3)_2$, $Mo(CO)_6$, $IrCl(CO)(PPh_3)_2$, and $Re_2(CO)_{10}$ showed no catalytic activity.

The ring-opening carbonylation of oxetane, a four-membered cyclic ether, also proceeded under the present reaction conditions to give *N*-benzyl-4-(trimethylsiloxy)butanamide in 75% yield (Eq. 1).



Isolated yield: 75% (1)

However, tetrahydrofuran(THF), a less strained five-membered cyclic ether, was not carbonylated at all under the same reaction conditions.

Mechanistic Consideration

Murai et al. have already reported the ring-opening carbonylation of cyclic ethers with *hydrosilanes* in the presence of $Co_2(CO)_8$ catalyst under 1 atm of carbon monoxide at room temperature.[7] They speculated that $R_3SiCo(CO)_4$ which would be generated from $Co_2(CO)_8$ and hydrosilanes is a key intermediate for their reactions and the ring-opening of oxiranes would be attained via the formation of silyloxonium ion intermediate owing to strong oxophilicity of silicon atom.[8] After the present reaction, however, a new cobalt carbonyl species was detected by FT-IR

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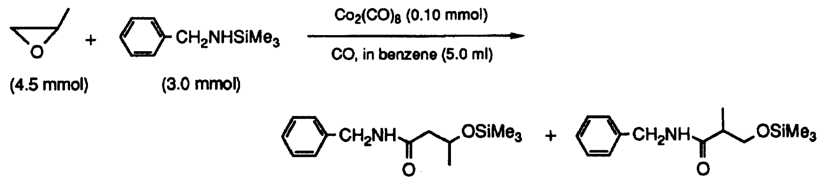
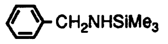
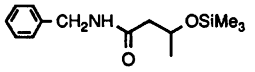
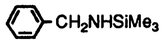
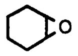
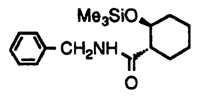
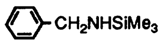
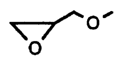
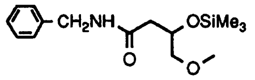
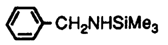
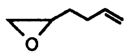
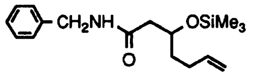
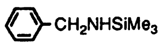
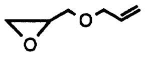
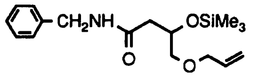
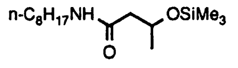
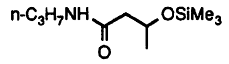
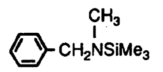
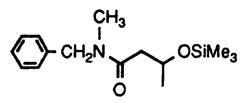
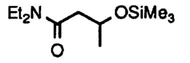
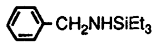
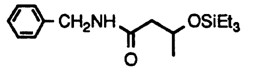


Conditions:	**GLC Yields:**	
CO 1 atm, r.t., 24 h	84%[a]	0%
CO 60 atm, r.t., 24 h	40%	11%
CO 60 atm, 120 °C, 15 h	56%	24%

a) Isolated yield.

Scheme 1.

Table 1. $Co_2(CO)_8$-Catalyzed Ring-Opening Carbonylation of Oxiranes Using *N*-Silylamines under 1 atm of Carbon Monoxide at Room Temperature[a]

Run	*N*-Silylamine	Oxirane	Time/h	Product	Isolated yields[b]/%
1			24		84
2			50		60
3			24		81
4			24		79
5			48		72
6	n-$C_8H_{17}NHSiMe_3$		24		83
7	n-$C_3H_7NHSiMe_3$		24		71
8			24		89
9	Et_2NSiMe_3		24		66
10			24		73

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a) *N*-Silylamine (3.0 mmol), oxirane (4.5 mmol), $Co_2(CO)_8$ (0.10 mmol), benzene (5.0 ml) under 1 atm of carbon monoxide (balloon) at room temperature. b) Based on the amount of *N*-silylamine charged.

measurement (absorption bands at 2006, 1960, and 1894 (vs) cm^{-1}, which were quite similar to those of $[\mathrm{Et_3NSiEt_3}]^+[\mathrm{Co(CO)_4}]^-$[9]), and the characteristic absorption bands of $\mathrm{(CH_3)_3SiCo(CO)_4}$[10] were not observed at all. Furthermore, when $\mathrm{Co_2(CO)_8}$ was treated with an excess amount of *N*-(trimethylsilyl)benzylamine in $\mathrm{CH_2Cl_2}$ without oxiranes at room temperature for 10 h, the generation of a similar cobalt carbonyl species was observed (FT-IR absorption band at 1898 cm^{-1} (vs)). Unfortunately, we could not isolate and identify this complex fully, but we believe that it would be $[\mathrm{(R_3Si)_2NR^1R^2}]^+[\mathrm{Co(CO)_4}]^-$ (**2**) generated from $\mathrm{R_3SiCo(CO)_4}$ (**1**) and *N*-silylamines. The steric hindrance around the metal center in **2** would become larger, and the carbonylation should occur at the less hindered carbon atom of unsymmetrically substituted oxiranes.[11] Under higher carbon monoxide pressure, however, both the carbonylation ability of cobalt catalyst and the rate of carbonylation were extremely enhanced and the regioselectivity did not manifest. Accordingly, the most plausible route to β-siloxy amides is illustrated in Scheme 2.

In conclusion, we succeeded in the regioselective syntheses of β- and γ-siloxy amides by $\mathrm{Co_2(CO)_8}$-catalyzed ring-opening carbonylation of oxiranes and oxetane, which involves the effective utilization of the novel reactivity of *N*-silylamines.

Experimental

Materials. Cyclic ethers and solvents were commercially available and distilled before use. *N*-Silylamines were prepared according to the procedure described later, except for *N*-(trimethylsilyl)diethylamine which was purchased from Shin-Etsu Chemical Industries Co., Ltd. Carbon monoxide (>99.9%) was used without further purification. $\mathrm{Co_2(CO)_8}$ purchased from Strem Chemicals was recrystallized from pentane at −10 °C before use. $\mathrm{CoCl_2(PPh_3)_2}$,[13] $\mathrm{[PPN]Co(CO)_4}$,[14] $\mathrm{Rh_6(CO)_{16}}$,[15] and $\mathrm{Pt(CO)_2(PPh_3)_2}$,[16] were prepared according to procedures in the literatures. $\mathrm{CoCl_2}$, $\mathrm{Ru_3(CO)_{12}}$, $\mathrm{Mn_2(CO)_{10}}$, $\mathrm{Fe_2(CO)_9}$, $\mathrm{Mo(CO)_6}$, $\mathrm{IrCl(CO)(PPh_3)_2}$, and $\mathrm{Re_2(CO)_{10}}$ were purchased from Strem Chemicals and used without further purification.

Preparation of *N*-(Trimethylsilyl)benzylamine. A solution of benzylamine (22 g) in tetrahydrofuran (50 ml) was placed in a 500 ml three-necked flask equipped with a 200 ml dropping funnel connected with a Schlenk line (under an argon atmosphere). Butyllithium (1.59 mol dm^{-3} in hexane; 140 ml) was added dropwise from the funnel at 0 °C with magnetically stirring, and the reaction mixture gradually became a red suspension. After complete addition of butyllithium, the resulting red solution was stirred at room temperature for 2 h. Then, from the dropping funnel, chlorotrimethylsilane (31 ml) was added to this red solution at room temperature. White powder, LiCl, slowly precipitated and red color of the solution disappeared. The resulting milky solution was still stirred overnight. White precipitate was filtered off by a glass filter and Celite under an argon atmosphere, followed by the concentration of the filtrate to give yellow liquid. This was carefully distilled under vacuum twice, affording 26 g of the colorless liquid, *N*-(trimethylsilyl)benzylamine (72% yield), bp 72.9—73.1 °C (3.6 mmHg, 1 mmHg=133.322 Pa). Other *N*-silylamines were also prepared in the similar manner.

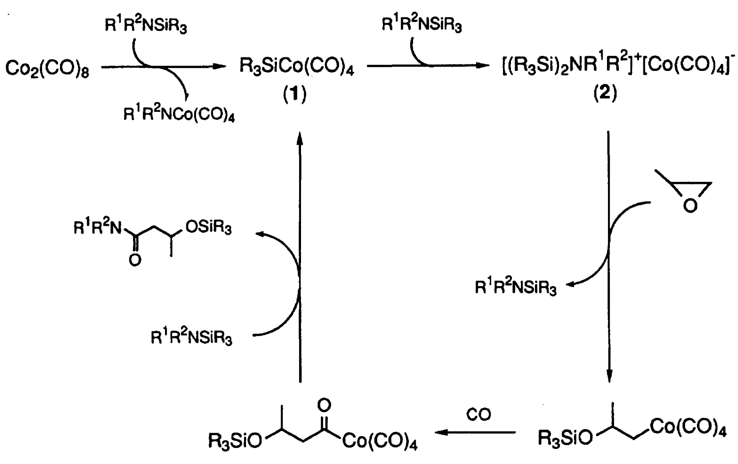
General Reaction Procedure. A typical reaction procedure is as follows. A mixture of *N*-silylamines (3.0 mmol), cyclic ethers (4.5 mmol), $\mathrm{Co_2(CO)_8}$ (0.10 mmol), and benzene (5.0 ml) was placed in a 50 ml Pyrex flask equipped with a balloon containing an atmospheric pressure of carbon monoxide. The solution was magnetically stirred under 1 atm of carbon monoxide at room temperature for 24—50 h. All products were isolated by Kugelrohr distillation and identified by ^{1}H NMR, ^{13}C NMR, FT-IR, GC-MS, and/or elemental analysis. The ^{1}H and ^{13}C NMR spectra were recorded in $\mathrm{CDCl_3}$ at 270 MHz with a JEOL GSX-270 and at 22.05 MHz with a JEOL JNM FX-100, respectively. IR spectra were recorded on a NICOLET 5-MX Fourier transform infrared spectrophotometer. Mass spectra were obtained with a Shimadzu GCMS-QP 2000. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Spectral and analytical data of the representative products are described below.

***N*-Benzyl-3-(trimethylsiloxy)butanamide:** Yellow oil; Kugelrohr distillation: bp 190 °C (0.1 mmHg); IR (neat) 1655 cm^{-1} (C=O); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.00 (9H, s, $\mathrm{-Si(CH_3)_3}$), 1.09 (3H, d, $\mathrm{-CHC}H_3$), 2.22 (2H, d, $\mathrm{-COCH_2-}$), 4.15 (1H, six, $\mathrm{-OC}H\mathrm{CH_3}$), 4.27 (2H, d, $\mathrm{C_6H_5C}H_2\mathrm{-}$), 7.09—7.27 (6H, m, $\mathrm{C_6H_5-}$ and −NH−); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=−0.234 (q, $\mathrm{-Si(CH_3)_3}$), 23.3 (q, $\mathrm{-CH}C\mathrm{H_3}$), 42.9 (t, $\mathrm{C_6H_5}C\mathrm{H_2-}$), 45.9 (t, $\mathrm{-CO}C\mathrm{H_2-}$), 65.6 (d, $\mathrm{-O}C\mathrm{HCH_3}$), 126.8 (d, phenyl 4), 127.2 (d, phenyl 2,6), 128.0 (d, phenyl 3,5), 138.1 (s, phenyl 1), 170.7 (s, −CONH−); MS (70 eV) *m/z* (rel intensity) 265 (M$^+$; 12), 250 (22), 106 (74), 91 (100), 73 (45).

***trans*-*N*-Benzyl-2-(trimethylsiloxy)-1-cyclohexanecarboxamide:** White solid; Kugelrohr distillation: 230 °C (0.5 mmHg); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=−0.04 (9H, s, $\mathrm{-Si(CH_3)_3}$), 0.90—2.10 (8H, m, cyclohexyl-CH_2), 1.94—2.04 (1H, m, −C*H*CO−), 3.67—3.76 (1H, m, −C*H*OSi−), 4.31 (2H, d, $\mathrm{C_6H_5C}H_2\mathrm{-}$), 6.54 (1H, t, −NH−), 7.12—7.28 (5H, m, $\mathrm{C_6H_5-}$) ^{13}C NMR ($\mathrm{CDCl_3}$) δ=0.41 (q, $\mathrm{-Si(CH_3)_3}$), 24.2, 24.4, 28.2, 35.4, (t, cyclohexyl-CH$_2$), 43.0 (t, $\mathrm{C_6H_5}C\mathrm{H_2-}$), 53.5 (d, −CO*C*H−), 72.0 (d, $-C\mathrm{HOSi(CH_3)_3}$), 126.9 (d, phenyl 4), 127.4 (d, phenyl 2,6), 128.2 (d, phenyl 3,5), 138.4 (s, phenyl 1), 174.1 (s, −NHCO−); MS (70 eV) *m/z* (rel intensity) 305 (M$^+$; 10), 290 (32), 106 (74), 91 (100), 73 (38).

***N*-Benzyl-4-methoxy-3-(trimethylsiloxy)butanamide:** Yellow oil; Kugelrohr distillation: bp 175 °C (0.05 mmHg); IR (neat) 1651 cm^{-1} (C=O); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.00 (9H, s, $\mathrm{-Si(CH_3)_3}$), 2.21—2.39 (2H, m, $\mathrm{-COCH_2-}$), 3.16—3.27 (7H, m, $\mathrm{C}H_3\mathrm{OC}H_2\mathrm{-}$ and $\mathrm{C_6H_5C}H_2\mathrm{-}$), 4.11—4.19 (1H, m, $\mathrm{-OC}H\mathrm{CH_2OCH_3}$), 6.56 (1H, br, −NH−), 7.12—7.24 (5H, m, $\mathrm{C_6H_5-}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=−0.117 (q, $\mathrm{-Si(CH_3)_3}$), 41.3 (t, $\mathrm{-CO}C\mathrm{H_2-}$), 43.1 (t, $\mathrm{C_6H_5}C\mathrm{H_2-}$), 58.7 (q, $\mathrm{CH_3O-}$) 68.5 (d, $\mathrm{-O}C\mathrm{HCH_2OCH_3}$), 76.1 (t, $\mathrm{CH_3O}C\mathrm{H_2-}$), 126.9 (d, phenyl 4), 127.3 (d phenyl 2,6), 128.2 (d, phenyl 3,5), 138.1 (s, phenyl 1), 170.4 (s, −CONH−).

***N*-Benzyl-3-(trimethylsiloxy)-6-heptenamide:** Yellow oil; Kugelrohr distillation: bp 179 °C (0.1 mmHg); IR (neat) 1649 cm $^{-1}$ (C=O); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.07 (9H, s, $\mathrm{-Si(CH_3)_3}$), 1.54 (2H, q, $\mathrm{-CHC}H_2\mathrm{-}$), 2.00—2.13 (2H, m, $\mathrm{CH_2{=}CHC}H_2\mathrm{-}$), 2.30 (1H, dd, $\mathrm{-COC}H\mathrm{H'-}$), 2.31 (1H,



Scheme 2.

dd, $-COHH'-$), 4.04—4.13 (1H, m, $-CHOSi-$), 4.24—4.42 (2H, m, $C_6H_5CH_2-$), 4.94 (1H, dd, $HH'C{=}CH-$), 4.98 (1H, dd, $HH'C{=}CH-$), 5.68—5.83 (1H, m, $CH_2{=}CH-$), 7.07 (1H, br, $-NH-$), 7.19—7.29 (5H, m, C_6H_5-); ^{13}C NMR ($CDCl_3$) $\delta=0.117$ (q, $-Si(CH_3)_3$), 29.4 (t, $CH_2{=}CHCH_2-$), 36.1 (t, $CH_2{=}CHCH_2CH_2-$), 43.1 (t, $C_6H_5CH_2-$), 44.0 (t, $-COCH_2-$), 69.0 (d, $-CHOSi-$), 114.3 ($CH_2{=}CH-$), 126.8 (d, phenyl 4), 127.2 (d, phenyl 2,6), 128.0 (d, phenyl 3,5), 137.5 (d, $CH_2{=}CH-$), 137.9 (s, phenyl 1), 170.4 (s, $-CONH-$).

***N*-Octyl-3-(trimethylsiloxy)butanamide:** Yellow oil; Kugelrohr distillation: bp 170 °C (0.3 mmHg); IR (neat) 1643 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) $\delta=0.06$ (q, $-Si(CH_3)_3$), 14.0 (q, CH_3CH_2-), 22.6 (t, CH_3CH_2-), 23.5 (q, CH_3CH-), 26.9 (t, $-NHCH_2CH_2CH_2-$), 29.1 (t, $CH_3CH_2CH_2CH_2CH_2-$), 29.5 (t, $CH_3CH_2CH_2-$), 31.7 (t, $-NHCH_2CH_2-$), 39.5 (t, $-NHCH_2-$), 46.3 (t, $-COCH_2-$), 65.9 (d, $-CHOSi(CH_3)_3$), 170.6 (s, $-CONH-$).

Found: C, 62.67; H, 11.57; N, 4.87%. Calcd for $C_{15}H_{33}NO_2Si$: C, 62.83; H, 11.97; N, 4.89%.

***N*-Benzyl-*N*-methyl-3-(trimethylsiloxy)butanamide:** Yellow oil; Kugelrohr distillation: bp 150 °C (0.10 mmHg); IR (neat) 1649 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) $\delta=-0.117$ (q, $-Si(CH_3)_3$), 23.9 (q, CH_3CHO-), 33.5 and 33.8 (q, CH_3N-), 42.6 and 42.9 (t, $-COCH_2-$), 50.4 and 53.2 (t, $C_6H_5CH_2-$), 66.3 and 66.4 (d, $-OCHCH_3$), 125.9, 126.8, 127.1, 127.6 128.1 and 128.4 (d, phenyl 2-6), 136.4 and 137.0 (s, phenyl 1), 170.8 and 171.3 (s, $-CONH-$).

Found: C, 64.47; H, 9.01; N, 5.01%. Calcd for $C_{15}H_{25}NO_2Si$: C, 64.40; H, 9.22; N, 5.14%.

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