# Cobalt Catalysed Ring-opening Carbonylation of Cyclic Ethers using *N*-(Trimethylsilyl)amines

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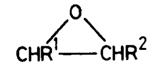
*N*-(Trimethylsilyl)amines direct ring-opening carbonylation of a variety of cyclic ethers such as oxiranes (**1**—**3**), oxetane (**4**), tetrahydrofuran (**5**), and 1,3-dioxolane (**6**) in the presence of a catalytic amount of $Co_2(CO)_8$ under carbon monoxide pressure to give siloxy amides.

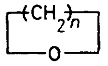
Silicon–nitrogen bonds are readily formed by various methods.[1,2] The resultant aminosilanes, thus far, are usually used as silyl transfer reagents or *N*-protected amines.[1] In this Communication, we wish to report the novel reactivity of *N*-(trimethylsilyl)amines [*N*-(TMS)amines], *i.e.*, ring-opening carbonylation of cyclic ethers[3,4] directed by the *N*-TMS functionality.

The results are listed in Table 1. In the presence of *N*-(TMS)amines and a catalytic amount of $Co_2(CO)_8$ under carbon monoxide, a variety of cyclic ethers such as oxiranes (**1**—**3**) (runs 1—6), oxetane (**4**) (run 7), and tetrahydrofuran (THF) (**5**) (run 8) are carbonylated to give the corresponding β-, γ- and δ-siloxyamides, respectively, in good yields. 1,3-Dioxolane (**6**) can also be employed (run 9). In these reactions, siloxyamines, simple products of ring-opening *via* nucleophilic attack of the amines, were afforded in only trace amounts. In some cases, ureas containing no TMS group are obtained as by-products. Among the cyclic ethers, oxiranes are the most reactive. The carbonylation of oxiranes took place even at room temperature under carbon monoxide as exemplified by run 5.

The importance of the *N*-TMS functionality is explicitly demonstrated by use of benzylamine in place of *N*-(trimethylsilyl)benzylamine. Under the same reaction conditions as runs 5 or 8, no carbonylation proceeded and the amine was recovered unchanged. Strong oxophilicity of silicon (bond

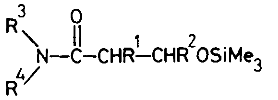


**(1)** R$^1$ = Me, R$^2$ = H
**(2)** R$^1$ = CH$_2$OMe, R$^2$ = H
**(3)** R$^1$ = R$^2$ = $-(CH_2)_4-$



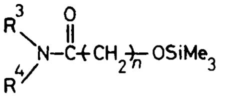
**(4)** $n$ = 3
**(5)** $n$ = 4

**(6)**



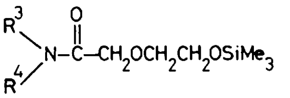
$R^3R^4N{-}C(O){-}CHR^1{-}CHR^2OSiMe_3$

**(7a)** R$^1$ = R$^4$ = H, R$^2$ = Me, R$^3$ = CH$_2$Ph
**(7b)** R$^2$ = R$^4$ = H, R$^1$ = Me, R$^3$ = CH$_2$Ph
**(8a)** R$^1$ = H, R$^2$ = Me, R$^3$ = R$^4$ = Et
**(8b)** R$^1$ = Me, R$^2$ = H, R$^3$ = R$^4$ = Et
**(9a)** R$^1$ = R$^4$ = H, R$^2$ = CH$_2$OMe, R$^3$ = CH$_2$Ph
**(9b)** R$^2$ = R$^4$ = H, R$^1$ = CH$_2$OMe, R$^3$ = CH$_2$Ph
**(10)** R$^1$ = R$^2$ = $-(CH_2)_4-$, R$^3$ = CH$_2$Ph, R$^4$ = H
**(11)** R$^1$ = R$^2$ = $-(CH_2)_4-$, R$^3$ = n-C$_8$H$_{17}$, R$^4$ = H



$R^3R^4N{-}C(O){-}(CH_2)_n{-}OSiMe_3$

**(12)** $n$ = 3, R$^3$ = CH$_2$Ph, R$^4$ = H
**(13)** $n$ = 4, R$^3$ = CH$_2$Ph, R$^4$ = H



$R^3R^4N{-}C(O){-}CH_2OCH_2CH_2OSiMe_3$

**(14)** R$^3$ = CH$_2$Ph, R$^4$ = H

dissociation energy;[5] Si–O 430—530 kJ mol$^{-1}$, Si–N 305—330 kJ mol$^{-1}$) will facilitate the ring opening, followed by carbonylation.

Dicobalt octacarbonyl, $Co_2(CO)_8$, is the only active catalyst precursor. Other transition metal carbonyls such as $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Mo(CO)_6$ are totally ineffective. It is well known that amines induce disproportionation of $Co_2(CO)_8$.[6—8] The similar disproportionation of $Co_2(CO)_8$ with *N*-(TMS)amines giving $Me_3Si{-}Co(CO)_4$ may be involved in the catalytic cycle.

**Table 1.** Ring-opening carbonylation of cyclic ethers with *N*-(trimethylsilyl)amines.[a]

| Run | *N*-(TMS)amine | Cyclic ether | Temp./ °C | Product | Yield/ %[b] |
|---|---|---|---|---|---|
| 1 | $PhCH_2NHSiMe_3$ | **(1)** | 120 | **(7a)**/**(7b)** | 80(7/3)[c] |
| 2 | $Et_2NSiMe_3$ | **(1)** | 120 | **(8a)**[d,e] | 72 |
| 3 | $PhCH_2NHSiMe_3$ | **(2)** | 120 | **(9a)**[d] | 64 |
| 4 | $PhCH_2NHSiMe_3$ | **(3)** | 100 | **(10)**[f] | 74 |
| 5[g] | $PhCH_2NHSiMe_3$ | **(3)** | Room temp. | **(10)**[f] | 60 |
| 6 | n-$C_8H_{17}NHSiMe_3$ | **(3)** | 100 | **(11)**[f] | 64 |
| 7 | $PhCH_2NHSiMe_3$ | **(4)** | 140 | **(12)** | 66[h] |
| 8 | $PhCH_2NHSiMe_3$ | **(5)**[i] | 160 | **(13)** | 51[h] |
| 9 | $PhCH_2NHSiMe_3$ | **(6)** | 160 | **(14)** | 30 |

[a] *N*-(Trimethylsilyl)amine (3.0 mmol), cyclic ether (4.5 mmol), $Co_2(CO)_8$ (0.075 mmol), benzene (3.0 ml), CO (60 kg cm$^{-2}$; initial pressure at room temp.) for 15 h. [b] Isolated yields based on the amines charged. [c] Ratio of two regioisomers. [d] Exclusively single regioisomer, without formation of **(8b)** or **(9b)**. [e] During the isolation, hydrolysis of the Si–O bond occurred. Ratio of the β-trimethylsiloxy- and β-hydroxy-amides is 6:4. [f] *Trans* isomer. [g] For 50 h. [h] By g.l.c. [i] THF (3.0 ml).

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