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COBALT CARBONYL CATALYSED REACTION OF OXETANES WITH A HYDROSILANE AND CARBON MONOXIDE

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Summary

The cobalt carbonyl catalyzed reaction of oxetanes with $HSiR_3$ and CO took place at 25°C under 1 atm to give not only 1,4-disiloxybutanes but also 1-siloxypropanes. The product ratio was highly dependent on the solvent used.

Introduction

In the study of the cobalt carbonyl catalyzed reaction of cyclic ethers with a hydrosilane and carbon monoxide [1], we found that the reaction of tetrahydrofuranes [1c] or oxiranes [1b] took place at 25°C under 1 atm of CO to form 1,5-disiloxypentanes or 1,3-disiloxypropanes, respectively, resulting from CO having been incorporated as an oxymethyl group. The high oxophilicity of the silicon atom in $R_3SiCo(CO)_4$, a key catalyst species generated in situ by the reaction of $HSiR_3$ with $Co_2(CO)_8$ [2], would be the driving force for cleavage of a carbon–oxygen bond in a cyclic ether to form an intermediate having a carbon–cobalt bond. This concept can likely be extended to the reaction of four-membered cyclic ethers (e.g., oxetane), since oxetane has more basic oxygen than ethylene oxide [3] and its strain energy is similar to that of ethylene oxide [4]. Curiously, however, we could obtain only a small amount of the expected disiloxybutane from oxetane under the same reaction conditions as used for the incorporation of carbon monoxide into oxiranes or tetrahydrofurans.

Now, in the study of the cobalt carbonyl catalyzed reaction of oxetanes with a hydrosilane and carbon monoxide, we have discovered an interesting side reaction

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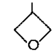
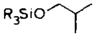
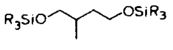
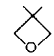
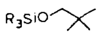
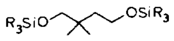
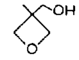
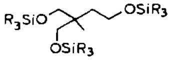
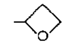
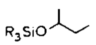
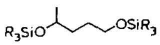
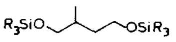
TABLE 1

COBALT CARBONYL CATALYZED REACTION OF OXETANES WITH HSiR$_3$ AND CO ^{a}

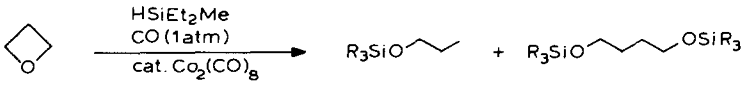
Oxetane	HSiR$_3$	Solvent	Temp. (°C)	Time (h)	Product (yield (%)) ^{b}		
 (1)					**2**	**3**	
	HSiEt$_2$Me	CH$_2$Cl$_2$	25	2	83	16	
	HSiEt$_2$Me	C$_6$H$_6$	25	7	17	63	
	HSiEt$_2$Me	DME	25	7	17	66	
	HSiEt$_2$Me	n-C$_6$H$_{14}$	25	7	trace	96	
 (6)							
	HSiEt$_2$Me	CH$_2$Cl$_2$	0	2	64	11	
	HSiEt$_2$Me	n-C$_6$H$_{14}$	25	20	1	95	
 (7)							
	HSiEt$_2$Me	CH$_2$Cl$_2$	0	7	68	12	
	HSiMe$_3$	n-C$_6$H$_{14}$	25	20	trace	67	
 (8)							
	HSiMe$_3$	CH$_2$Cl$_2$	25	20	61	0	
	HSiMe$_3$	n-C$_6$H$_{14}$	25	20	7	76	
 (9)					 (10)	 (11)	 (12)
	HSiEt$_2$Me	CH$_2$Cl$_2$	0	20	85	13	0
	HSiEt$_2$Me	n-C$_6$H$_{14}$	25	20	0	89	0
	HSiMe$_3$	n-C$_6$H$_{14}$	25	20	0	53	7

^{a} Reaction conditions: Oxetane (2.5 mmol), HSiEt$_2$Me (7.5 mmol) [or HSiMe$_3$ (25 mmol)], Co$_2$(CO)$_8$ (0.1 mmol), solvent (5 ml) under 1 atm of CO. ^{b} Determined by GLC analysis.

and a remarkable solvent dependence of the product distribution. These are the subjects of the present report.

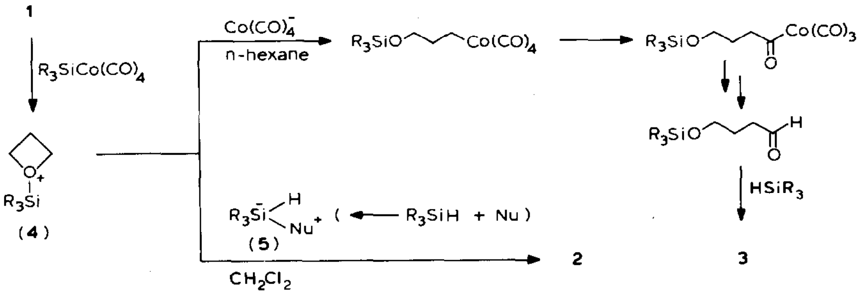
Results and discussion

The reaction of oxetane (**1**) with HSiEt$_2$Me and CO in CH$_2$Cl$_2$ at 25°C under 1 atm (the standard reaction conditions for oxymethylative ring opening of oxiranes or tetrahydrofurans [1b,c]) was completed within 2 h according to GLC monitoring.



(1) (2) (3) (1)

The products obtained were 1-siloxypropane (**2**) (83% yield) and 1,4-disiloxybutane (**3**) (16% yield) (eq. 1). The results showed that the principal reaction took place without incorporation of carbon monoxide. Interestingly, the product distribution of this reaction was highly dependent on the solvent used. The results obtained for **1** are given in Table 1. Incorporation of carbon monoxide to give **3** became an exclusive reaction course when n-hexane was employed as the solvent.



SCHEME 1

A plausible reaction pathway is outlined in Scheme 1. The oxetane may react with $R_3SiCo(CO)_4$ to form the silyloxonium ion intermediate **4** and $Co(CO)_4^-$ *. Nucleophilic attack of $Co(CO)_4^-$ on **4** may result in the formation of an alkylcobalt complex, which may give product **3** via the 3-siloxy aldehyde intermediate **. On the other hand product **2** may be obtained by hydrogen transfer from $HSiR_3$ ***. The hydrogen transfer may require activation of $HSiR_3$ into a pentacoordinate form [8] such as **5**. These processes may be accelarated in a polar solvent and the nucleophile Nu in **5** could be **1** itself ****.

The results of the reaction of substituted oxetanes are also shown in Table 1. Although the alkyl substituents in **6**, **7**, and **8** seemed to decrease the reaction rates, similar product distributions were obtained. The reaction of 2-methyloxetane (**9**) proceeded smoothly both in CH_2Cl_2 and in n-hexane to give similar results as with oxetane. In CH_2Cl_2 **10** and **11** were obtained in 85 and 13% yields, respectively, both of which did not contain the regio-isomers. The ring opening of **9** with $HSiMe_3$ and CO in n-hexane took place predominantly at the less-substituted carbon center (**11**: 53%, **12**: 7%). The regioselectivity was improved in the reaction of **9** with $HSiEt_2Me$ and CO in n-hexane, only **11** being obtained in 89% yield. Steric hindrance in the silyloxonium ion similar to **4** may be responsible for the better regioselectivity ‡.

These results demonstrate a new possibility for the catalytic incorporation of carbon monoxide using the cobalt complex under 1 atm of CO.

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[*] Gladysz et al. observed related process in stoichiometric reaction of $(CH_3)_3SiMn(CO)_5$ [5].

[**] An alternative path involving a cobalt carbenoid intermediate may exist [1c].

[***] The ability of hydrogen transfer of hydrosilanes to a electropositively charged carbon center is well-known [6].

[****] The products obtainable from hydrogen transfer were not found in significant amounts in the reactions of tetrahydrofurans. Oxetane might play a role as the nucleophile to form the pentacoordinated intermediate **5**. After transferring hydride, **5** may be converted to **4** [7].

[‡] Compared with the regioselectivity of ring opening in 1-butene oxide [1b] or 2-methyltetrahydrofuran [1c], which gave a mixture of regioisomers in a ratio of about 1/3, 2-methyloxetane seems to be a special case exhibiting high regioselectivity. Although no clear explanation for the high regioselectivity can be offered at the present time, similar high regioselectivity was observed by Weber et al. in the ring opening of 2-methyloxetane with Me_3SiCl [8].

Experimental

General

Infrared spectra were recorded with Shimazu IR-400 or JASCO grating IR spectrophotometers IR-G; absorptions are reported in cm^{-1}. ^1H NMR were recorded on a Japan Electron Optics JNM-PS-100 spectrometer or Japan Electron Optics JNM-GX 270 FT-NMR spectrometer operating at 100 and 270 MHz, respectively, with Me_4Si or $CHCl_3$ as internal standard. The position of Me_4Si was recognized by adding the standard after the spectrum was recorded without it. Otherwise the signal of the standard may be confused with that of organosilicon compounds. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, c = complex, br = broad), coupling constant (Hz), integration, and interpretation. Mass spectra were recorded on a model RMU-6E instrument operating at 70 eV. Elemental analyses were performed by the Elemental Analyses Center of Osaka University. Analytical gas chromatography (GLC) was carried out on a Shimazu GC-3BF or a Hitachi Model 163 equipped with a flame ionization detector, using a 6 m × 3 mm stainless steel column packed with 5% Silicone OV-1 supported in 60–80 mesh Chromosorb W(AW). Preparative GLC was carried out using a Hitachi Model K 53 gas chromatograph using a 2 m × 10 mm stainless steel column packed with 5% Silicone OV-1 supported on 60–80 mesh Chromosorb W.

Benzene, toluene, 1,2-dimethoxyethane (DME), and n-hexane were distilled from a sodium/lead alloy. Dichloromethane was distilled from CaH_2. Carbon monoxide was purchased from the Neriki Gas Co. and used as received. $Co_2(CO)_8$ was purchased from Strem Chemical Co., recrystallized from n-hexane (25 to −20°C) and stored under carbon monoxide in a refrigerator. Hydrosilanes were prepared from chlorosilanes following literature procedures [9]. Oxetane, 2-methyloxetane, and 3,3-dimethyloxetane were purchased from the Nakarai Chemical Co., and distilled before use. The other oxetanes were prepared according to the literature: 3-methyloxetane [10], 3-hydroxymethyl-3-methyloxetane [11].

General procedure for the cobalt carbonyl catalyzed reaction of oxetanes with a hydrosilane and carbon monoxide

A 10 ml two-necked round-bottom flask equipped with a Teflon-coated magnetic stirring bar was flame dried and then charged with 0.0342 g (0.1 mmol) of $Co_2(CO)_8$, fitted with a serum cap and a CO balloon and flushed with carbon monoxide. $HSiEt_2Me$ (1.1 ml, 7.5 mmol) was added to the flask with a syringe. After five minutes, 5 ml of solvent and 2.5 mmol of oxetane were added to this solution. The solution was stirred for an appropriate period, a few drops of pyridine were added, and air was bubbled through for about 15 min. The precipitates were separated by use of a centrifuge. The solvent was evaporated in vacuo and distillation gave a pure sample of the product. When necessary, purification by preparative GLC was carried out. For GLC yields, appropriate hydrocarbons ($n\text{-}C_nH_{2n+2}$) calibrated against purified products were added before or immediately after the reaction.

Spectroscopic properties of the products are as follows. ^1H NMR data without indication were obtained at 100 MHz.

3,10-Diethyl-3,10-dimethyl-4,9-dioxa-3,10-disiladodecane: for a sample obtained by bulb to bulb distillation; b.p. 100°C (oven)/0.4 Torr; IR (neat): 2950, 2880, 1460, 1420, 1390, 1260, 1100, 1010, 800, 760 cm^{-1}; ^{1}H NMR (CCl_4): δ (ppm) 0.01(s, 6H, Si–CH_3), 0.6(m, 8H, Si–CH_2), 1.2(m, 12H, Si–C–CH_3), 1.33 (m, 4H, CH_2), 3.64(m, 4H, CH_2O); Mass: m/e 261(M^+ – Et, 26), 190(100), 161(51). Found: C, 57.72; H, 12.00. $C_{14}H_{34}O_2Si_2$ calcd.: C, 57.87; H, 11.79%.

3,10-Diethyl-3,6,10-trimethyl-4,9-dioxa-3,10-disiladodecane: for a sample obtained by bulb to bulb distillation; b.p. 120°C (oven)/3 Torr; IR (neat): 2950, 2880, 1460, 1420, 1400, 1260, 1100, 800, 760 cm^{-1}; ^{1}H NMR (CCl_4): δ (ppm) 0.04(s, 6H, Si–CH_3), 0.6(m, 8H, Si–CH_2), 0.9(m, 15H, Si–C–CH_3, and CH_3), 1.3(m, 2H, CH_2), 1.6(m, 1H, $CH(C)_2$), 3.50(dd, J 6 Hz, 2 Hz, CH_2–O), 3.70(t, J 6 Hz, 2H, CH_2O); Mass: m/e 285(M^+ – Et, 10), 217(14), 187(100), 172(50). Found: C, 58.97; H, 12.13. $C_{15}H_{36}O_2Si_2$ calcd.: C, 59.14; H, 11.91%.

3,10-Diethyl-3,6,6,10-tetramethyl-4,9-dioxa-3,10-disiladodecane: for a sample obtained by bulb to bulb distillation; b.p. 97°C (oven)/1 Torr: IR (neat): 2940, 2860, 1460, 1250, 1090, 1000, 830, 800, 780 cm^{-1}; ^{1}H NMR (CCl_4): δ (ppm) 0.1(s, 6H, Si–CH_3), 0.8(m, 8H, Si–CH_2), 1.2(complex, 18H, Si–C–CH_3, and CH_3), 1.68(t, J 6 Hz, 2H, CH_2), 3.42(s, 2H, CH_2–O), 3.84(t, J 6 Hz, CH_2–O); Mass: m/e 289(M^+ – Et, 15), 287(10), 201(5), 187(100). Found: C, 60.05; H, 12.11. $C_{16}H_{38}O_2Si_2$ cslcd.: C, 68.30; H, 12.01%.

2,2,5,5,9,9-Hexamethyl-3,8-dioxa-2,9-disiladecane: for a sample obtained by bulb to bulb distillation: b.p. 150°C (oven)/20 Torr; IR (neat): 2950, 2800, 1475, 1395, 1365, 1250, 1080, 990, 870, 830, 750 cm^{-1}; ^{1}H NMR (CCl_4) δ (ppm) 0.02(s, 18H, Si–CH_3), 0.9(s, 6H, CH_3), 1.46(t, J 8 Hz, 2H, CH_2), 3.22(s, 2H, CH_2–O), 3.62(t, J 8 Hz, 2H, CH_2–O); Mass: m/e 262(M^+, 3), 177(17), 157(28), 147(100), 144(72). Found: C, 54.96; H, 11.71. $C_{12}H_{30}O_2Si_2$ calcd.: C, 54.90; H, 11.52%.

2,2,5,5,8,8-Hexamethyl-3,7-dioxa-2,8-disilanonane: for a sample obtained by bulb to bulb distillation; b.p. 120°C (oven)/12 Torr; IR (neat): 2910, 2856, 2821, 1475, 1398, 1359, 1258, 1087, 1000, 913, 874, 843, 748 cm^{-1}; ^{1}H NMR (CCl_4); δ (ppm) 0.09(s, 18H, Si–CH_3), 0.80(s, 6H, CH_3), 3.25(s, 4H, CH_2–O); Mass m/e 233(M^+ – CH_3, 3), 191(7), 168(22), 157(92), 153(89), 133(11), 103(27), 73(100). Found: C, 52.96; H, 11.37. $C_{11}H_{28}O_2Si_2$ calcd. C, 53.16; H, 11.35%.

((5-β,β-Dimethyl)-α-oxa-β-sila)heptyl-2,2,5,9,9-pentamethyl-3,8-dioxa-2,9-disiladecane: for a sample obtained by bulb to bulb distillation; b.p. 150°C (oven)/15 Torr; IR (neat): 2910, 2846, 2821, 1475, 1401, 1259, 1245, 1077, 1038, 906, 871, 843, 759 cm^{-1}; ^{1}H NMR (CCl_4): δ (ppm) 0.09(s, 27H, Si–CH_3), 0.80(s, 3H, CH_3), 1.42(t, 2H, J 7.5 Hz, CH_3), 3.30(s, 4H, CH_2–O), 3.60(t, 2H, J 7.0 Hz, CH_2–O); Mass: m/e 335(M^+ – CH_3, 2). 245(4), 217(5), 191(9), 170(10), 155(98), 147(44), 143(17), 103(31), 73(100). Found: C, 51.34; H, 10.87. $C_{15}H_{38}O_3Si_3$ calcd. C, 51,36; H, 10.92%.

3,10-Diethyl-3,5,10-trimethyl-4,9-dioxa-3,10-disiladodecane: for a sample obtained by bulb to bulb distillation: b.p. 150°C (oven)/1.2 Torr; IR (neat) 2900, 2750, 1460, 1415, 1350, 1250, 1100, 1000, 790, 760 cm^{-1}; 270 MHz ^{1}H NMR ($CDCl_3$) δ (ppm) 0.02(s, 3H, Si–CH_3), 0.025(s, 3H, Si–CH_3), 0.54(q, J 8 Hz, Si–CH_3), 0.92(t, J 8 Hz, Si–C–CH_3), 1.14(d, J 6 Hz, 3H, CH_3), 1.5(complex, 4H, CH_2), 3.55 (complex, 2H, CH_2–O), 3.767(sextet, J 6 Hz, 1H, CH–O); Mass m/e 275(M^+ – Et, 27), 233(33), 189(100), 161(53). Found: C, 59.25; H, 12.11. $C_{15}H_{36}O_2Si_2$ calcd. C, 59.14; H, 11.92%. The product obtained showed identical spectroscopic and GLC properties with the authentic sample.

3,10-Diethyl-3,5,10-trimethyl-4,9-dioxa-3,10-disiladodecane: for an authentic sample prepared by silylation of parent diol; b.p. 115°C/3 Torr; IR (neat) 2950, 2860, 1460, 1410, 1390, 1260, 1100, 1050, 1000, 800, 750 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$): δ (ppm) 0.02(s, 3H, Si–CH_3), 0.025(s, 3H, Si–CH_3), 0.54(q, *J* 7 Hz, 8H, Si–CH_2), 0.92(t, *J* 7 Hz, 12H, Si–C–CH_3), 1.1(d, *J* 6 Hz, 3H, CH_3), 1.5(complex, 4H, CH_2), 3.55(complex, 2H, CH_2–O), 3.767(sextet, *J* 6 Hz, 1H, CH–O); Mass: *m/e* 276(M^+ – Et, 18), 232(29), 187(100). Found: C, 58.88; H, 12.07. $C_{15}H_{36}O_2Si_2$ calcd.: C, 59.14; H, 11.92%.

3,10-Diethyl-3,6,10-trimethyl-4,9-dioxa-3,10-disiladodecane: for an authentic sample prepared by silylation of the parent diol: IR (neat): 2950, 2880, 1470, 1260, 1100, 1010, 800, 760 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$): δ (ppm) 0.02(s, 3H, Si–CH_3), 0.025 (s, 3H, Si–CH_3), 0.55(q, *J* 7 Hz, 8H, Si–CH_2), 0.86(d, *J* 6.5 Hz, 3H, CH_3), 0.92(t, *J* 7 Hz, Si–C–CH_3), 1.28(m, 2H, CH_2), 1.68(m, 1H, CH), 3.34(dd, *J* 4.6, 3 Hz, 1H, CH_2–O), 3.422(dd, *J* 4.6, 3 Hz, 1H, CH_2–O), 3.616(m, 2H, CH_2–O); Mass *m/e* 276(M^+ – Et, 18), 218(11), 203(3), 187(100). Found: C, 59,05; H, 12.20. $C_{15}H_{36}O_2Si_2$ calcd.: C, 59.14; H, 11.91%.

2,2,4,9,9-Pentamethyl-3,8-dioxa-2,9-disiladecane (**11**) and 2,2,5,9,9-pentamethyl-3,8-dioxa-2,9-disiladecane (**12**): for a mixture (88/12) obtained by bulb to bulb distillation; b.p. 160°C (oven)/20 Torr; IR (neat): 2918, 1378, 1248, 1094, 842, 755 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$): δ (ppm) 0.016(s, 18H, Si–CH_3), 0.85(d, *J* 6 Hz, 0.36H, CH_3 of **12**), 1.11(d, *J* 6 Hz, 2.64H, CH_3 of **11**), 1.5(complex, 3.88H, CH_2 of **11**, CH and CH_2 of **12**), 3.34(dd, *J* 4.6 Hz, 3 Hz, 0.1H, CH_2–O of **12**), 3.422(dd, *J* 4.6 Hz, 3Hz, 0.1H, CH_2–O of **12**), 3.55(complex, 2H, CH_2–O of **11** and CH_2–O of **12**), 3.76(sextet, *J* 6 Hz, 1H, CH–O of **11**). Found: C, 52.89; H, 11.56. $C_{11}H_{28}O_2Si_2$ calcd.: C, 53.16; H, 11.36%.

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References

1 (a) T. Murai, S. Kato, S. Murai, Y. Hatayama and N. Sonoda, Tetrahedron Lett., 26 (1985) 2683; (b) T. Murai, S. Kato, S. Murai, T. Toki, S. Suzuki and N. Sonoda, J. Am. Chem. Soc., 106 (1984) 6093; (c) T. Murai, Y. Hatayama, S. Murai and N. Sonoda, Organometallics, 2 (1983) 1883; (d) Y. Seki, S. Murai and N. Sonoda, Angew. Chem. Int. Ed. Engl., 16 (1977) 789.

2 (a) A.J. Chalk and J.F. Harrod, J. Am. Chem. Soc., 89 (1967) 1640; (b) Y.L. Baay and A.G. MacDiarmic, Inorg. Chem., 8 (1969) 986.

3 R.L. Gritter, in S. Patai (Ed.), Chemistry of Ether Linkage, Interscience, New York, 1967, p. 378.

4 (a) H.K. Eigenmann, D.M. Golden and S.W. Benson, J. Phys. Chem., 77 (1973) 1687; (b) A.S. Pell and G. Dilcher, J. Chem. Soc., Faraday Trans., 61 (1965) 71.

5 (a) K.G. Brinkman and J.A. Gladysz, J. Chem. Soc., Chem. Commun., 1980 (1260); (b) K.G. Brinkman and J.A. Gladysz, Organometallics, 3 (1984) 147.

6 (a) E. Colvin, Silicon in Organic Synthesis, Butterworth and Co Ltd, London, 1981; (b) Y. Nagai, Org. Prep. and Proc. Int., 12 (1980) 13.

7 (a) J.L. Fry and M.A. Mcadam, Tetrahedron Lett., 25 (1984) 5859; (b) R.J.P. Corriu, R. Perz and C. Reye, Tetrahedron, 39 (1983) 999.

8 P. Tzeng and W.P. Weber, J. Org. Chem., 47 (1982) 1976.

9 O.W. Steward and O.R. Pierce, J. Am. Chem. Soc., 83 (1961) 1916.

10 S. Scott, Jr., A.P. Kenneth and F.L. Eugene, J. Am. Chem. Soc., 79 (1957) 948.

11 E.J. Corey and N. Raju, Tetrahedron Lett., 24 (1983) 5571.