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**Registry No.** **1**, 93752-54-6; **1a**, 121055-91-2; **1b**, 121055-92-3; **1d**, 121055-94-5; **2**, 548-93-6; **4**, 4053-51-4; **4a**, 121055-95-6; **4b**, 121055-96-7; **5**, 93525-28-1; **5a**, 121055-97-8; **5b**, 121055-98-9; **6**, 102-56-7; **6a**, 121055-99-0; **7**, 3467-59-2; **7a**, 121056-00-6; **8**, 20734-68-3; **8a**, 121056-01-7; **9**, 614-80-2; **9a**, 121056-02-8; **9a** (methyl ether), 121056-05-1; **9b**, 121056-03-9; **10**, 90-04-0; **10a**, 121056-04-0; **11**, 95-55-6; **11b**, 121056-06-2; **12**, 88-75-5; **13**, 15969-09-2; **14**, 10539-14-7; **15**, 121055-90-1; **15a**, 121056-07-3; **16**, 112458-00-1.

# Cobalt Carbonyl Catalyzed Reactions of Cyclic Ethers with a Hydrosilane and Carbon Monoxide. A New Synthetic Reaction Equivalent to Nucleophilic Oxymethylation[1]

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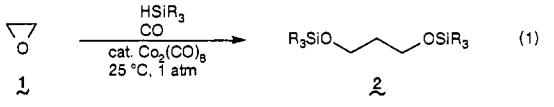
**Abstract:** Siloxymethylative ring opening of cyclic ethers has been attained by a new catalytic system of $HSiR_3/CO/Co_2(CO)_8$. The reaction generally proceeded at room temperatures under 1 atm of CO. The carbon monoxide was incorporated into the product as a part of siloxymethyl group. The reactivity of cyclic ethers decreased in the order of 4 > 3 > 5 >> 6 and 7 membered ring. Among the hydrosilanes ($HSiMe_3$, $HSiEt_2Me$, and $HSiEt_3$), the highly reactive $HSiMe_3$ allowed the use of lower reaction temperature leading to high product selectivities. The regiochemical course of the reaction depended on the substituents of the oxiranes. The reaction of monosubstituted oxiranes having electron-withdrawing groups, such as hydroxy, acetoxy, and benzoyloxy, resulted in a highly regioselective ring opening at the primary carbon center. While *tert*-butylethylene oxide reacted at the primary carbon, styrene oxide reacted at the secondary center. The stereochemical course of the reaction was demonstrated to be trans in the cases of cycloalkene oxides and *cis*- and *trans*-2-butene oxides. The regio- and stereoselective ring opening of allylic alcohol epoxide derivatives has been attained when their hydroxy group was converted into monochloroacetoxy group. Rare examples of incorporation of carbon monoxide into tertiary carbon centers were observed for the ring opening of geminal dialkyl-substituted oxiranes. The importance of $R_3SiCo(CO)_4$ (**3**) as a key catalyst species and the reaction mechanism have been discussed. An acylcobalt carbonyl intermediate generated by the stoichiometric reaction of $R_3SiCo(CO)_4$ (**3**) with *tert*-butylethylene oxide was intercepted by a 1,3-diene.

The new catalytic reaction system of $HSiR_3/CO/Co_2(CO)_8$ can bring about incorporation of carbon monoxide into olefins and various oxygen-containing compounds.[2] It has been shown that carbon monoxide is incorporated into the products in the form of formyl, siloxymethylidene (=$CHOSiR_3$), or other carbafunctional groups. For example, conversions of alkenes to siloxymethylidene alkanes,[2,3] aldehydes to higher $\alpha$-siloxy aldehydes,[2,4] alkyl acetates to siloxymethylidene alkanes,[5] and cyclobutanones to disiloxycyclopentenes[6] have been attained by the reaction of these substrates with $HSiR_3$ and CO in the presence of $Co_2(CO)_8$. These reactions proceed generally at 140 °C and 50 atm of carbon monoxide, and in some cases[1,5] at 200 °C and 50 atm.

In contrast to these results, we have found that a catalytic reaction of oxiranes with $HSiR_3/CO/Co_2(CO)_8$ takes place under surprisingly mild conditions, i.e., at 25 °C under 1 atm.[7] More interesting is the form of the carbafunctional group introduced. The incorporated carbon monoxide is converted to a siloxymethyl group in the product (eq 1) instead of previously observed formyl or siloxymethylidene group.




(1)

1 2

From the synthetic point of view, the present reaction can be regarded formally as a nucleophilic oxymethylation ($ROCH_2^-$). The reaction should provide a simple method for the construction of 1,3-diol units, an important building block in natural product

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(7) Preliminary results have been reported: Murai, T.; Kato, S.; Murai, S.; Toki, T.; Suzuki, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 6093.

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**Table I.** Reaction of Unsubstituted Cyclic Ethers with $HSiR_3/CO/Co_2(CO)_8$ (eq 3)

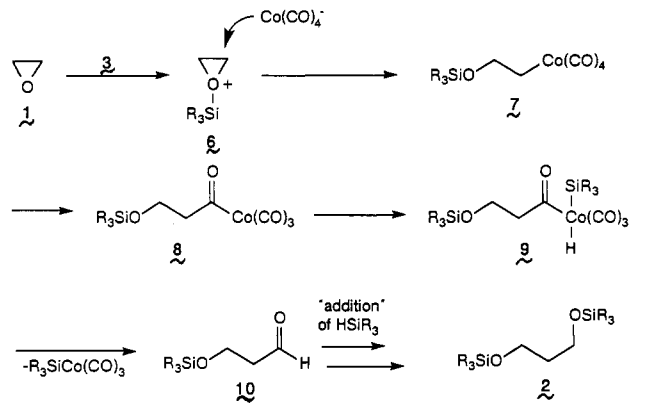
| cyclic ether | $R_3$ in $HSiR_3$ | conditions | yield of product (**5**), %[a] |
|---|---|---|---|
| **4a**, $n = 3$ | $Et_2Me$ | $n$-$C_6H_{14}$/25 °C/7 h | 96[b] |
| **4b**, $n = 4$ | $Et_3$ | $CH_2Cl_2$/25 °C/20 h | 81[c] |
| **4c**, $n = 5$ | $Et_2Me$ | $CH_3C_6H_5$/80 °C/3 days | 56 |
| **4d**, $n = 6$ | $Et_2Me$ | $CH_3C_6H_5$/80 °C/3 days | 14[d] |

[a] GLC yields. [b] $CH_3(CH_2)_2OSiR_3$ was a major byproduct under some reaction conditions (ref 14). [c] $R_3SiO(CH_2)_4$-$C(OSiR_3)$=$CHOSiR_3$ was a minor byproduct under a different run with $CH_2Cl_2/HSiEt_2Me$/25 °C/20 h. [d] $R_3SiO(CH_2)_5CH$=$CH(OSiR_3)$ was also formed in 29% yield.

synthesis.[8] In this context, various synthetic equivalents of $ROCH_2^-$ have been devised,[9] but only a few have been applied to the transformation equivalent to eq 1.[9i,j,n]

From the view point of homogeneous catalysis, the present reaction (1) represents a rare example of the incorporation of carbon monoxide under exceptionally mild conditions with cleavage of a carbon–oxygen bond in the starting material. Continuous efforts have been devoted to find the catalytic reaction of carbon monoxide at low pressures, and representative examples of a successful catalyst system involve metal species of rhodium[10] and palladium.[11] For cobalt, a phase-transfer system or a base system involving $Co(CO)_4^-$ as a chain carrier[12] has been found effective. Among these, only two systems, i.e., vinyl triflate/$Pd$[11u,x] and styrene oxide/$Co$,[12e,f] involve cleavage of the C–O bond in the starting material at room temperature under 1 atm of CO, to the best of our knowledge.

**Scheme I**




In this paper we present the results of our detailed studies on the scope and limitation of the catalytic reaction of cyclic ethers with $HSiR_3$ and CO in the presence of $Co_2(CO)_8$.[7]

## Results and Discussion

**Catalytic Reactions of Unsubstituted Oxirane and Other Cyclic Ethers and Possible Reaction Mechanisms.** Since the catalytic reaction proceeds at a room temperature under 1 atm of CO, the reaction requires no special equipment and is operationally simple. General experimental procedures are given below. To $Co_2(CO)_8$ (0.1 mmol) placed in a flask connected with a CO balloon was added $HSiEt_2Me$ (7.5 mmol). In several minutes, gas ($H_2$) evolution ceased, and a homogeneous pale brown solution resulted. This operation corresponds to the conversion of $Co_2(CO)_8$ to silylcobalt carbonyl (**3**, eq 2).[13] Then, an oxirane (2.5 mmol)

$$Co_2(CO)_8 + 2HSiR_3 \longrightarrow \underset{\underset{\sim}{3}}{2R_3SiCo(CO)_4} + H_2 \quad (2)$$

dissolved in a solvent (5 mL) was added. In the case of ethylene oxide (**1**), it was transferred by trap-to-trap distillation. After the reaction, simple nonaqueous workup made the isolation of the product very easy (see the Experimental Section).

Ethylene oxide (**1**) gives 1,3-disiloxypropane (**2**) in a very good yield when reacted with $HSiEt_2Me$ and CO (1 atm) in $CH_2Cl_2$ in the presence of a catalytic amount of $Co_2(CO)_8$ (eq 1). The results obtained for the catalytic reaction of oxetane,[14] tetrahydrofuran,[15] and those for six- and seven-membered cyclic ethers are given in the eq 3 and Table I. Fortunately among cyclic

$$\underset{\underset{\sim}{4a\text{-}d}}{\underset{n=3-6}{\text{cyclic ether}}} + HSiR_3 + CO \xrightarrow[Co_2(CO)_8]{} \underset{\underset{\sim}{5a\text{-}d}}{\underset{n=3-6}{R_3SiO\text{-}(CH_2)_{n+1}\text{-}OSiR_3}} \quad (3)$$

ethers, unsubstituted and substituted (vide infra) oxiranes that are synthetically most important react most cleanly. Oxetane (**4a**) experienced reduction to give $CH_3(CH_2)_2OSiR_3$[16] and tetrahydrofuran yielded a byproduct, unless proper reaction conditions were not employed (Table I). The reactions of **4c** and **4d** were somewhat sluggish.

The speculative mechanism is proposed in Scheme I. The reaction would begin with the attack of an unshared electron pair of oxirane oxygen onto the silicon atom of silylcobalt carbonyl

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(16) Recently, Kang and Weber reported that the use of a bulky silane ($HSiMe_2Bu$-*t*) in the reaction of oxetane resulted in the introduction of a siloxymethylidene group: see ref 17. We have reported the similar steric effect in the reaction of 2,5-dimethyltetrahydrofuran.[15a]

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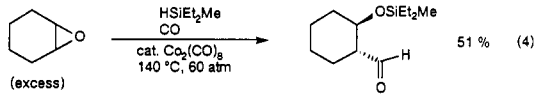
3, a key catalyst species generated initially by reaction 2 and regenerated at the final step of the catalytic reaction. The thus-formed silyloxonium ion **6** undergoes cleavage of the carbon–oxygen bond by the nucleophilic attack of $Co(CO)_4^-$ to give an alkylcobalt complex **7**. Migratory insertion of CO would follow to afford the acylcobalt complex **8**. This pathway from **1** to **8** seems to be quite reasonable. MacDiarmid has isolated silylammonium and silylphosphonium salts similar to **6** by the reaction of trimethylamine and trimethylphosphine with (trimethylsilyl)cobalt carbonyl.[18] Gladysz has reported the reaction of oxiranes with $Me_3SiMn(CO)_5$ under 250 psi of CO to give an acylmanganese pentacarbonyl similar to **8**.[19] An acylcobalt complex similar to **8** can be trapped with a diene (see below).

Oxidative addition of $HSiR_3$ to **8** would give **9**, which could then undergo reductive elimination to produce an aldehyde, **10**. Hydrosilylation of **10** by a well-known process would afford the final product **2**.

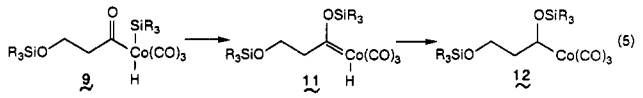
It should be emphasized that we have at present no conclusive evidence for or against the formation of an aldehyde intermediate such as **10**. The facts in favor of the aldehyde intermediacy include (i) isolation of aldehydes from cyclic ethers under different reaction conditions, i.e., using substrates (oxiranes) in excess and at 70–140 °C and 60 atm of CO (eq 4)[2,20] and (ii) recent finding by Wegman




51 % (4)

of the reaction of an acylcobalt phosphine complex with $HSiEt_3$ giving rise to an aldehyde through steps similar to those for **8** to **10**.[21] Curiously, however, aldehydes that are expected to be formed from oxiranes in the present reaction have not been detected even when a different aldehyde has been added into the reaction system.[22]

Instead of an aldehyde, carbene complex **11** could be an alternative intermediate as suggested previously.[2,5,7] The 1,3-migration of silicon in **9** and subsequent $\alpha$-insertion of the carbene ligand to the H-Co in **11** would convert **9** into **12** without intervention of the aldehyde **10** as an intermediate (eq 5). Recently,

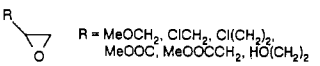



(5)

Gladysz demonstrated that such silicon migration did occur in the similar iron complex.[23] Marko et al. have suggested in their study on the stoichiometric reaction of isobutanoylcobalt tetracarbonyl with $HSiEt_3$ that an $\alpha$-siloxyalkyl complex corresponding to **12** would be a likely intermediate possibly formed via a carbene complex.[24]

As another alternative, catalyzed addition of $HSiR_3$ to the acyl carbonyl group of an acylcobalt (**8** but with additional CO) leading to $\alpha$-siloxyalkyl cobalt (**12** but with additional CO) could be envisaged.[25]

**Chart I**




Interestingly, the catalytic reaction did not take place when the reaction was carried out at 25 °C but under pressure of CO, i.e., 50 atm. This suggests a 16-electron complex such as **8** may be involved in the catalytic cycle.

In short, the finding of the present catalytic reactions has raised many interesting questions.

**Catalytic Reaction of Oxiranes: General Features.** We have carried out the reaction of various oxiranes with hydrosilanes and carbon monoxide in the presence of catalytic amounts of $Co_2(CO)_8$. The results are listed in Table II in the order of increasing number of substituents. For each run the reaction conditions have been semioptimized by changing the hydrosilane ($HSiMe_3$ to $HSiEt_3$), the solvent ($C_6H_6$, $CH_2Cl_2$, or $n$-$C_6H_{14}$), the reaction temperature, and the reaction time (monitored by GLC for the completion of the reaction), and these are given in the Experimental Section. Generally, the reaction was faster in the order $HSiMe_3$ > $HSiEtMe_2$ > $HSiEt_2Me$ > $HSiEt_3$ and in $CH_2Cl_2$ > in $C_6H_6$ > in $n$-$C_6H_{14}$. The fast reaction enabled us to use lower temperatures affording better selectivity. However, when a given oxirane was very reactive and the reaction was very fast, the reaction suffered from reduction such as that observed for **4a** leading to $CH_3(CH_2)_2OSiR_3$. The reduction became most significant for $HSiMe_3$, partly because it was the smallest silane used and partly because the concentration of $HSiMe_3$ was possibly the highest (see below).

For the reaction employing $HSiMe_3$, a large excess amount of $HSiMe_3$ over an oxirane (10:1 in molar ratio) was charged, and an efficient dry ice reflux condenser was used because of the low boiling point of this silane (bp 6.7 °C). The reaction went under gentle reflux of $HSiMe_3$, and therefore the exact concentration of $HSiMe_3$ in the solution was somewhat difficult to estimate. For handling of $HSiMe_3$ we have devised a special syringe described in the Experimental Section (Figure 1). This syringe should also be useful for storing and handling other low boiling materials. For other silanes a molar ratio of 3:1 to an oxirane was generally used (note that one oxirane molecular unit consumes 2 mol of $HSiR_3$). In one case (run 14 of Table II), the reaction with a 50-g scale is reported to proceed equally well without any problem.[26]

**Regio- and Stereoselectivity of the Ring Opening of Oxiranes.** First, the regioselectivity of the ring opening of monosubstituted oxiranes has been examined. Both electronic and steric factors of substituents have affected the regioselectivity significantly. Although the changes in solvents and reaction temperatures had only small effects on the regioselectivity, these factors affected the formation of byproducts such as that produced by reduction or by incorporation of two molecules of carbon monoxide.

Noteworthy is that the ring opening of oxiranes having an electron-withdrawing group, such as hydroxy, acetoxy, benzoyl, phenoxy, and allyloxy, occurred predominantly at the primary carbon centers (runs 6–12 and 26–28 of Table II). The oxiranes shown in Chart I also underwent essentially complete regioselective reaction (see a preliminary communication[7]). Styrene oxide exhibited an opposite selectivity due to the stabilization of a transition state (see below) with a partial positive charge on the internal carbon atom (run 5). Kang and Weber[27] reported the reaction of styrene oxide with $HSiEt_3/CO/Co_2(CO)_8$ system to give $\beta$-siloxystyrene without incorporation of CO. However, as shown (run 5, Table II), the use of $HSiMe_3$ and $n$-$C_6H_{14}$ as a solvent enabled incorporation of CO.

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(20) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, S. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 789.

(21) Wegman, R. W. *Organometallics* **1986**, *5*, 707. See, however, also footnote 5 of ref. 23.

(22) For example, when the catalytic reaction of cyclopentene oxide was carried out under the same reaction conditions as for run 14 of Table II but in the presence of an equimolar amount (to the oxirane) of 2,2-dimethylpropanal, the products were only the same one in run 14 (Table II) and $(CH_3)_3CH_2OSiEt_2Me$ (80%).

(23) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmit, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1326.

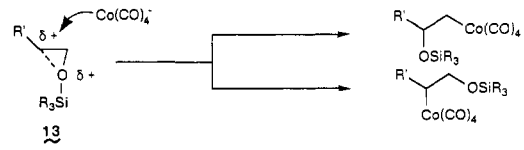
(24) The products obtained from the reaction of $(CH_3)_2CHCOCo(CO)_4$ with $HSiEt_3$ have been reported to involve $(CH_3)_2CHCHO$ in addition to $(CH_3)_2C{=}CHOSiEt_3$ and $(CH_3)CHCH_2OSiEt_3$. They suggested that the aldehyde $(CH_3)_2CHCHO$ would not give the latter two silyl ethers because the reaction of the aldehyde with $Et_3SiCo(CO)_4$ is slow. However, their results cannot be applied directly to the possibility of the aldehyde intermediate in our catalytic reaction where a hydrosilane is always present in excess and overall reaction is quite slow: Kovacs, I.; Sisak, A.; Ungvary, F.; Marko, L. *Organometallics* **1988**, *7*, 1025.

(25) **Note Added in Proof**: See a very recent paper: Akita, M.; Mitani, O.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 527.

(26) Rüedi, P.; Merckling, F. Private communication.

(27) Kang, K.-T.; Weber, W. P. *Tetrahedron Lett.* **1985**, *26*, 5414.

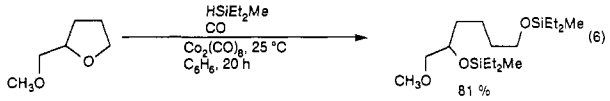
**Scheme II**



The oxirane having a bulky group reacted exclusively at the primary carbon center at 0 °C (run 4). Even under more forcing conditions, i.e., at 25 °C, the ring opening at the internal carbon was not observed, and instead a byproduct, $(CH_3)_3CCH(OSiR_3)CH_3$, arising from reduction at the terminal carbon was produced in addition to the desired product.

The regiodetermining step of the reaction would involve the attack of $Co(CO)_4^-$ on silyloxonium ion intermediate **13** as shown in Scheme II. The primary carbon–oxygen bond would be cleaved by an $S_N2$ mechanism, whereas the ring opening at a secondary center, where the partial positive charge would be developed in the transition state, would proceed by a borderline $S_N2$ mechanism (but with some positive charge on the reacting carbon atom).[28] The ability of the electron-withdrawing group to suppress the development of the partial positive charge on the secondary center would have resulted in the highly regioselective attack of $Co(CO)_4^-$ to the primary center.

A similar electronic effect can operate in the case of a five-membered cyclic ether. The complete regioselection at the carbon away from the methoxymethyl group paralleled the results of oxiranes (eq 6).



As shown in Table II, functional groups such as an ester group or chloride remain intact due to the mild reaction conditions of the present catalytic reaction.

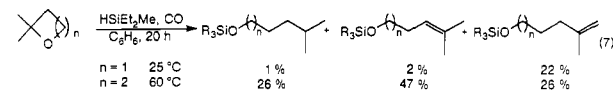
The carbon–carbon double bond was hydrosilylated obviously prior to the ring opening of oxirane (runs 11 and 12). This seems rather exceptional for $Co_2(CO)_8$-catalyzed hydrosilylation since the $Co_2(CO)_8$-catalyzed hydrosilylation of simple olefins did not proceed in the presence of an excess amount of $HSiR_3$.[29] Indeed, when the reaction of 1-hexene oxide was carried out similarly as in run 2 except in the presence of 1-hexene, the products obtained in run 2 were obtained with almost complete recovery of 1-hexene. The unusual hydrosilylation observed in runs 11 and 12 is under study.

The ring opening of the oxirane shown in run 13 gave a tetrahydrofuran derivative selectively. The intramolecular nucleophilic attack of the carbonyl oxygen to the silyloxonium ion followed by the hydride transfer from $HSiR_3$ or $HSiR_3Nu^-$[30] ($Nu^-$ stands for a nucleophile), a pentacoordinate silicon where $Nu^-$ may be $Co(CO)_4^-$ or any heteroatom present in the system, would give the product. This result shows that the reactivity of the oxirane to silylcobalt carbonyl **3** appears to be higher than that of the carbonyl group and that the $Co(CO)_4^-$ is a less powerful nucleophile than the intramolecular carbonyl oxygen. The higher reactivity of an oxirane ring than that of a tetrahydrofuran was indicated in run 18 which was in accordance with the results in Table I.

Secondarily, the stereochemical course of this catalytic reaction was shown in runs 14–17.[31] According to these results, the reaction would have proceeded with the inversion of the configuration at the carbon atom,[32] indicating back side attack of $Co(CO)_4^-$ to the silyloxonium ion like **6**.

Finally, the regio- and stereoselective ring opening of allylic alcohol epoxide derivatives has been studied because of the synthetic potential of these reactions reinforced by recent progress in the chiral synthesis of these epoxides.[34] In contrast to the case of the simple allylic alcohol epoxide (run 6), the regioselectivity of the ring opening of such an oxirane bearing an additional alkyl group (run 20) was as low as that of the dialkyl-substituted oxirane (run 19). To improve the regioselectivity, the hydroxy group of crotyl alcohol epoxide was modified by electron-withdrawing groups. The oxirane in which the hydroxy group was protected with an acetyl group (run 21) was ring-opened at the carbon atom having methyl group predominantly.[35] The protection of the hydroxy group with a *monochloroacetyl group* dramatically enhanced the selectivity. Namely, the ring opening proceeded highly regio- and stereoselectively to give a *threo*-2-hydroxy-3-methyl-1,4-butanediol derivative in 67% yield as a major product (run 22). The effect of the monochloroacetyl group was further demonstrated with a homoallylic alcohol epoxide (run 23) and a cyclic allylic alcohol epoxide (run 24). The product in run 24 has the three successive carbons stereochemically defined.

Additionally, incorporation of carbon monoxide at a tertiary carbon center, which is extremely rare,[36] was observed for geminally dialkyl-substituted oxiranes. Although the yield and the selectivity were still low, the formation of the quarternary carbon center[37] was attained via CO incorporation (runs 25, 26, 29, and 30). Even in these cases, the electron-withdrawing group dramatically changed the regiochemical course of the ring opening (runs 27 and 28). Interestingly, similar reactions using 2,2-dimethyltetrahydrofuran and 2,2-dimethyloxetane gave only the products without incorporation of carbon monoxide, although the ring opening took place only at the tertiary carbon centers (eq 7). The acyl complex formed from the oxirane might be stabilized



by the intramolecular coordination of oxygen to cobalt to form five-membered ring **14**. This would be the reason why the CO incorporated products into tertiary centers was obtained only from the oxirane.

**Stoichiometric Reaction of $R_3SiCo(CO)_4$.** For the better understanding of the reaction pathway, the stoichiometric reaction of silylcobalt carbonyl with an oxirane has been examined. To simplify the product selectivity, *tert*-butylethylene oxide was chosen as the substrate. Acylcobalt complexes can be trapped by dienes at or even below room temperature.[38] We attempted the interception of an acylcobalt intermediate obtainable from oxirane

(28) (a) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737. (b) Beherns, C. H.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67.

(29) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 1133.

(30) (a) Nagai, Y. *Org. Prep. Proc. Int.* **1980**, *12*, 13. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983; p 277. (c) Kato, J.; Iwasawa, N.; Mukaiyama, T. *Chem. Lett.* **1985**, 743.

(31) It should be added that cycloheptene oxide cannot be employed as a substrate. Numerous attempts to achieve the same transformation resulted in the formation of complex mixture. The rather good result was obtained by the reaction of cycloheptene oxide with $HSiMe_3$ and CO in toluene at 0 °C under 1 atm of CO to give 53% of the corresponding 1,3-diol disilyl ether along with 26% yield of cyclohexanemethanol silyl ether and 10% yield of (cycloheptylidenemethoxy)trimethylsilane.

(32) This mechanism is derived because the subsequent insertion of carbon monoxide has been known to proceed with retention of configuration.[33]

(33) Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

(34) (a) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. (b) Sharpless, K. B.; Beherns, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodward, S. S. *Pure. Appl. Chem.* **1983**, *55*, 583. (c) Pfenninger, A. *Synthesis* **1986**, 89.

(35) The benzoyl and methoxycarbonyl groups were also employed as the protective group to result in regioselectivity similar to that of acetyl group.

(36) Catalytic reactions: (a) Pittmann, Jr., C. U.; Honnick, W. D.; Yang, J. J. *J. Org. Chem.* **1980**, *45*, 684. (b) Tanaka, M.; Hayashi, T.; Ogata, I. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2351. (c) Pruett, R. L.; Smith, J. A. *J. Org. Chem.* **1969**, *34*, 327; see also ref 5b. Stoichiometric reactions: Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 4023.

(37) Martin, S. F. *Tetrahedron* **1980**, *36*, 419.

(38) (a) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3381. (b) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

**Table II.** Reaction of Substituted Oxiranes with $HSiR'_3/CO/Co_2(CO)_8$[a]

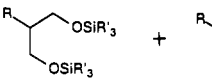
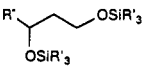
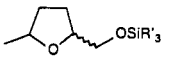
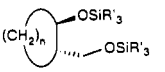
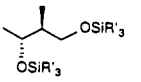
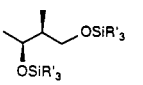
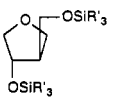
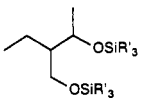
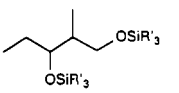
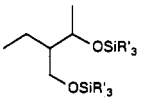
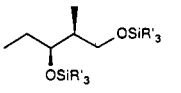
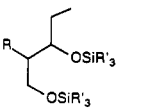
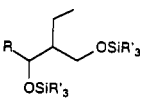
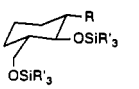
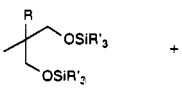
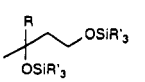
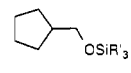
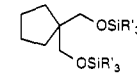
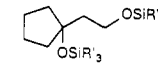
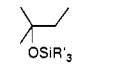
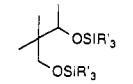
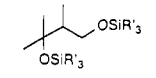
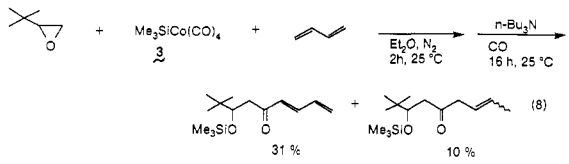
| run | oxirane and its R | $R'_3$ in $HSiR'_3$ | products[b] yield, %[c] | | |
|---|---|---|---|---|---|
| |  | |  | | |
| | R = | | | | |
| 1 | Me | $Et_2Me$ | 25 | | 75 |
| 2 | n-Bu | $Et_2Me$ | 36 | | 63 |
| 3 | sec-Bu | $Me_3$ | 21 | | 60 |
| 4 | t-Bu | $Me_3$ | 0 | | 73 |
| 5 | Ph | $Me_3$ | 60[d] | | 0 |
| 6 | $HOCH_2$ | $Me_3$ | 0 | | 92[e] |
| 7 | $MeCO_2CH_2$ | $Me_3$ | 9 | | 76 |
| 8 | $PhCO_2CH_2$ | $Me_3$ | 11 | | 87 |
| 9 | $PhOCH_2$ | $Et_2Me$ | 3 | | 63 |
| 10 | $HOCMe_2$ | $Me_3$ | 0 | | 76[f] |
| | | |  | |  |
| 11 | $CH_2{=}CHCH_2OCH_2$ | $Et_2Me$ | 66[g] | | 16[g] |
| 12 | $CH_2{=}CHCH_2OCH_2$ | $Me_3$ | 0 | | 84[g,h] |
| | | |  | | |
| 13 | $CH_3CO(CH_2)_2$ | $Et_2Me$ | 82[i] | | |
| |  | |  | | |
| 14 | $n = 3$ | $Et_2Me$ | 88 | | |
| 15 | $n = 4$ | $Et_2Me$ | 65 | | |
| 16 |  | $Et_2Me$ |  | | |
| | | | 60 | | |
| 17 |  | $Et_2Me$ |  | | |
| | | | 73 | | |
| 18 |  | $Et_2Me$ |  | | |
| | | | 100[j] | | |
| 19 |  | $Me_3$ |  | |  |
| | | | 32[j] | | 40[j] |
| |  | |  | |  |
| | R = | | | | |
| 20 | $HOCH_2$ | $Me_3$ | 34[e,j] | | 56 |
| 21 | $MeCO_2CH_2$ | $Me_3$ | 17[j] | | 62 |
| 22 | $ClCH_2CO_2CH_2$ | $Me_3$ | 3[j] | | 67 |
| 23 |  | $Me_3$ |  | |  |
| | $R = ClCH_2CO_2(CH_2)_2$ | | 7[l] | | 60[l] |
| 24 |  | $Me_3$ |  | | |
| | $R = ClCH_2CO_2$ | | 56 | | |
| |  | |  |  |  |
| | R = | | | | |
| 25 | Me | $Et_2Me$ | 30 | 10 | 10[k] |
| 26 | $HOCH_2$ | $Et_2Me$ | 0 | 20[e] | 61[e] |
| 27 | $ClCH_2$ | $Me_3$ | 0 | 0 | 56 |
| 28 | MeOOC | $Et_2Me$ | 0 | 0 | 89 |

**Table II** (Continued)

| run | oxirane and its R | $R'_3$ in $HSiR'_3$ | products[b] yield, %[c] | | |
|---|---|---|---|---|---|
| 29 |  | $Me_3$ |  68 |  17 |  9 |
| 30 |  | $Me_3$ |  58 |  21 |  2 |

[a] The reaction conditions are in the Experimental Section. [b] $R'_3Si$ stands for $Et_2MeSi$ or $Me_3Si$. [c] GLC yields. [d] $PhC(CH_2OSiR'_3)=CHOSiR'_3$ was also formed in 10% yield. [e] $R = R'_3SiOCH_2$. [f] $R = R'_3SiOCMe_2$. [g] $R'' = R'_3Si(CH_2)_3OCH_2$. [h] The regioisomer was also formed in 9% yield. [i] The cis/trans ratio (3.6/1) was determined by GLC analysis: see the Experimental Section. [j] The stereochemistry was not determined. [k] $Me_2CH(CH_2)_2OSiR'_3$ (7%) and $R'_3SiOCH_2Me_2CC(OSiR'_3)=CH(OSiR'_3)$ (10%) were also obtained.

(Scheme I) with a diene.[39] The reaction of *tert*-butyl ethylene oxide with a slightly excess amount (1.6 equiv) of silylcobalt carbonyl **3** in the presence of butadiene (16 equiv) followed by treatment with an amine resulted in the trapping of the acyl moiety by the diene, as shown in eq 8. Although reaction conditions had



(8)

not been optimized yet, the products arising from acyl group transfer were isolated in a combined yield of 41%. This result may open a synthetically useful new entry to acylcobalt carbonyl complexes under mild reaction conditions.

## Summary

The new catalytic reaction system of $HSiR_3/CO/Co_2(CO)_8$ enabled the incorporation of carbon monoxide into cyclic ethers at room temperature under 1 atm of CO (Table I). Oxiranes, the preparative methods of which are widely developed, could be converted into 1,3-diol derivatives, which are important synthetic units (Table II). Carbon monoxide was selectively transformed into the form of an oxymethyl group in the final product. Functional groups such as hydroxy, acetoxy, benzoyloxy, phenoxy, and chloro could not only tolerate the reaction conditions but also control the regioselectivity of the ring opening. Highly regio- and stereoselective ring opening of allylic alcohol epoxide derivatives could be achieved by protecting the hydroxy group with a monochloroacetyl group. Mechanistically, the intermediacy of acylcobalt carbonyl was demonstrated by the stoichiometric reaction. Further applications of this catalytic system will be reported in the near future.

## Experimental Section

Infrared spectra were recorded with a Shimazu IR-400 or JASCO grating IR spectrophotometer IR-G; absorptions are reported in reciprocal centimeters. The $^1H$ NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer or JEOL JNM 270 FT-NMR spectrometer operating at 100 and 270 MHz, respectively, in $CCl_4$ or $CDCl_3$ with $Me_4Si$ or $CHCl_3$ as an 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 (hertz), integration, and interpretation. $^{13}C$ NMR spectra were recorded on a JEOL JNM-FX-60s spectrometer and were reported in ppm from tetramethylsilane on the $\delta$ scale. The structural assignments of some products were supported by irradiation experiments. Mass spectra were recorded on a Hitachi Model RMU-6E instrument operating at 70 eV. Elemental analyses were performed by Analysis Center at Osaka University. Analytical gas chromatographies (GLC) were 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 on 60–80 mesh Chromosorb W (AW). Preparative GLC was carried out by using a Hitachi Model K 53 gas chromatograph using 2 m × 10 mm stainless steel column packed with 5% silicon OV-1 supported on 60–80 mesh Chromosorb W.

Benzene, toluene, and *n*-hexane were distilled from sodium–lead alloy. Dichloromethane was distilled from $CaH_2$. Carbon monoxide was purchased from 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. 1-Oxiranyl-3-butanone, 3,6-dioxabicyclo[3.1.0]hexane, 1,1-dimethyloxiranemethanol, and 2-methyloxiranemethanol were prepared by the oxidation of the corresponding olefins using *m*-chloroperoxybenzoic acid. Oxirane (ethylene oxide), butyloxirane, (2-methylpropyl)oxirane, and (1,1-dimethylethyl)oxirane were prepared by the cyclization of the corresponding bromohydrins. 1-Oxaspiro[2.4]heptane was prepared according to Corey's procedure.[40] The other cyclic esters were purchased from the Nacalai Tesque Co., Wako Pure Chemical Indistries Ltd., or Tokyo Chemical Industry Co. and distilled before use. The oxiranyl ethers were prepared by the reaction of the parent oxiranemethanol with an appropriate acid chloride in the presence of pyridine in ether at 0 °C for 1 h, the reaction time being critical to obtain good results. These oxiranes were purified by distillation. Boiling points were for the oxirane in run 21 65–67 °C/18 mmHg, that in run 22 122–126 °C/30 mmHg, that in run 23 138–141 °C/15 mmHg, that in run 24 141–145 °C/15 mmHg, for benzoyl[34] 155–157 °C/20 mmHg, and for methoxycarbonyl[34] 74–76 °C/20 mmHg.

Hydrosilanes were prepared from chlorosilanes following literature procedures.[41] We have designed a special apparatus shown in Figure 1 for handling $HSiMe_3$, which has low boiling point (bp 6.7 °C). This apparatus may be conveniently used for any other low boiling substance that has a vapor pressure below 20 atm at a room temperature. It is assembled with a stainless steel reservoir A in sizes from 50 to 200 mL, needle valve B, a thick-wall calibrated glass barrel of 10 mm × 150 mm C, another needle bulb having a needle locking tip (Luer-Lok) D, and Luer-Lok syringe needle E. The $HSiMe_3$ is transferred into A through B and an appropriate connector by trap-to-trap distillation for stock. (Do not fill container A more than 80% by trap-to-trap distillation for safety.) Then C, D, and E are connected to A while B is closed. Holding the apparatus with E upward, the needle valves D and B are opened in this order for a while until the glass tube C is filled with the vapor of $HSiMe_3$. After D is closed, the whole apparatus is held upside down, so that $HSiMe_3$ is transferred into C as a liquid. Slight cooling of C was sometimes helpful. When the desired amount of $HSiMe_3$ is collected in C, the valve B is closed. The needle E is then inserted through the septum of the reaction vessel, and the liquid $HSiMe_3$ can be injected by opening the bulb D just as when a normal syringe technique is used. It may be convenient for the next use not to disconnect the whole apparatus A–E.

**General Procedure for Cobalt Carbonyl Catalyzed Reaction of Cyclic Ethers with a Hydrosilane and Carbon Monoxide.** A 10-mL two-necked round-bottom flask equipped with a Teflon-coated magnetic stirrer bar was flame dried and then charged with 0.0342 g (0.1 mmol) of $Co_2(CO)_8$, fitted with a septum rubber and CO balloon, and flashed with carbon monoxide. $HSiEt_2Me$ (1.1 mL, 7.5 mmol) was added to the flask with a syringe. After 5 min, 5 mL of solvent and 2.5 mmol of cyclic ether were added to the flask with a syringe. The solution was stirred for an appropriate period, a few drops of pyridine were added, and air was bubbled

(39) Very recently, Deshong et al. have reported the insertion reaction of alkenes to $\beta$-siloxyacylmanganese complex derived from the oxirane and silylmanganese complex: Deshong, P.; Sidler, D. R. *J. Org. Chem.* **1988**, *53*, 4894.

(40) Corey, E. J.; Chaykovsky, M. *Org. Synth. V* **1973**, 755.
(41) Steward, O. W.; Pierce, O. R. *J. Am. Chem. Soc.* **1961**, *83*, 1916.

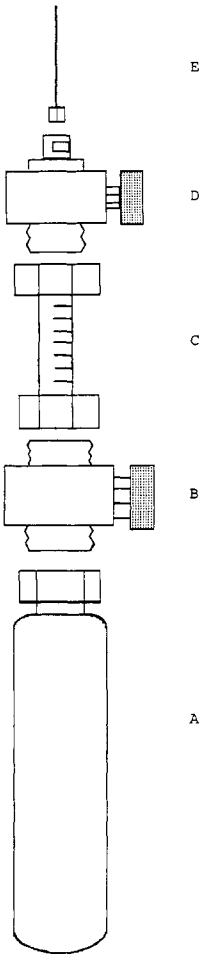



Figure 1.

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 ($n$-$C_nH_{2n+2}$) calibrated against purified products were added before or immediately after the reaction. For the reaction using $HSiMe_3$, 2.83 mL (25 mmol) of $HSiMe_3$ was injected to the reaction vessel equipped with an efficient dry ice acetone condenser for reflux of $HSiMe_3$.

**Spectroscopic Properties of the Products in Table I. 3,12-Diethyl-3,12-dimethyl-4,11-dioxa-3,12-disilatetradecane obtained from 4c**: bp 180 °C (oven)/5 mmHg; IR (neat) 2950, 2910, 2870, 1453, 1230, 1120, 1090, 1055, 1000, 960, 942, 815, 792, 750, 673 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.03 (s, 6 H, $SiCH_3$), 0.58 (q, 8 H, $J$ = 7.8 Hz, $SiCH_2$), 0.96 (t, 12 H, $J$ = 7.8 Hz, $SiCCH_3$), 1.31 (m, 4 H, $CH_2C$), 1.51 (m, 4 H, $CH_2$), 3.56 (t, 4 H, $J$ = 7.1 Hz, $CH_2O$); mass $m/e$ 289 ($M^+$ - Et, 11), 189 (53), 177 (16), 161 (30), 133 (10), 101 (12), 83 (100), 73 (23). Anal. Calcd for $C_{16}H_{38}O_2Si_2$: C, 60.31; H, 12.02. Found: C, 60.29; H, 12.35.

**3,13-Diethyl-3,13-dimethyl-4,12-dioxa-3,13-disilapentadecane obtained from 4d**: bp 180 °C (oven)/5 mmHg; IR (neat) 2950, 2948, 1453, 1406, 1382, 1248, 1230, 1110, 1095, 1000, 958, 940, 815, 795, 790, 750, 673 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.05 (s, 3 H, $SiCH_3$), 0.09 (s, 3 H, $SiCH_3$), 0.58 (q, 4 H, $J$ = 7.3 Hz, $SiCH_2$), 0.59 (q, 4 H, $J$ = 7.3 Hz, $SiCH_2$), 0.95 (t, 6 H, $J$ = 7.3 Hz, $SiCCH_3$), 0.97 (t, 6 H, $J$ = 7.3 Hz, $SiCCH_3$), 1.42 (m, 10 H, $CH_2$), 3.57 (t, 4 H, $J$ = 6.6 Hz, $CH_2OSi$); mass $m/e$ 303 ($M^+$ - Et), 273 (7), 189 (75), 177 (24), 161 (45), 97 (100), 83 (47), 73 (36). Anal. Calcd for $C_{17}H_{40}O_2Si_2$: C, 61.38; H, 12.12. Found: C, 61.72; H, 12.48.

**3,13-Diethyl-3,13-dimethyl-4,12-dioxa-3,13-disila-5-pentadecene obtained from 4d**: bp 180 °C (oven)/5 mmHg; $^1H$ NMR $\delta$ 0.05 (s, 3 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$), 0.61 (q, 8 H, $J$ = 7.5 and 8.1 Hz, $SiCH_2$), 0.95 (t, 6 H, $J$ = 7.5 Hz, $SiCCH_3$), 0.98 (t, 6 H, $J$ = 8.1 Hz, $SiCCH_3$), 1.43 (m, 6 H, $CH_2$), 2.17 (m, 2 H, $CH_2$), 3.58 (t, 2 H, $J$ = 7.1 Hz, $CH_2OSi$), 4.44–4.95 (m, 1 H, CH=C—OSi), 6.16 (td, 1 H, $J$ = 1.5 and 6.0 Hz, C=CH—OSi); mass $m/e$ 301 ($M^+$ - Et, 11), 212 (15), 189 (70), 161 (52), 133 (20), 101 (65), 89 (72), 73 (74), 54 (100).

**Spectroscopic Data of the Products in Table II (with the Reaction Conditions Employed). Mixture of 3,9-Diethyl-3,6,9-trimethyl-4,8-dioxa-3,9-disilaundecane** (25:75, run 1, $HSiEt_2Me$, $C_6H_6$, 25 °C, 20 h): bp 87 °C/25 mmHg; IR (neat) 3060, 3030, 2880, 1470, 1410, 1395, 1220, 1100, 1050, 1030, 995, 800 $cm^{-1}$; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.00 (s, 6 H, $SiCH_3$), 0.56 (m, 8 H, $SiCH_2$), 0.96 (m, 15 H, $SiCCH_3$ and $CH_3$), 1.54 (m, 1.75 H, CH and $CH_2$), 3.56 (c, 2.5 H, $CH_2O$), 3.96 (m, $J$ = 6 Hz, 0.75 H, CHO); mass $m/e$ 275 ($M^+$ - $CH_3$, 1), 261 (31), 233 (16), 191 (28), 189 (100), 161 (54), 133 (19), 101 (23), 89 (11). Anal. Calcd for $C_{14}H_{34}O_2Si_2$: C, 57.85; H, 11.81. Found: C, 57.67; H, 12.23.

**Mixture of 6-butyl-3,9-diethyl-3,9-dimethyl-4,8-dioxa-3,9-disilaundecane and 5-butyl-3,9-diethyl-3,9-dimethyl-4,8-dioxa-3,9-disilaundecane** (33:66, run 2, $HSiEt_2Me$, $C_6H_6$, 25 °C, 20 h): bp 100 °C (oven)/1 mmHg; IR (neat) 2950, 2910, 2880, 1460, 1420, 1380, 1270, 1090 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.04 (s, 6 H, $SiCH_3$), 0.55–0.59 (m, 8 H, $SiCH_2$), 0.89–0.94 (m, 12 H, $SiCCH_3$), 1.27 (m, 7.38 H, $CH_3$ and $CH_2$), 1.65 (m, 0.31 H, CH), 3.53 (dd, $J$ = 1.9 and 5.6 Hz, 1.24 H, $CH_2O$), 3.65 (t, $J$ = 7.0 Hz, 1.38 H, $CH_2O$), 3.72–3.89 (m, 0.69 H, CHO); mass $m/e$ 303 ($M^+$ - Et, 20), 275 (29), 189 (100), 161 (69), 101 (37). Anal. Calcd for $C_{17}H_{40}O_2Si_2$: C, 61.38; H, 12.12. Found: C, 61.20; H, 12.26.

**Mixture of 5-(2-methylpropyl)-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane and 4-(2-methylpropyl)-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane** (25:75, run 3, $HSiMe_3$, $CH_2Cl_2$, 25 °C, 48 h): bp 130 °C (oven)/20 mmHg; IR (neat) 2950, 2900, 1460, 1380, 1360, 1245, 1080, 875, 830, 740 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.05 (s, 18 H, $SiCH_3$), 0.88 (m, 6 H, $CH_3$), 1.2–1.7 (c, 4.74 H, $CH_2$ and CH), 3.50 (d, $J$ = 6.9 Hz, 2.96 H, $CH_2$), 3.65 (t, $J$ = 6.88 Hz, 0.51 H, $CH_2$), 3.8–3.9 (m, 0.75 H, CH); mass $m/e$ 231 ($M^+$ - Me, 3), 159 (11) 147 (16), 103 (24), 97 (18), 75 (100). Anal. Calcd for $C_{13}H_{32}O_2Si_2$: C, 56.46; H, 11.66. Found: C, 56.26; H, 11.82.

**4-(1,1-Dimethylethyl)-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane** (run 4, $HSiMe_3$, $CH_3C_6H_5$, 0 °C, 10 h): bp 150 °C (oven)/2 mmHg; IR (neat) 2990, 1490, 1400, 1370, 1250, 1100, 1030, 880, 840, 750 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.02 (s, 18 H, $SiCH_3$), 0.74 (s, 9 H, $CH_3$), 1.4 (m, 2 H, $CH_2$), 3.38 (m, 1 H, CHO), 3.60 (c, 2 H, $CH_2O$); $^{13}C$ NMR ($CDCl_3$) $\delta$ $SiMe_3$ (0.0324, 0.811), 26.314, 35.288, 35.532, 60.750, 77.682; mass $m/e$ 261 ($M^+$ - $CH_3$, 5), 233 (8), 219 (83), 158 (18), 147 (21), 103 (100). Anal. Calcd for $C_{13}H_{32}O_2Si_2$: C, 56.46; H, 11.66. Found: C, 56.31; H, 11.77.

**5-Phenyl-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane** (run 5, $HSiMe_3$, $n$-$C_6H_{14}$, 25 °C, 20 h); bp 160 °C (oven)/2 mmHg; IR (neat) 3075, 3000, 2980, 1500, 1455, 1250, 1100, 870, 840, 750, 700 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.00 (s, 18 H, $SiCH_3$), 2.85 (quintet, $J$ = 6.2 Hz, 1 H, CH), 3.75 (dd, $J$ = 10.3 Hz and 5.68 Hz, 2 H, $CH_2O$), 3.83 (dd, $J$ = 10.3 and 5.68 Hz, 2 H, $CH_2O$), 7.26 (c, 5 H, Ph); mass $m/e$ 206 (40, $M^+$ - $Me_6$), 181 (25), 179 (20), 147 (65), 103 (100). Anal. Calcd for $C_{15}H_{28}O_2Si_2$: C, 60.75; H, 9.52. Found: C, 60.64;, H, 9.68.

**5-Phenyl-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanon-4-ene** (run 5): bp 160 °C(oven)/2 mmHg; IR (neat) 2890, 2800, 1635, 1445, 1295, 1247, 1170, 1060, 1040, 965, 860, 830, 750, 695 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.09 (s, 9 H, $SiCH_3$), 0.22 (s, 9 H, $SiCH_3$), 4.60 (s, 2 H, $CH_2$), 6.64 (s, 1 H, CH), 7.14–7.42 (c, 5 H, Ph); mass $m/e$ 294 ($M^+$, 25), 147 (63), 104 (25), 73 (100).

**Mixture of acetic acid 2-(3,3-dimethyl-2-oxa-3-silabutyl)-5,5-dimethyl-4-oxa-5-silahexyl ester and acetic acid 2-(2,2-dimethyl-1-oxa-2-silapropyl)-6,6-dimethyl-5-oxa-6-silaheptyl ester** (12:88, run 7, $HSiMe_3$, $CH_3C_6H_5$, 0 °C, 20 h): bp 135 °C (oven)/8 mmHg; IR (neat) 2950, 2900, 2870, 1750, 1425, 1370, 1240, 1090, 840, 750 $cm^{-1}$; $^1H$ NMR ($CCl_4$ + Eu(thd)$_3$) $\delta$ 0.016 (s, 9 H, $SiCH_3$), 0.036 (s, 9 H, $SiCH_3$), 1.90 (m, 1.88 H, CH and $CH_2$), 3.30 (s, 2.64 H, $CH_3C$=O), 3.42 (s, 0.36 H, $CH_3C$=O), 3.80 (t, $J$ = 6.38 Hz, 1.76 H, $CH_2O$), 3.98 (d, $J$ = 4.25 Hz, 0.48 H, $CH_2O$), 4.60 (m, 0.88 H, CHO), 6.44 (dd, $J$ = 12.77 and 5.53 Hz, 0.24 H, $CH_2O$); mass $m/e$ 277 ($M^+$ - Me, 6), 219 (4), 189 (11), 175 (10), 117 (43), 103 (91), 73 (100).

**Mixture of benzoic acid 2-(3,3-dimethyl-2-oxa-3-silabutyl)-5,5-dimethyl-4-oxa-5-silahexyl ester and benzoic acid 2-(2,2-dimethyl-1-oxa-2-silapropyl)-6,6-dimethyl-5-oxa-6-silaheptyl ester** (11:89, run 8, $HSiMe_3$, $CH_2Cl_2$, 25 °C, 20 h): 160 °C (oven)/6 mmHg; IR (neat) 2950, 2900, 2875, 1730, 1605, 1460, 1260, 1100, 850, 750, 710 $cm^{-1}$; $^1H$ NMR ($CCl_4$ + Eu(thd)$_3$) $\delta$ 0.12 (s, 9 H, $SiCH_3$), 0.28 (s, 9 H, $SiCH_3$), 1.89 (c, 1.89 H, CH and $CH_2$), 3.77 (t, $J$ = 6.38 Hz, 1.78 H, $CH_2O$), 4.00 (d, $J$ = 8.51 Hz, 0.44 H, $CH_2O$), 4.62 (m, 0.89 H, CHO), 5.56 (d, $J$ = 5.96 Hz, 1.78 H, $CH_2O$), 5.86 (d, $J$ = 6.38 Hz, 0.22 H, $CH_2O$); mass $m/e$ 339 ($M^+$ - Me, 9), 219 (57), 179 (34), 105 (100), 103 (97), 73 (74). Anal. Calcd for $C_{17}H_{30}O_4Si_2$: C, 57.38; H, 8.53. Found: C, 57.25; H, 8.46.

**Mixture of 3,9-diethyl-3,9-dimethyl-6-(2-phenyl-2-oxaethyl)-4,8-dioxa-3,9-disilaundecane and 3,9-diethyl-3,9-dimethyl-5-(2-phenyl-1-oxaethyl)-dioxa-3,9-disilaundecane** (5:95, run 9, $HSiEt_2Me$, $C_6H_6$, 40 °C, 20 h): bp 150 °C/2 mmHg; IR (neat) 2950, 2900, 2880, 1601, 1500, 1460, 1250, 1100, 800 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.00 (s, 3 H, $SiCH_3$), 0.03 (s, 3 H, $SiCH_3$), 0.50–0.60 (m, 8 H, $SiCH_2$), 0.87–0.93 (m,

12 H, $SiCCH_3$), 1.73 (m, 2 H, CH and $CH_2$), 3.68 (t, $J$ = 6.2 Hz, 2.1 H, $CH_2OSi$), 3.81 (d, $J$ = 5.1 Hz, 1.9 H, $CH_2OPh$), 3.93 (d, $J$ = 6.3 Hz, 0.1 H, $CH_2OPh$), 4.14 (m, 0.95 H, CHOSi); mass $m/e$ 353 ($M^+$ – Et, 73), 275 (20), 235 (30), 103 (100). Anal. Calcd for $C_{17}H_{30}O_4Si_4$: C, 57.38; H, 8.53. Found: C, 57.25; H, 8.46.

**5-(2,2-Dimethyl-1-oxa-2-silapropyl)-2,2,4,4,9,9-hexamethyl-3,8-dioxa-2,9-disiladecane** (run 10, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 48 h): bp 150 °C (oven)/2 mmHg; IR (neat) 3000, 1475, 1445, 1385, 1365, 1250, 1180, 1160, 1105, 1030, 945, 875, 830, 755, 685 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.01 (s, 27 H, $SiCH_3$), 1.12 (s, 3 H, $CH_3$), 1.19 (s, 3 H, $CH_3$), 1.5 (m, 1 H, $CH_2$), 1.9 (m, 1 H, $CH_2$), 3.51 (dd, $J$ = 4.0 and 9.4 Hz, CHO), 3.65 (c, 2 H, $CH_2O$); mass $m/e$ 335 ($M^+$ – Me, 0.3), 245 (3), 171 (2), 147 (9), 131 (100), 103 (7), 73 (33). Anal. Calcd for $C_{15}H_{38}O_3Si_3$: C, 51.37; H, 10.92. Found: C, 51.30; H, 11.14.

**3-Ethyl-3-methyl-7-oxa-8-oxiranyl-3-silaoctane** (run 11, $HSiEt_2Me$, $CH_2Cl_2$, 25 °C, 20 h): IR (neat) 2975, 2950, 1470, 1425, 1350, 1260, 1110, 1015, 910, 840, 790, 755 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ –0.08 (s, 3 H, $SiCH_3$), 0.46 (m, 4 H, $SiCH_2$), 0.91 (t, $J$ = 7.7 Hz, 6 H, $SiCCH_3$), 1.55 (m, 2 H, $CH_2$), 2.60 (dd, $J$ = 2.56 and 5.13 Hz, 1 H, $CH_2O$), 2.79 (t, $J$ = 5.12 Hz, 1 H, $CH_2O$), 3.13 (m, 1 H, CHO), 3.45 (m, 2 H, $CH_2O$), 3.70 (dd, $J$ = 2.93 and 11.5 Hz, 2 H, $CH_2O$); mass $m/e$ ($M^+$ – Et, 3), 157 (18), 115 (100), 101 (25), 87 (36), 73 (30).

**Mixture of 5-(3,3-dimethyl-2-oxa-3-silabutyl)-2,2,11,11-tetramethyl-3,7-dioxa-2,11-disiladodecane and 6-(2,2-dimethyl-1-oxa-2-silapropyl)-2,2,12,12-tetramethyl-3,8-dioxa-2,12-disilatridecane** (run 12, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 48 h): bp 170 °C (oven)/2 mmHg; IR (neat) 3000, 2800, 1455, 1425, 1385, 1250, 1110, 1045, 835, 760, 695 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ –0.03 (s, 9 H, $SiCH_3$), 0.09 (s, 18 H, $SiCH_3$), 0.50 (m, 2 H, $SiCH_2$), 1.45–1.80 (c, 4 H, $CH_2$), 3.32 (d, 2 H, $J$ = 5.80 Hz, $CH_2O$), 3.35 (t, 2 H, $J$ = 6.94 Hz, $CH_2O$), 3.60 (d, $J$ = 6.2 Hz, 0.4 H, $CH_2O$), 3.65 (dd, $J$ = 6.9 and 5.8 Hz, 1.8 H, $CH_2OSi$), 3.95 (m, 0.9 H, CHOSi); mass $m/e$ 349 ($M^+$ – Me, 6), 274 (21), 233 (13), 219 (100), 189 (13), 147 (100), 129 (50), 103 (78), 73 (100). Anal. Calcd for $C_{16}H_{40}O_3Si_3$: C, 52.69; H, 11.05. Found: C, 52.37; H, 11.06.

**Tetrahydro-2-((diethylmethylsiloxy)methyl)-5-methylfuran** (run 13, $HSiEt_2Me$, $CH_2Cl_2$, 25 °C, 48 h): bp 91 °C (oven)/17 mmHg; IR (neat) 2950, 2875, 1465, 1420, 1390, 1255, 1150, 1010, 820, 800, 760 $cm^{-1}$; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.04 (s, 3 H, $SiCH_3$), 0.58 (q, 4 H, $SiCH_2$), 0.91 (t, 6 H, $SiCCH_3$), 1.15 (d, $J$ = 6 Hz, 3 H, $CH_3$), 1.22–2.02 (m, 4 H, $CH_2$), 3.43 (dd, $J$ = 6 and 10 Hz, 1 H, CHO), 3.49 (dd, $J$ = 4.5 and 10 Hz, 1 H, CHO), 3.82 (m, 2 H, $CH_2O$); mass $m/e$ 201 ($M^+$, 6), 186 (100), 131 (59), 85 (100). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.06; H, 11.18. Found: C, 60.71; H, 11.31.

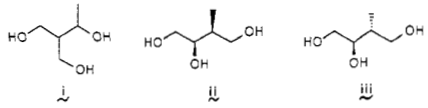
This sample was shown to contain cis and trans isomers in a ratio of 3.6:1 by GLC analysis after desilylation ($KF/CH_3OH$, 25 °C, 2 h). Authentic samples of the parent alcohols were prepared.[42] The first-eluting (GLC Carbowax 20 M) alcohol has been reported to be the cis isomer.[43]

**Tetrahydro-2-(diethylmethylsiloxy)-3-((diethylmethylsiloxy)methyl)-furan** (run 18, $HSiEt_2Me$, $C_6H_6$, 25 °C, 20 h): bp 150 °C (oven)/0.3 mmHg; IR (neat) 2950, 2905, 2875, 1460, 1420, 1250, 1090, 1005, 800, 750 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$ 0.04 (s, 6 H, $SiCH_3$), 0.52 (m, 8 H, $SiCH_2$), 0.98 (m, 12 H, $SiC(CH_3)$, 2.12 (m, 1 H, CH), 3.50 (m, 4 H, $CH_2O$), 3.80 (dd, $J$ = 4.6 and 8.9 Hz, 1 H, $CCCH_2O$), 3.95 (dd, $J$ = 7 and 8.9 Hz, 1 H, $CCCH_2O$), 4.18 (m, 1 H, CHO); mass $m/e$ 289 ($M^+$ – Et, 64), 231 (10), 189 (100), 171 (41), 161 (67), 131 (82). Anal. Calcd for $C_{15}H_{34}O_2Si_2$: C, 56.55; H, 10.76. Found: C, 56.56; H, 10.92.

**Mixture of 5-ethyl-2,2,4,8,8-pentamethyl-3,7-dioxa-2,8-disilanonane and 6-ethyl-2,2,5,8,8-pentamethyl-3,7-dioxa-2,8-disilanonane** (run 19, $HSiEt_2Me$, $CH_3C_6H_5$, 0 °C, 20 h): bp 120 °C (oven)/20 mmHg; IR (neat) 2950, 2680, 1450, 1370, 1080, 1050, 1005, 870, 830, 675 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.09 (s, 18 H, $SiCH_3$), 0.89–0.90 (c, 4.5 H, $CH_3$), 1.09 (d, $J$ = 6.23 Hz, 1.5 H, $CH_3$), 1.22–1.45 (c, 2.5 H, $CH_2$ and CH), 1.73 (m, $J$ = 7.2 Hz, 0.5 H, CH), 3.38 (dd, $J$ = 6.96 and 9.99 Hz, 1 H, $CH_2$), 3.51–3.59 (c, 1.5 H, $CH_2$ and CH), 3.89 (quintet, $J$ = 5.5 Hz, 0.5 H, CH); mass $m/e$ 247 ($M^+$ – Me, 3), 232 (6), 172 (23), 147 (45), 143 (38), 131 (67), 117 (83), 103 (22), 75 (28), 73 (100).

**Mixture of 5-(3,3-dimethyl-2-oxa-3-silabutyl)-2,2,4,8,8-pentamethyl-3,7-dioxa-2,8-disilanonane and *threo*-5-(2,2-dimethyl-1-oxa-2-silapropyl)-2,2,6,9,9-pentamethyl-3,8-dioxa-2,9-disiladecane** (run 20, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 72 h): bp 100 °C (oven)/0.5 mmHg; IR (neat) 2955, 1380, 1250, 1080, 840, 740 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.12 (s, 27 H, $SiCH_3$), 0.81 (d, $J$ = 7.0 Hz, 1.2 H, $CH_3$), 1.14 (d, $J$ = 6.46 Hz, 0.8 H, $CH_3$), 1.61 (c, 0.4 H, CH), 1.79 (m, 0.6 H, CH), 3.36 (dd, $J$ = 10.2 and 7.2 Hz, 1.2 H, $CH_2O$), 3.43–3.75 (c, 2.8 H, $CH_2O$), 3.81 (td, $J$ = 6.0 and 3.12 Hz, 0.6 H, CHO), 3.98 (quintet, $J$ = 6.0 Hz, 0.4 H, CHO); mass $m/e$ 336 ($M^+$, 1), 321 ($M^+$ – Me, 1), 246 (6), 233 (45), 147 (38), 143 (95), 117 (100), 103 (93). Thus, the structures of the mixture (4:6) were established unequivocally except for the stereochemistry (see below).

Desilylation was done as follows. To 20 $\mu$L of a mixture (4:6) was added 10 drops of 10% aqueous HCl. After stirring at room temperature for 20 min, water and hexamethyldisiloxane formed were evaporated to give a mixture of triols i and ii. That the mixture contained i and ii[44]



was shown by 270-MHz $^1H$ NMR, in $CDCl_3$ and $D_2O$, except for their stereochemistry (see below). The threo stereochemistry for ii ($CDCl_3$, $\delta$ 0.99 for $CH_3$) was assigned by comparison of the NMR data with that of erythro-triol iii ($CDCl_3$, $\delta$ 0.88 for $CH_3$).[45]

$^1H$ NMR ($CDCl_3$, 270 MHz) for a mixture of i and ii (4:6) $\delta$ 0.99 (d, $J$ = 7.2 Hz, 1.8 H, $CH_3$ of ii), 1.33 (d, $J$ = 7.6 Hz, 1.2 H, $CH_3$ of i), 1.62–1.93 (br, 4 H, OH, CH), 3.62–4.13 (c, 4.6 H, $CH_2O$ of i and ii, CHO of ii), 4.18 (m, 0.4 H, CHO of i). $^1H$ NMR ($D_2O$, 270 MHz) of the same sample: $\delta$ 0.78 (d, $J$ = 7.00 Hz, 1.8 H, $CH_3$ of ii), 1.09 (d, $J$ = 7.00 Hz, 1.2 H, CH of i), 1.55–1.73 (m, 1 H, CHO), 3.36 (dd, $J$ = 10.8 and 6.3 Hz, 1.2 H, $CH_2$ of ii), 3.41–3.67 (c, 3.4 H, $CH_2$ of i, $CH_2$ and CH of ii), 3.84 (quintet, $J$ = 6.3 Hz, 0.4 H, CH of i). The $^1H$ NMR signals (in $D_2O$) of the major product ii were identical with those of the triol obtained by the hydrolysis of the chloroacetate (vide infra).

**Mixture of acetic acid 2-(3,3-dimethyl-2-oxa-3-silabutyl)-3,5,5-trimethyl-4-oxa-5-silahexyl ester and acetic acid 2-(2,2-dimethyl-1-oxa-2-silapropyl)-3,6,6-trimethyl-5-oxa-6-silaheptyl ester** (run 21, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 72 h) for a mixture (22:78) obtained by bulb-to-bulb distillation: bp 100 °C (oven)/0.7 mmHg; IR (neat) 2950, 2880, 1740, 1440, 1370, 1250, 1060, 960, 840, 750 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$ 0.08 (s, 18 H, $SiCH_3$), 0.70 (d, $J$ = 6 Hz, 2.34 H, $CH_3$), 1.06 (d, $J$ = 6.0 Hz, 0.66 H, $CH_3$), 1.32–1.72 (m, 1 H, CH), 1.90 (s, 3 H, $CH_3C{=}O$), 3.28 (d, $J$ = 6 Hz, 1.56 H, $CH_2O$), 3.44 (d, $J$ = 6 Hz, 0.44 H, $CH_2O$)8, 3.68–4.12 (c, 3 H, $CH_2O$ and CHO); mass $m/e$ 291 ($M^+$ – Me, 4), 261 (1), 233 (41), 175 (29), 147 (53), 117 (62), 103 (62), 73 (100). Anal. Calcd for $C_{13}H_{40}O_4Si_2$: C, 50.94; H, 9.86. Found: C, 51.21; H, 9.62.

**Mixture of chloroacetic acid 2-(3,3-dimethyl-2-oxa-3-silabutyl)-3,5,5-trimethyl-4-oxa-5-silahexyl ester and chloroacetic acid 2-(2,2-dimethyl-1-oxa-2-silapropyl)-3,6,6-trimethyl-5-oxa-6-silaheptyl ester** (run 22, $HSiMe_3$, $CH_2L_2$, 0 °C, 72 h) for a mixture (4:96) obtained by bulb-to-bulb distillation: bp 170 °C (oven)/1 mmHg; IR (neat) 2975, 2910, 1750, 1400, 1280, 1245, 1170, 1080, 980, 830, 740, 675 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.09 (s, 9 H, $SiCH_3$), 0.12 (s, 9 H, $SiCH_3$), 0.84 (d, $J$ = 6.28 Hz, 2.84 H, $CH_3$), 1.17 (d, $J$ = 6.28 Hz, 0.16 H, $CH_3$), 1.69 (m, 1 H, CH), 3.39 (dd, $J$ = 5.0 and 8.5 Hz, 1 H, $CH_2OSi$), 3.45 (dd, $J$ = 3.6 and 10.0 Hz, 1 H, CHOSi), 4.02 (m, 1 H, CH) overlapping with a singlet at $\delta$ 4.05. 4.05 (s, 2 H, $ClCH_2$), 4.12 (dd, $J$ = 3.6 and 7.8 Hz, 1 H, $CH_2O$). 4.18 (dd, $J$ = 3.6 and 11.4 Hz, 1 H, $CH_2O$); mass $m/e$ 327 ($M^+$ – Me, 1.7), 325 (3.3), 297 (1.3), 295 (2.3), 233 (0.8), 231 (13), 211 (12), 209 (25), 189 (17), 103 (100); high resolution MS, $M^+$ 340.1277 (calcd for $C_{13}H_{29}ClO_4Si_2$ 340.1294).

Hydrolysis to a triol ii (see structure under the data for the product obtained in run 20) was performed by standing a mixture (20 $\mu$L), $H_2O$ (five drops), and pyridine (five drops) overnight at room temperature. This is a standard procedure for the deprotection of chloroacetate.[46] The NMR spectrum of the thus-obtained triol ii was almost identical with that in run 20 (see the experimental part for run 20): $^1H$ NMR ($D_2O$, 270 MHz) $\delta$ 0.77 (d, $J$ = 7.7 Hz, 3 H, $CH_3$), 1.69 (c, 1 H) 3.38 (dd, $J$ = 5.8 and 11.2 Hz, 2 H, $CH_2O$), 3.52 (m, 2 H, $CH_2O$), 3.65 (m, 1 H, CHO).

**Mixture of chloroacetic acid 3-(3,3-dimethyl-2-oxa-3-silabutyl)-4-ethyl-6,6-dimethyl-5-oxa-6-silaheptyl ester and chloroacetic acid 3-(3,3-dimethyl-1-oxa-2-silapropyl)-4-ethyl-7,7-dimethyl-6-oxa-7-silaoctyl ester** (run 23, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 72 h) for a mixture (11:89) obtained by bulb-to-bulb distillation: bp 170 °C (oven)/2 mmHg; IR (neat) 3000, 1750, 1465, 1415, 1310, 1250, 1160, 1080, 1055, 832, 750, 690 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.09 (s, 9 H, $SiCH_3$), 0.10 (s, 9 H, $SiCH_3$), 0.90 (t, $J$ = 7.0 Hz, 2.68 H, $CH_3$), 1.00 (t, $J$ = 7.3 Hz, 0.32 H, $CH_3$), 1.35–1.60 (c, 3 H, $CH_2$ and CH), 1.65–1.85 (c, 2 H, $CH_2$), 3.44 (dd, $J$ = 11.7 and 5.87 Hz, 1 H, $CH_2OSi$), 3.52 (dd, $J$ = 11.7 and 5.87 Hz, 1 H, $CH_2OSi$), 3.97 (td, $J$ = 8.8 and 2.9 Hz, 1 H, CHOSi), 4.03

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(s, 2 H, $CH_2Cl$), 4.13–4.39 (c, 2 H, $CH_2$—OC=O); mass *m/e* 355 ($M^+$ – Me, 0.5), 353 (1), 280 (1.5), 278 (3), 147 (34), 129 (60), 103 (12), 73 (100); high-resolution MS, $M^+$ 368.16158 (calcd for $C_{15}H_{33}O_4Si_2Cl$, 368.1606).

**Chloroacetic acid 2-*trans*-(2,2-dimethyl-1-oxa-2-silapropyl)-3-*cis*-(3,3-dimethyl-2-oxa-3-silabutyl)cyclohexyl ester** (run 24, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 72 h): bp 150 °C (oven)/2 mmHg; IR (neat) 2900, 2770, 1730, 1440, 1260, 1245, 1170, 1100, 1010, 830, 730, 680 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.08 (s, 9 H, $SiCH_3$), 0.09 (s, 9 H, $SiCH_3$), 1.20–1.90 (c, 7 H, $CH_2$ and CH), 3.53 (d, $J$ = 4.0 Hz, 2 H, $CH_2O$), 3.58 (dd, $J$ = 9.9 and 2.9 Hz, 1 H, CHOSi), 4.08 (s, 2 H, $CH_2$, $CH_2$(C=O)), 5.19 (br, 1 H, CHO); $^{13}C$ NMR ($CDCl_3$) $\delta$ –0.53 (SiC), 0.05 (SiC), 19.56, 27.00, 29.10, 41.26, 41.39, 63.07, 70.98, 75.16, 167.00 (C=O); mass *m/e* 353 ($M^+$ – Me, 1), 351 (2), 323 (1), 321 (1), 217 (14), 183 (51), 103 (27), 73 (100); high-resolution MS, $M^+$ 366.14210 (calcd for $C_{15}H_{31}O_{41}Si_2Cl$ 366.144943).

**3,9-Diethyl-3,6,6,9-tetramethyl-4,8-dioxa-3,9-disilaundecane** (run 25, $HSiEt_2Me$, $C_6H_6$, 25 °C, 20 h): bp 115 °C (oven)/3 mmHg; IR (neat) 2950, 2900, 2880, 1465, 1420, 1360, 1255, 1090, 1005, 830, 795, 765 $cm^{-1}$; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.04 (s, 6 H, $SiCH_3$), 0.56 (m, 8 H, $SiCH_2$), 1.00 (m, 18 H, $SiCCH_3$ and $CH_3$), 3.25 (s, 4 H, $CH_2O$); mass *m/e* 304 ($M^+$, 1), 285 (45), 189 (100), 161 (72), 133 (21). Anal. Calcd for $C_{15}H_{36}O_2Si_2$: C, 59.14; H, 11.91. Found: C, 58.92; H, 12.21.

**3,9-Diethyl-3,5,5,9-tetramethyl-4,8-dioxa-3,9-disilaundecane** (run 25): bp 115 °C (oven)/3 mmHg; IR (neat) 2960, 2925, 2900, 1470, 1430, 1400, 1380, 1270 $cm^{-1}$; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.09 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$), 0.50 (t, $J$ = 6 Hz, 8 H, $SiCH_2$), 0.09 (t, $J$ = 6 Hz, 12 H, $SiCCH_3$), 1.10 (s, 6 H, $CH_3$), 1.58 (t, $J$ = 6 Hz, 2 H, $CH_2$), 3.62 (t, $J$ = 6 Hz, $CH_2O$); mass *m/e* 299 ($M^+$ – Me, 9), 285 (45), 256 (33), 189 (100), 159 (58).

**3,10-Diethyl-3,7,7,10-tetramethyl-6-(2-ethyl-2-methyl-1-oxa-2-silabutyl)-4,9-dioxa-3,10-disiladodec-5-ene** (run 25): bp 198 °C (oven)/22 mmHg; 2950, 2850, 2780, 1670, 1455, 1410, 1342, 1200, 1150, 1115, 1085, 1005, 960, 850, 830, 790, 750, 680 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.02 (s, 6 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$), 0.48–0.68 (m, 12 H, $SiCH_2$), 0.87–0.99 (m, 24 H, $SiCCH_3$ and $CH_3$), 3.36 (s, 2 H, $OCH_2$), 5.68 (s, 1 H, =CH); mass *m/e* 432 ($M^+$, 9), 417 ($M^+$ – Me, trace), 403 (4), 301 (100), 101 (46), 73 (61).

**Mixture of 6-(3-ethyl-3-methyl-2-oxa-3-silapentyl)-3,9-diethyl-3,6,9-trimethyl-4,8-dioxa-3,9-disilaundecane and 6-(3-ethyl-3-methyl-2-oxa-3-silapropyl)-3,10-diethyl-3,6,10-trimethyl-4,9-dioxa-3,10-disiladodecane** (run 26 $HSiEt_2Me$, $CH_2Cl_2$, 25 °C, 20 h, for a 25:75 mixture obtained by bulb-to-bulb distillation): bp 110 °C (oven)/0.6 mmHg; IR (neat) 2950, 2920, 2880, 1465, 1420, 1260, 1095, 1005, 965, 800, 783 $cm^{-1}$; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.02 (s, 6.75 H, $SiCH_3$), 0.06 (s, 2.25 H, $SiCH_3$), 0.40–0.84 (m, 12 H, $SiCH_2$), 0.94 (c, 18.75 H, $SiCCH_3$ and $CH_3$), 1.16 (s, 2.25 H, $CH_3$), 1.4 (t, $J$ = 8.0 Hz, 1.5 H, $CH_2$), 3.38 (s, 1.5 H, $CH_2$), 3.73 (t, $J$ = 8.0 Hz, 1.5 H, $CH_2O$); mass *m/e* 391 ($M^+$ – Et, 16), 289 (100), 189 (69), 185 (49). Anal. Calcd for $C_{20}H_{48}O_3Si_3$: C, 57.08; H, 11.50. Found: C, 57.22; H, 11.78.

**4-(1-(3,3-Dimethyl-2-oxa-3-silabutyl)cyclopentyl)-2,2-dimethyl-3-oxa-2-silabutane** (run 29, $HSiMe_3$, $CH_3C_6H_5$, 25 °C, 20 h): bp 112 °C (oven)/10 mmHg; IR (neat) 2950, 2850, 2780, 1469, 1388, 1260, 1250, 1130, 1080, 872, 833, 751, 687 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.07 (s, 18 H, $SiCH_3$), 1.28–1.35 (br, 4 H, $CH_2$), 1.48–1.57 (br, 4 H, $CH_2$), 3.33 (s, 4 H, $OCH_2$); mass *m/e* 274 ($M^+$, 1), 259 (8), 184 (95), 147 (89), 94 (89), 73 (100). Anal. Calcd for $C_{13}H_{30}O_2Si_2$: C, 56.87; H, 11.01. Found: C, 56.61; H, 11.22.

**5-(1-(2,2-Dimethyl-1-oxa-2-silapropyl)cyclopentyl)-2,2-dimethyl-3-oxa-2-silapentane** (run 29): bp 112 °C (oven)/10 mmHg; IR (neat) 2950, 2850, 2780, 1450, 1400, 1370, 1340, 1248, 1121, 1088, 1003, 968, 880, 831, 755, 685 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.09 (s, 9 H, $SiCH_3$), 0.10 (s, 9 H, $SiCH_3$), 1.54 (m, 8 H, $CH_2$), 1.83 (m, 2 H, $CH_2$), 3.72 (m, 2 H, $OCH_2$); mass *m/e* 274 ($M^+$, 1), 259 (8), 184 (12), 171 (100), 73 (88). Anal. Calcd for $C_{13}H_{30}O_2Si_2$: C, 56.87; H, 11.01. Found: C, 56.56; H, 11.19.

**2,2,4,5,5,8,8-Heptamethyl-3,7-dioxa-2,8-disilanonane** (run 30, $HSiMe_3$, $CH_3C_6H_5$, 25 °C, 20 h): bp 40 °C (oven)/20 mmHg; IR (neat) 2950, 2875, 2850, 1470, 1386, 1315, 1305, 1252, 1242, 1110, 1108, 1080, 1045, 1000, 960, 870, 830, 740, 675, 610 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.08 (s, 9 H, $SiCH_3$), 0.76 (s, 3 H, $CH_3$), 0.79 (s, 3 H, $CH_3$), 1.04 (d, $J$ = 6.4 Hz, 3 H, $CH_3$), 3.24 (d, $J$ = 10.2 Hz, 1 H, $CH_2$), 3.36 (d, $J$ = 10.2 Hz, 1 H, $CH_2$), 3.72 (q, $J$ = 6.4 Hz, 1 H, CH); mass *m/e* 262 ($M^+$, trace), 247 (4), 172 (6), 117 (100), 73 (65). Anal. Calcd for $C_{12}H_{30}O_2Si_2$: C, 54.90; H, 11.52. Found: C, 54.81; H, 11.81.

**2,2,4,4,5,8,8-Heptamethyl-3,7-dioxa-2,8-disilanonane** (run 30): bp 40 °C (oven)/20 mmHg; IR (neat) 2950, 2875, 1445, 1410, 1370, 1253, 1242, 1210, 1180, 1110, 1085, 1070, 1020, 1445, 1410, 1370, 1253, 1242, 1210, 1180, 1110, 1085, 1070, 1020, 995, 956, 908, 830, 745, 680, 610 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.00 (s, 9 H, $SiCH_3$), 0.10 (s, 9 H, $SiCH_3$), 0.83 (s, 3 H, $CH_3$), 0.87 (s, 3 H, $CH_3$), 1.04 (d, $J$ = 6.1 Hz, 3 H, $CH_3$), 1.57 (m, 1 H, CH), 3.55 (m, 2 H, $OCH_2$); mass *m/e* 245 ($M^+$ – 17, 4), 147 (37), 73 (100). Anal. Calcd for $C_{12}H_{30}O_2Si_2$: C, 54.90; H, 11.52. Found: C, 54.72; H, 11.87.

**Spectroscopic Data for the Products Appearing in Equations and Notes. 3,11-Diethyl-3,11-dimethyl-5-(2-oxapropyl)-4,10-dioxa-3,11-disilatridecane** (eq 6): bp 116–117 °C/0.6 mmHg; IR (neat) 2950, 2900, 2880, 1460, 1255, 1100, 1010, 800, 760 $cm^{-1}$; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.01 (s, 3 H, $SiCH_3$), 0.02 (s, 3 H, $SiCH_3$), 0.37–0.75 (m, 8 H, $SiCH_2$), 0.81–1.09 (m, 12 H, $SiCCH_3$), 1.19–1.65 (c, 6 H, $CH_2$), 3.16 (d, $J$ = 5.8 Hz, 2 H, $CH_2O$), 3.27 (s, 3 H, $CH_3O$), 3.39–3.85 (m, 3 H, $CH_2O$ and CHO); mass *m/e* 319 ($M^+$ – Et, 11), 303 (11), 157 (44), 103 (87), 101 (100), 81 (93). Anal. Calcd for $C_{17}H_{40}O_3Si_2$: C, 58.56; H, 11.56. Found: C, 58.70; H, 11.76.

**4-(1,1-Dimethylethyl)-2,2-dimethyl-3-oxa-2-siladeca-7,9-dien-6-one** (eq 8): IR 2960, 2900, 2875, 1700, 1670, 1610, 1595, 1370, 1250, 1100, 840, 955 $cm^{-1}$; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.01 (s, 9 H, $SiCH_3$), 0.85 (s, 9 H, $CH_3$), 2.39 (d, $J$ = 3.5 Hz, 1 H, $CH_2$), 2.65 (d, $J$ = 8 Hz, 1 H, $CH_2$), 3.90 (dd, $J$ = 3.5 and 8 Hz, 1 H, CH), 5.46 (d, $J$ = 10 Hz, 1 H, $CH_2$=), 5.60 (d, $J$ = 17 Hz, 1 H, $CH_2$=), 6.09 (d, $J$ = 15 Hz, 1 H, CH=), 6.40 (dt, $J$ = 17 and 10 Hz, 1 H, CH=), 7.01 (dd, $J$ = 10 and 15 Hz, 1 H, CH=); mass *m/e* 254 ($M^+$, 2), 239 (13), 197 (53), 153 (53), 81 (100), 75 (30), 73 (16), 53 (11). Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 66.08; H, 10.30. Found: C, 66.05; H, 10.50.

**4-(1,1-Dimethylethyl)-2,2-dimethyl-3-oxa-2-siladeca-8-en-6-one** (eq 8): IR 2950, 1725, 1365, 1100, 1030, 840; 100-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.03 (s, 9 H, $SiCH_3$), 0.82 (s, 9 H, $CH_3$), 1.68 (m, 3 H, $CH_3$), 2.25 (dd, $J$ = 17 and 4 Hz, 1 H, $CH_2$), 2.48 (dd, $J$ = 17 and 7 Hz, 1 H, $CH_2$), 2.96 (m, 1.8 H, 2 H, $CH_2$), 3.82 (dd, $J$ = 4 and 7 Hz, 1 H, CH), 5.44 (m, 2 H, CH=CH).

**Mixture of benzoic acid 2-(3,3-dimethyl-2-oxa-3-silabutyl)-3,5,5-trimethyl-4-oxa-5-silahexyl ester and benzoic acid 2-(2,2-dimethyl-1-oxa-2-silapropyl)-3,6,6-trimethyl-5-oxa-6-silaheptyl ester** (ref 34, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 20 h): for a mixture (22:78) obtained by bulb-to-bulb distillation: bp 200 °C (oven)/0.5 mmHg; IR (neat) 3000, 2950, 1725, 1250, 1680, 1615, 1590, 1455, 1385, 1320, 1270, 1250, 1100, 965, 830, 755, 675, 690 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.13 (s, 18 H, $SiCH_3$), 0.88 (d, $J$ = 7.17 Hz, 2.34 H, $CH_3$), 1.22 (d, $J$ = 5.97 Hz, 0.66 H, $CH_3$), 1.76–1.99 (m, 1 H, CH), 3.42 (dd, $J$ = 6 and 10.4 Hz, 0.78 H, $CH_2$), 3.51 (dd, $J$ = 7.2 and 10.4 Hz, 0.78 H, $CH_2$), 3.64 (dd, $J$ = 5.4 Hz and 9.6 Hz, 0.22 H, $CH_2$), 3.71 (dd, $J$ = 6 and 9.6 Hz, 0.22 H, $CH_2$), 4.12–4.21 (m, 1 H, CH), 4.24–4.39 (c, 2 H, $CH_2$), 7.35–7.36 (c, 3 H, Ar), 7.95–8.11 (c, 2 H, Ar); mass *m/e* 353 ($M^+$ – Me, 3), 233 (40), 231 (31), 189 (29), 105 (100), 103 (71). Anal. Calcd for $C_{18}H_{32}O_4Si_2$: C, 58.65; H, 8.75. Found: C, 58.41; H, 8.71.

**Mixture of methyl 2-(3,3-dimethyl-2-oxa-3-silabutyl)-3,5,5-trimethyl-4-oxa-5-silahexyl carbonate and methyl 2-(2,2-dimethyl-1-oxa-2-sila-3,6,6-trimethyl-5-oxa-6-silaheptyl) carbonate** (ref 34, $HSiMe_3$, $CH_2Cl_2$, 0 °C, 48 h) for a mixture (17:83) obtained by bulb-to-bulb distillation: bp 170 °C (oven)/1 mmHg; IR (neat) 2990, 2950, 1750, 1445, 1250, 1090, 975, 840, 750, 700 $cm^{-1}$; 270-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.12 (s, 18 H, $SiCH_3$), 0.81 (d, $J$ = 7.4 Hz, 2.49 H, $CH_3$), 1.16 (d, $J$ = 6.6 Hz, 0.51 H, $CH_3$), 1.66–1.89 (c, 1 H, CH), 3.37 (dd, $J$ = 6.13 and 9.82 Hz, 0.83 H, $CH_2$), 3.43 (dd, $J$ = 7.36 and 9.82 Hz, 0.83 H, $CH_2$), 3.54 (dd, $J$ = 6.55 and 9.82 Hz, 0.17 H, $CH_2$), 3.60 (dd, $J$ = 5.7 Hz, 0.17 H, $CH_2$), 3.73–3.83 (m, 1 H, CH) overlapping with a singlet at $\delta$ 3.76, 3.76 (s, 3 H, $CH_3O$), 4.01 (dd, $J$ = 3.03 and 5.32 Hz, 0.83 H, $CH_2$), 4.11 (d, $J$ = 6.5 Hz, 0.17 H, $CH_2$); mass *m/e* 307 ($M^+$ – Me, 10), 233 (52), 231 (54), 191 (24), 133 (32), 103 (84), 73 (100). Anal. Calcd for $C_{13}H_{30}O_5Si_2$: C, 48.41; H, 9.37. Found: C, 48.40; H, 9.45.

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