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Ring-Opening Reactions of Cyclic Acetals and 1,3-Oxazolidines with Halosilane Equivalents

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Reactions of acetal and 1,3-oxazolidine rings were examined using two kinds of iodosilane equivalent reagents, a 1:2 mixture of Me₃SiNEt₂ and MeI (reagent 1a) and a 1:1 mixture of Et₃SiH and MeI containing a catalytic amount of $PdCl_2$ (reagent **1b**). In the reactions of alkanone ethylene acetals with reagent 1a, a C-O bond in the acetal ring readily cleaved to give 2-(trimethylsiloxy)ethyl enol ethers. Similarly, the C-O bond of 1,3-oxazolidine rings cleaved to give ring-opened imine or enamine derivatives. The reactions of aromatic ketone ethylene acetals and cyclohexanone trimethylene acetal led to deprotection of the acetal unit to liberate free ketones. With reagent **1b**, cycloalkanone ethylene acetal afforded a dimeric product with 2-iodoethyl alkenoate moieties, while aromatic ketone ethylene or trimethylene acetals produced deprotected ketones.

Introduction

Halosilanes are widely used in areas of synthetic organic chemistry.¹ For example, it has been reported that the reactions of cyclic ethers² and lactones³ with iodo- and bromosilanes produce α -halo- ω -siloxy compounds in good yields. It has also been reported that deprotection of acetal moieties with trimethyliodosilane takes place to give free ketones under neutral conditions.⁴ However, in contrast to fluoro- and chlorosilanes, the use of iodosilanes is rather limited due to their strong tendency to undergo hydrolytic cleavage of the siliconhalogen bonds even with atmospheric moisture.⁵

Recently, we have demonstrated that a 1:2 mixture of Me₃SiNEt₂ and MeI (reagent 1a) and a 1:1 mixture of Et₃SiH and MeI containing a catalytic amount of PdCl₂ (reagent 1b) act as synthetic equivalents of Me₃SiI and Et₃SiI, respectively.^{6–9} These reagents can be handled

without special care and react readily with several organic substrates containing a C-O bond. Their reactions with cyclic ethers afford ring-opened α -iodo- ω siloxyalkanes in good yield.⁶ It has also been reported that treatment of alkyl esters of alkanoic acids with reagent 1a affords trimethylsilyl alkanoates with the liberation of alkyl iodides,⁷ while similar reactions of alkanones give trimethylsilyl enol ethers.⁸ To further explore the scope of the synthetic utilities of the iodosilane equivalents, we examined the reactions of acetals¹⁰ and 1,3-oxazolidines that have a five- or six-membered ring with reagents 1a and 1b.

Results and Discussion

Reactions of Alkanone Acetal Rings with Reagent 1a. Reactions of cyclic acetals 2a-g derived from cyclic or acyclic alkanones were examined, as listed in Table 1. All these reactions were carried out using 1 equiv of reagent 1a in toluene at 80-90 °C for 12 h, and the products were isolated by distillation and verified on the basis of spectroscopic and elemental analyses.

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 TABLE 1. Reactions of Alkanone Acetal Rings with 1

 Equiv of Reagent 1a^a

+ Et₂NSiMe₃ + 2Mel toluene, 80-90 °C Product



^{*a*} All reactions were carried out using 1 equiv of **1a** in toluene at 80-90 °C for 12 h. ^{*b*} Isolated yield.

When ethylene acetals **2a**-**f** were treated with **1a**, preferential C-O bond cleavage took place at one of the O-C-O bonds in the acetal ring, and the corresponding ring-opened 2-(trimethylsiloxy)ethyl enol ethers 3a-f were obtained in good yields, respectively. Thus, the reaction of cyclohexanone ethylene acetal (2a) for 12 h gave 2-(trimethylsiloxy)ethyl 1-cyclohexenyl ether (3a) as the sole volatile product in 76% isolated yield. Similar reactions of alkanone dimethyl acetals with Me₃SiI in the presence of hexamethyldisilazane, which give the corresponding methyl vinyl ethers, have been reported previously.¹¹ Recently, we reported that a 1:2 mixture of Me₃SiNEt₂ and allyl bromide (reagent 1a') acts as a synthetic equivalent of Me₃SiBr,^{6,7,9} and the reactions with cyclic ethers, such as tetrahydrofuran and tetrahydropyran, give ring-opened products, α -bromo- ω -trimethylsiloxyalkanes. However, the acetal ring of 2a did not react with 1a'.

Treatment of 2-methylcyclohexanone ethylene acetal (**2b**) that has an unsymmetrically substituted cyclohexane ring with **1a** gave a mixture of double-bond isomers, 2-methyl- and 6-methyl-1-cyclohexenyl ethers **3b-1** and **3b-2**, respectively, in a ratio of 59/41 in 75% combined yield. Ethylene acetals of cyclopentanone (**2c**), 3-pentanone (**2d**), and 4-methyl-2-pentanone (**2e**) also under-







went ring-opening reactions to give the corresponding siloxyethyl enol ethers **3c** (75%), **3d** (62%), and **3e** (72%), respectively. Traces of 1,2-bis(trimethylsiloxy)ethane and 1-iodo-2-(trimethylsiloxy)ethane were detected by GC/MS analysis in these reactions. The reaction of cyclohexanone propylene acetal (**2f**), which bears an unsymmetrical acetal ring, led to preferential cleavage on the less hindered C-O bond to give an 87/13 mixture of **3f-1** and **3f-2** in 84% yield.

In the reaction of **2d**, the products were obtained as a mixture of (E)-3d and (Z)-3d (80/20), whose ratio was determined on the basis of integrated ratios of proton signals in ¹H NMR spectra. Their configurations around C=C double bonds could be confirmed by NOESY experiments. For the major component, clear NOEs were observed between a signal due to vinylmethyl protons (δ 1.56, d) and signals due to methyl (δ 1.03, t) and methylene (δ 2.14, q) protons in an ethyl group, respectively. On the other hand, the vinylmethyl protons (δ 1.66, d) of the minor component showed NOE with protons in an OCH₂CH₂OSi unit, but not with the ethyl protons. The reaction of 2e with 1a afforded also a mixture of 3e-1, (E)-3e-2, and (Z)-3e-2 (60/30/10), and the assignment of E/Z for **3e-2** was similarly made by NOESY measurements: NOEs were observed between signals of *i*-Pr and Me(-Vi) groups in (*E*)-**3e-2** and between those of H(-Vi) and Me(-Vi) groups in (Z)-3e-2

Strangely, six-membered ring acetals did not produce enol ethers. Thus, the reaction of cyclohexanone trimethylene acetal (**2g**) with **1a** would give a 40/60 mixture of 1,3-bis(trimethylsiloxy)propane (**3g-1**) and 1-iodo-3-(trimethylsiloxy)propane (**3g-2**) in 64% yield, although no products due to the cyclohexyl moiety were found in the volatile products. Moreover, attempted reaction of the parent ring compound, 1,3-dioxolane, with **1a** was unsuccessful.

These reactions may be initiated by silylation on one of two oxygen atoms forming a ring-opened cationic species (**A**), as shown in Scheme 1, and subsequent proton elimination from **A** produces enol ethers $3\mathbf{a} - \mathbf{e}$ (similarly **3f**). It is also possible to assume an iodosiloxy compound (**B**) as the intermediate, in analogy with the reaction of cyclic ethers,⁶ although we have not yet obtained evidences for the formation of **B** in the present reactions. Thus, the formation of **3g-1** can be understood by assuming **B**: further silylation to **B** produces bissilylated product **3g-1**, while iodosiloxylpropane **3g-2** is produced

 TABLE 2.
 Reactions of Phenyl-Substituted Acetal Rings

 with Reagent $1a^a$ a^a



^{*a*} Reactions were carried out in toluene under the following conditions: (A) **1a**/**4** = 2/1, 12 h; (B) **1a**/**4** = 1/1, 12 h; or (C) **1a**/**4** = 1/1, 48 h. ^{*b*} Isolated yield. ^{*c*} Benzophenone was also obtained as the coproduct in 67, ^{*d*} 75, ^{*e*} and 70% ^{*f*} yields, respectively.

from **A**, as discussed later. A failure to isolate a counterpart of **3g**, possibly cyclohexylidene iodide or cyclohexanone, is presumably due to further reactions such as acid-catalyzed self-condensation or reaction with diethylamine liberated in the reaction pathway, forming nonvolatile products. The iodide **B** may be in equilibrium with **A** and seems to be formed only from trimethylene acetal **2g** and not from ethylene acetals due to steric hindrance. Deprotonation from **A** thus proceeds in cases of ethylene acetals to give enol ethers.

Reactions of Phenyl-Substituted Acetal Rings with Reagent 1a. Table 2 summarizes results for the reactions of cyclic acetals 4a-e bearing phenyl group(s) on the ring with reagent 1a. The reactions were carried out at 80-90 °C in a manner similar to that described above. In all cases, iodosiloxyalkanes and/or bis(siloxy)alkanes were obtained in good yields. Thus, when benzaldehyde ethylene acetal (4a) was treated with 2 equiv of 1a for 12 h, 1,2-bis(trimethylsiloxy)ethane (5) was isolated in 79% yield as the sole volatile product. Benzylidene iodide, which is expected to be formed along with 5, was not detected by GLC analysis of the reaction mixture. This is presumably due to the same reason discussed in Scheme 1 before.

In the reaction of acetophenone ethylene acetal (4b) with 2 equiv of 1a for 12 h, an enol ether that can be generated was not detected in the reaction mixture, but an 80/20 mixture of 5 and 1-iodo-2-(trimethylsiloxy)-ethane (6a) was isolated in 61% total yield. The reaction of benzophenone ethylene acetal (4c) with 1 equiv of 1a for 12 h gave 6a as the main product in 62% yield, together with 67% yield of benzophenone, while similar reaction of benzophenone trimethylene acetal (4d) for 48 h gave 1-iodo-3-(trimethylsiloxy)propane (3g-2) and benzophenone in 71 and 75% isolated yields, respectively. In the reaction of benzophenone acetal 4e with a methyl substituent on the ring for 48 h, silylation occurred on the less hindered oxygen atom to give an 83/17 mixture of iodosiloxypropanes 6b and 6c (73%) and benzophenone

TABLE 3. Reactions of Oxazolidine Rings with 1 Equivof Reagent $1a^a$



 a All reactions were carried out using 1 equiv of ${\bf 1a}$ in toluene. b Isolated yield.

(70%). These compounds **6b** and **6c** were also given by the ring-opening iodosilation of propylene oxide with **1a**. In this reaction, **6c** was obtained as the major product (**6b/6c** = 8/92), in contrast to the reaction of cyclic acetal **4e**.

These results can be understood by analogy with the reactions of acetal **2**. As illustrated in the bottom part of Scheme 1, two pathways (**a** and **b**) from a cation **A'** may compete, and their ratio seems to depend on the bulkiness of the substituents. In the case of benzaldehyde ethylene acetal ($\mathbf{R} = \mathbf{H}$), addition of an iodide anion to the sp² carbon in **A'** is possible to give an iodosiloxy intermediate **B'** (path **b**), from which bissiloxyethane **5** is produced. On the other hand, benzophenone acetal ($\mathbf{R} = \mathbf{Ph}$) do not form **B'** due to steric hindrance, and the iodide anion attacks preferentially on the less hindered ethylene carbon to liberate **6a** and benzophenone (path **a**). Acetophenone acetal ($\mathbf{R} = \mathbf{Me}$) undergoes both reactions through **a** and **b** and results in a mixture of **6a** and **5**.

Reactions of Oxazolidine Rings with Reagent 1a. The reactivity of a series of 2,2-dialkyl-1,3-oxazolidines 7a-d with 1a was also examined. The results are summarized in Table 3. The reaction of 7a with 1a at room temperature gave an 81/19 isomeric mixture of *N*-[2-(trimethylsiloxy)ethyl]cyclohexanimine (**8a**) and a simple N-trimethylsilylated product **8a**' in 89% combined yield, while heating **7a** and **1a** at 80–90 °C for 5 h led to the exclusive formation of **8a** as the sole product in 83% yield, suggesting that **8a**' is a primary product, which then isomerizes to **8a**. The isomerization may proceed via an intermediate **C**, as indicated in Scheme 2, details of which are discussed below.

To confirm isomerization pathways, we carried out related experiments. When allyl bromide was used instead of MeI in reagent **1a** as the halogen source (reagent **1a'**), the reaction of **7a** at 80–90 °C proceeded less selectively to give a 63/37 mixture of **8a** and **8a'** in 85% yield, while the reaction of **7a** with trimethylchlorosilane in ether under reflux gave a 69/31 ratio of **8a** and **8a'** in 82% yield. When the isolated mixture (69/31) was heated at 100 °C overnight, the mixture was

SCHEME 2



recovered in 92% yield with no noticeable change in the ratio (71/29). This clearly indicates that the isomerization of **8a**' to **8a** does not proceed by a simple thermal process but needs some interaction with iodosilane or its equivalent, as indicated in Scheme 2.

As can be seen in Table 3, the reactions of other oxazolidines, **7b** and **7c** with **1a**, also proceeded quite smoothly. Thus, the reactions of **7b** and **7c** went to completion at room temperature within 2 h to give respective ring-opened imines **8b** (82%) and **8c** (73%) as the sole products. The higher reactivity of oxazolidines **7a**-**c** compared to that of ethylene acetals may be understood by the formation of iminium ions that are more stable than oxonium ions, as represented with **C** in Scheme 2. The silylated iminium salt **C** further converts to an imine with a loss of the trimethylsilyl group, which is presumably released as iodosilane.

On the other hand, the reaction of N-methylated oxazolidine **7d** at 80-90 °C for 5 h produced enamine **8d** in 72% yield. In this reaction, a similar iminium intermediate **C**' may also be produced, but **C**' prefers proton elimination, since its *N*-methyl group is hard to leave compared with the trimethylsilyl group in **C**.

Reactions of Acetal Rings with Reagent 1b. Unlike the reaction with reagent **1a**, a completely different type of product was obtained in the reaction of cyclohexanone ethylene acetal (**2a**) with reagent **1b**. This is in marked contrast to the previous observation that both of **1a** and **1b** produced similar ring-opened iodosiloxyalkanes upon reactions with cyclic ethers.⁶

As shown in Table 4, the reaction of **2a** with 1 equiv of **1b** produced a dimeric compound, 2-iodoethyl 6-(1cyclohexenyl)hexanoate (9a), in 63% isolated yield, together with an 85% yield of Et₃SiOSiEt₃ (run 1). When Pd(acac)₂/dppe was used as the catalyst, in place of PdCl₂ of reagent 1b, the yield of 9a increased to 73%. In these reactions, no enol ethers analogous to 3a were detected in the reaction mixtures by GLC analysis. When allyl bromide was used instead of MeI in 1b, an 80/20 mixture of bromoester 9b-1 and its dehydrogenated product 9b-2 was obtained in 79% combined yield after distillation (run 2), and the products could be separated by recycling GPC. Similar reaction of acetal 2b with 1b proceeded regioselectively to give also the dimeric product, 2-iodoethyl 2-methyl-6-(2-methyl-1-cyclohexenyl)hexanoate (9c, 76%), and Et₃SiOSiEt₃ (98%) (run 3).

On the other hand, attempted reactions of other alkanone acetals 2c, 2d, and 2f with 1b gave complex mixtures, from which no main products were separated. In contrast, deprotection reaction of acetal rings proceeded cleanly for diaryl-substituted acetals (runs 4-7). Thus, the reactions of benzophenone acetals 4c and 4d

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TABLE 4. Reactions of Acetal Rings with Reagent 1b^a



^{*a*} Reactions were carried out in a 1:1 ratio of **1b**/acetal in toluene at 80–90 °C. ^{*b*} In most cases, Et₃SiOSiEt₃ was obtained as the coproduct in nearly quantitative yield. ^{*c*} Isolated yield. ^{*d*} Pd(acac)₂/ dppe was used instead of PdCl₂.

SCHEME 3



with **1b** gave deprotected benzophenone (**10a**) in 87 and 82% yields, respectively, along with high yields of Et_3 -SiOSiEt₃. Deprotection of the acetal moiety also proceeded for ethylene acetals of phenyl styryl ketone and distyryl ketone (**4f** and **4g**) to give the corresponding free ketones **10b** and **10c** in 74 and 80% yields, respectively.

Although a pathway leading to dimeric product **9a** from **2a** is uncertain at present, we tentatively assume 2-(1-cyclohexenyl)cyclohexanone ethylene acetal **(11)** as an intermediate (Scheme 3), which is possibly produced from **2a** by acid-catalyzed condensation. If this is the case, Pd-assisted C–C bond cleavage on the acetal carbon of **11** may follow to produce a π -allyl intermediate **D**, which then reacts with HI to give **9a**. The Pd-assisted cleavage of C–C bonds adjacent to a C–O unit has been reported.¹²

To check this possibility, we prepared acetal **11** by aldol condensation of cyclohexanone followed by acetalization and examined the reaction with **1b**. As expected, the reaction of **11** with 1 equiv of **1b** gave **9a** in 43% yield. On the other hand, the reaction of **11** with pure Et_3SiI

alone gave a quantitative yield of a deacetalized product, 2-(1-cyclohexenyl)cyclohexanone, without formation of **9a**, suggesting that the presence of a Pd catalyst is essential for production of **9a**.

Deprotection reactions of diaryl-substituted acetals with **1b** might proceed in manners similar to those with **1a**, but no products derived from acetal rings would be detected in the volatile products. It should be stressed again that hexaethyldisiloxane is always obtained in high yields, and no silicon units are incorporated into the products from acetal rings. These facts suggest that some followup reactions with remaining iodosilane occur in the present system to make the reaction more complicated.

Conclusions

We studied the reactivity of two types of iodosilane equivalent reagents, 1a and 1b, toward acetal and 1,3oxazolidine rings. Specific reactions proceeded depending on the reagents and structures of substrates. With reagent 1a, ethylene acetals and 1,3-oxazolidines bearing dialkyl substituents on the ring underwent ring-opening deprotosilation reactions, giving rise to the formation of siloxyethyl enol ethers and siloxyethylimines (or enamines) bearing a silyl-protected hydroxylethyl group, respectively, providing one-step synthetic routes to the products. On the other hand, the reactions of alkanone acetals with reagent 1b gave rather complex results. Among them, the reaction of cyclohexanone ethylene acetal with **1b** gave a dimeric product in good yield, which could be explained by assuming acid-catalyzed condensation of the starting acetal and subsequent Pd-catalyzed ring-opening reaction.

In marked contrast to these alkyl derivatives, those with diaryl substituents on the acetal ring led to a significant change in the reaction course, i.e., reactions with both **1a** and **1b** gave deprotected ketones in high yields. In the reaction with **1a**, iodosiloxyalkanes were also obtained as coproducts. This seems to be of importance as a method not only for deprotection of aromatic acetals under neutral conditions but also for preparation of α, ω -iodosiloxyalkanes, which are useful in synthetic chemistry as bifunctional materials.

Experimental Section

General Considerations. Methyl iodide and allyl bromide were dried over P_2O_5 and distilled just before use. Toluene was dried over sodium and distilled just before use. All reactions were carried out under an atmosphere of dry argon. Typical procedures for the reactions with reagents **1a** and **1b** are shown below. The ratio of isomers was determined by integration of ¹H NMR signals of the mixture.

Reaction of 2a with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (5.95 g, 41.0 mmol), **2a** (5.79 g, 40.8 mmol), and methyl iodide (12.2 g, 86.1 mmol) in 20 mL of toluene was stirred at 80–90 °C for 12 h. The resulting ammonium salts were filtered off, and the solvent was evaporated. The residue was fractionally distilled under reduced pressure to give **3a** (6.63 g, 31.0 mmol, 76%), bp 73– 75 °C/1 mmHg. For **3a**: IR (neat) 1667, 1107 cm⁻¹; ¹H NMR (CDCl₃) δ 4.58 (s, 1H), 3.81 (t, J = 5.1 Hz, 2H), 3.69 (t, J = 5.1 Hz, 2H), 2.15–2.02 (m, 4H), 1.68–1.62 (m, 2H), 1.55–1.49 (m, 2H), 0.12 (s, 9H); ^{13}C NMR (CDCl₃) δ 154.48, 93.85, 67.37, 61.46, 27.78, 23.49, 22.87, 22.72, -0.38; GC/MS m/z 214 (M⁺), 199 (M⁺ - Me). Anal. Calcd for C $_{11}H_{22}O_2Si;$ C, 61.63; H, 10.34. Found: C, 61.51; H, 10.49.

Reaction of 4c with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (5.95 g, 41.0 mmol), **4c** (5.79 g, 40.8 mmol), and methyl iodide (12.2 g, 86.1 mmol) in 20 mL of toluene was treated as described above. The products were distilled to give benzophenone (2.57 g, 14.1 mmol, 67%) and **6a** (3.19 g, 13.1 mmol, 62%). For **6a**: bp 70–71 °C/ 25 mmHg; IR (neat) 1103 cm⁻¹; ¹H NMR (CDCl₃) δ 3.80 (t, J = 6.8 Hz, 2H), 3.18 (t, J = 6.8 Hz, 2H), 0.11 (s, 9H); ¹³C NMR (CDCl₃) δ 63.79, 6.55, -0.44; GC/MS *m*/*z* 229 (M⁺ – Me). Anal. Calcd for C₅H₁₃IOSi: C, 24.60; H, 5.37. Found: C, 24.39; H, 5.33.

Reaction of 7a with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (21.2 g, 146 mmol), **7a** (19.0 g, 135 mmol), and methyl iodide (20.8 g, 146 mmol) in 100 mL of toluene was treated for 5 h as described above, and then triethylamine (16.0 g, 158 mmol) was added. The products were distilled to give **8a** (23.9 g, 112 mmol, 83%), bp 65–68 °C/1 mmHg. For **8a**: IR (neat) 1665, 1108 cm⁻¹; ¹H NMR (CDCl₃) δ 3.77 (t, *J* = 6.5 Hz, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 2.27–2.26 (m, 4H), 1.78–1.60 (m, 6H), 0.09 (s, 9H); ¹³C NMR (CDCl₃) δ 174.53, 62.91, 52.49, 39.94, 29.14, 27.66, 26.94, 26.00, -0.47; GC/MS *m*/*z* 213 (M⁺), 198 (M⁺ – Me). Anal. Calcd for C₁₁H₂₃NOSi: C, 61.91; H, 10.86; N, 6.56. Found: C, 61.52; H, 10.85; N, 6.51.

Reaction of 7d with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (14.7 g, 101 mmol), **7d** (15.5 g, 100 mmol), and methyl iodide (14.6 g, 103 mmol) in 100 mL of toluene was treated as described above. The products were distilled to give **8d** (16.3 g, 72.0 mmol, 72%), bp 75 °C/1 mmHg. For **8d**: IR (neat) 1641, 1097 cm⁻¹; ¹H NMR (CDCl₃) δ 4.41 (brs, 1H), 3.58 (t, J = 6.5 Hz, 2H), 3.08 (t, J = 6.5 Hz, 2H), 2.63 (s, 3H), 2.15–2.00 (m, 4H), 1.70–1.60 (m, 2H), 1.55–1.45 (m, 2H), 0.09 (s, 9H); ¹³C NMR (CDCl₃) δ 143.99, 96.45, 59.93, 52.99, 38.32, 26.92, 24.63, 23.46, 22.86, -0.53; GC/MS *m*/*z* 227 (M⁺), 212 (M⁺ - Me). Anal. Calcd for C₁₂H₂₅NOSi: C, 63.38; H, 11.08; N, 6.16. Found: C, 63.32; H, 10.86; N, 6.14.

Reaction of 2a with Et₃SiH/MeI(Pd(acac)₂/dppe). A mixture of triethylsilane (3.08 g, 26.6 mmol), 2a (3.75 g, 26.4 mmol), methyl iodide (7.94 g, 55.9 mmol), palladium acetylacetonate (40 mg, 0.13 mmol), and 1,2-bis(diphenylphosphino)ethane (60 mg, 0.15 mmol) was stirred at 80-90 °C for 5 h. The products were fractionally distilled with a Kügel-Rohr distillation apparatus to give hexaethyldisiloxane (2.68 g, 10.9 mmol, 82%) and 9a (3.37 g, 9.64 mmol, 73%). For 9a: bp 170 °C/1 mmHg (oven temp); IŘ (neat) 1740 cm⁻¹; ¹H NMR (CDCl₃) δ 5.36 (s, 1H), 4.31 (t, J = 6.8 Hz, 2H), 3.28 (t, J = 6.8 Hz, 2H), 2.32 (t, J = 7.5 Hz, 2H), 2.00–1.89 (m, 6H), 1.67–1.50 (m, 6H), 1.43–1.27 (m, 4H); ¹³C NMR (CDCl₃) & 173.15, 137.67, 120.79, 64.31, 37.78, 34.13, 28.79, 28.23, 27.24, 25.22, 24.82, 23.01, 22.58, 0.50; GC/MS m/z 350 (M⁺), 223 (M⁺ – I). Anal. Calcd for C14H23IO2: C, 48.01; H, 6.62. Found: C, 48.31; H, 6.68.

Reaction of 2b with Et₃SiH/MeI(PdCl₂). A mixture of triethylsilane (3.52 g, 30.3 mmol), **2b** (4.56 g, 29.2 mmol), methyl iodide (6.74 g, 47.5 mmol), and palladium dichloride (20 mg, 0.11 mmol) was treated as described above. The products were distilled to give hexaethyldisiloxane (3.66 g, 14.9 mmol, 98%) and **9c** (4.20 g, 11.1 mmol, 76%). For **9c**: bp 170–175 °C/1 mmHg (oven temp); IR (neat) 1740 cm⁻¹; ¹H NMR (CDCl₃) δ 4.32 (t, J = 6.8 Hz, 2H), 3.28 (t, J = 6.8 Hz, 2H), 2.50–2.40 (m, 1H), 2.00–1.20 (m, 16H), 1.57 (s, 3H), 1.15 (d, J = 7.0 Hz, 3H); ¹³C NMR (CDCl₃) δ 176.20, 129.93, 125.92, 64.22, 39.46, 33.70, 33.24, 31.81, 29.51, 28.06, 27.28, 23.50, 23.40, 19.02, 17.03, 0.58; GC/MS *m*/*z* 378 (M⁺), 251 (M⁺ – I). Anal. Calcd for C₁₆H₂₇IO₂: C, 50.80; H, 7.19. Found: C, 50.60; H, 7.20.

Reaction of 2a with Et₃SiH/AllylBr(PdCl₂). A mixture of triethylsilane (4.81 g, 41.5 mmol), **2a** (5.94 g, 41.8 mmol), allyl bromide (8.01 g, 66.2 mmol), and palladium dichloride

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(20 mg, 0.11 mmol) was treated for 10 h. The products were distilled to give hexaethyldisiloxane (4.13 g, 16.7 mmol, 81%) and an 80/20 mixture of **9b-1** and **9b-2** (4.95 g, 16.4 mmol, 79%), bp 150 °C/1 mmHg (oven temp). Recycling GPC separation of the mixture eluting with benzene afforded **9b-1** and **9b-2** in pure forms. For **9b-1**: IR (neat) 1738 cm⁻¹; ¹H NMR (CDCl₃) δ 5.36 (s, 1H), 4.36 (t, J = 6.8 Hz, 2H), 3.50 (t, J = 6.8 Hz, 2H), 2.33 (t, J = 7.5 Hz, 2H), 2.00–1.80 (m, 6H), 1.67–1.40 (m, 6H), 1.40–1.25 (m, 4H); ¹³C NMR (CDCl₃) δ 173.27, 137.62, 120.76, 63.53, 37.76, 34.03, 28.75, 28.75, 28.21, 27.21, 25.19, 24.77, 22.99, 22.56; GC/MS *m*/*z* 302 (M⁺ for ⁷⁹Br). Anal. Calcd for C₁₄H₂₃BrO₂: C, 55.45; H, 7.65. Found: C, 55.63; H, 7.81. For **9b-2**: IR (neat) 1738 cm⁻¹; ¹H NMR (CDCl₃) δ 7.19–7.14 (m, 2H), 7.08–7.05 (m, 3H), 4.26 (t, J = 6.3 Hz, 2H), 3.38 (t, J = 6.3 Hz, 2H), 2.51 (t, J = 7.7 Hz, 2H), 2.24 (t, J = 7.5 Hz, 2H), 1.61–1.50 (m, 4H), 1.32–1.16 (m, 2H); ¹³C NMR

 $(CDCl_3)~\delta$ 173.15, 142.37, 128.32, 128.21, 125.62, 63.53, 35.64, 33.93, 30.98, 28.73, 28.60, 24.69; GC/MS $\it{m/z}$ 298 (M+ for ^{79}Br). Anal. Calcd for $C_{14}H_{19}BrO_2$: C, 56.20; H, 6.40. Found: C, 56.04; H, 6.55.

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Supporting Information Available: Detailed experimental procedures and spectral and analytical data for products. This material is available free of charge via the Internet at http://pubs.acs.org.

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