A Novel Type of Dyotropic Rearrangement. Palladium-Catalyzed Rearrangement of Alkoxymethyl-Substituted Silanes to Alkyl Silyl Ethers

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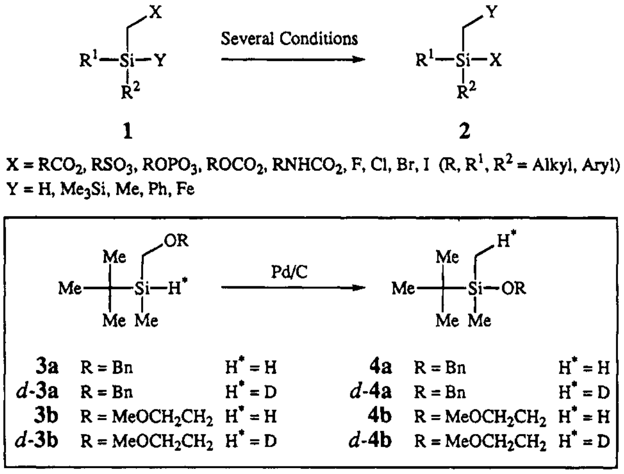
The treatment of alkoxymethyl-substituted hydrosilanes with palladium on charcoal gave rise to the corresponding alkyl silyl ethers by the migration of the silicon-bound hydrogen atom to the α-carbon atom and of the alkoxy group to the silicon center. Kinetic investigations revealed that two parallel reactions are involved in the rearrangement: an intramolecular reaction, following pseudo-first-order kinetics and showing an inverse kinetic deuterium isotope effect, is dominant in the initial phase of the transformation, and an intermolecular reaction becomes important in the later course of the transformation. The dominant reaction in the first phase of the transformation has to be classified as a dyotropic arrangement of type I, due to the intramolecular course and the reaction order, and it represents the first catalyzed example of a rearrangement of this type.

Introduction

Acetoxymethyl silanes of type **1** (Y = H, X = $MeCO_2$) are known to undergo dyotropic rearrangements[2,3] to the corresponding silyl acetates **2** (Y = H, X = $MeCO_2$) by simultaneous migration of a silicon-bound hydrogen atom to the adjacent carbon atom and of an acetoxy group to the silicon center[4-9] (Scheme 1). Similar rearrangements—proceeding by thermal means[9-14] or by the action of Lewis acids[15] or induced by nucleophiles or bases[16-22] or by radicals[5]—were observed with other compounds of type **1**, where a hydrogen atom, a silyl, an alkyl, or an aryl group migrates to the α-carbon atom with displacement of an acetoxy or another good leaving group.

Scheme 1



1 **2**

X = RCO_2, RSO_3, $ROPO_3$, $ROCO_2$, $RNHCO_2$, F, Cl, Br, I (R, R^1, R^2 = Alkyl, Aryl)
Y = H, Me_3Si, Me, Ph, Fe

3a	R = Bn	H* = H	**4a**	R = Bn	H* = H
d-**3a**	R = Bn	H* = D	*d*-**4a**	R = Bn	H* = D
3b	R = $MeOCH_2CH_2$	H* = H	**4b**	R = $MeOCH_2CH_2$	H* = H
d-**3b**	R = $MeOCH_2CH_2$	H* = D	*d*-**4b**	R = $MeOCH_2CH_2$	H* = D

In the course of our continuing investigations concerning the synthesis and the use of silicon-based chiral auxiliaries,[23,24] we encountered a similar reaction, namely, the palladium-catalyzed mild transformation of alkoxymethyl-substituted silanes of type **3** to alkyl silyl ethers of type **4**, which is a process that cannot be performed thermally but nevertheless could follow a intramolecular course similar to the dyotropic rearrangement. The results of a thorough study of the reaction, including kinetic measurements and the determination of kinetic isotope effects, are presented in the following paper.

Results and Discussion

The hydrosilanes **3a,b** and the corresponding deuteriosilanes *d*-**3a** and *d*-**3b** utilized in our investigation were

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prepared by successive substitution of the three chloro groups of commercially available dichloro(chloromethyl)-methylsilane, according to a reaction scheme described earlier.[23] For the preparation of the deuterated silanes *d*-**3a** and *d*-**3b**, the procedure was slightly modified: the labeled products were obtained with high isotopic purity, >95% as determined by mass spectrometry (MS), by reduction of the respective chloro- and alkoxysilane precursors with $LiAlD_4$ (>99% isotopically pure) instead of $LiAlH_4$.

Treatment of the silanes **3a,b** with Pd/C (10%)[25] in dry pentane for several hours at ambient temperature—the reaction of **3b** being characteristically more rapid than that of **3a**—delivered, after chromatography, the respective silyl ethers **4a,b** in 70 and 60% yield (Scheme 1), together with the corresponding silanols (20–30%). Similar yields on rearranged products were obtained with *d*-**3a** and *d*-**3b** as the starting materials. Surprisingly, however, these isotopically labeled silanes did not lead exclusively to the corresponding deuteriomethyl-substituted silyl ethers *d*-**4a** and *d*-**4b**, as would be expected for a single-step intramolecular reaction, but rather to mixtures of deuterated and nondeuterated products of type **4** in ratios of approximately 1.5:1. This finding suggested that, at least partially, a multistep intermolecular reaction path has to be involved in the formation of the rearranged products. The participation of such an intermolecular reaction was supported by the result of a cross experiment: the reaction of a mixture of the nondeuterated (benzyloxy)methyl-substituted silane **3a** and the deuterated (2-methoxyethoxy)methyl-substituted compound *d*-**3b** afforded, along with **4a,b** and *d*-**4b**, the deuterated silyl ether *d*-**4a** as well, which can only arise from an intermolecular process by deuterium transfer either from *d*-**3b** directly or via a mediator. The rearrangement reaction of compounds of type **3** to products of type **4**, however, is not purely intermolecular, as a closer examination revealed.

It became rapidly evident that at least two parallel reactions have to be involved in the formation of the rearrangement products, namely, an intramolecular reaction, being dominant in an initial phase of the transformation, and an intermolecular reaction, becoming more important in the later course of the rearrangement. This could be shown with the investigation of the kinetics of the reactions and, by means of the deuterated rearrangement precursors, with the evaluation of the isotopomeric compositions of the product mixtures. When several samples were drawn in defined time intervals from the reaction mixture containing, *e.g.*, **3a** or *d*-**3a**, and when these samples were examined by quantitative gas chromatography (GC) and by GC–MS, it was found that the rearrangement follows at first pseudo-first-order kinetics (*cf.* Figure 1, linear portion of the graph $\ln([3]_t/[3]_0)$ *vs* reaction time (t)), from which it departs markedly after approximately 50–60 min. The kinetics obtained by the separate investigations of

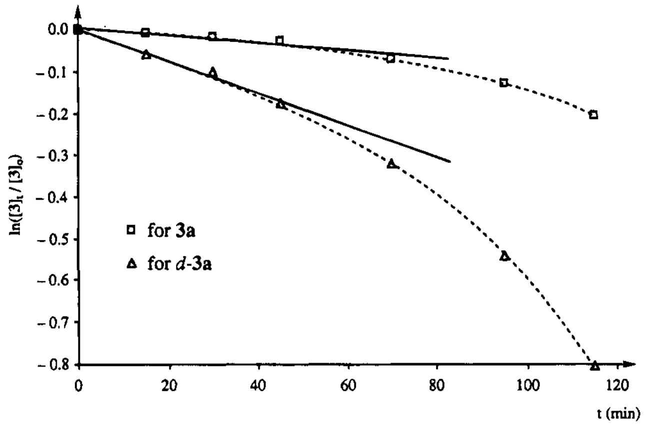

Figure 1. Plots of $\ln([3]_t/[3]_0)$, which should correspond to $-kt$ for a reaction of first order, *vs* the reaction time (t) for the separately investigated conversions of the silanes **3a** and *d*-**3a**.

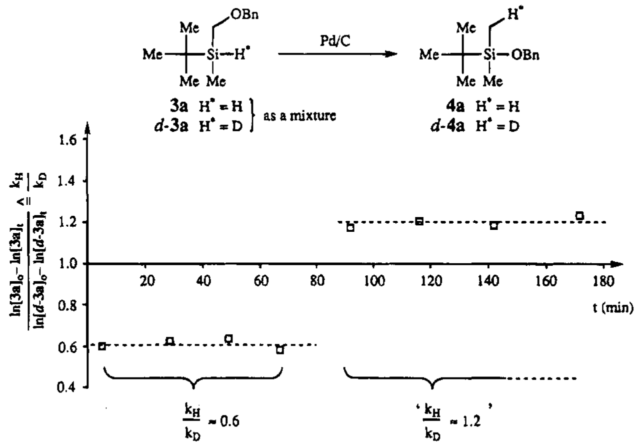

Figure 2. Determination of the kinetic deuterium isotope effect by plotting the values $(\ln[\mathbf{3a}]_0 - \ln[\mathbf{3a}]_t)/(\ln[d\text{-}\mathbf{3a}]_0 - \ln[d\text{-}\mathbf{3a}]_t)$, which should correspond to k_H/k_D for a reaction of first order, *vs* the reaction time (t). The reaction was performed with a 1:1 molar mixture of **3a** and *d*-**3a**, and the respective concentrations were determined by the combined analysis of samples by quantitative GC and GC–MS.

3a and *d*-**3a** implied additionally an inverse kinetic deuterium isotope effect ($k_D > k_H$), as recognized by the faster consumption of the deuteriosilane as compared to the hydrosilane (Figure 1). The GC–MS analysis further revealed the almost exclusive formation of the deuterated product *d*-**4a** in the starting phase of the reaction, the nondeuterated product **4a** not being formed until later in the course of the reaction.

An inverse kinetic deuterium isotope effect could indeed be ascertained ($k_H/k_D \approx 0.6$, with $k_H = 5.0 \times 10^{-5}$ s^{-1} and $k_D = 8.3 \times 10^{-5}$ s^{-1}) for the intramolecular portion of the transformations of **3a** and *d*-**3a** by interpretation of kinetic experiments performed with the mixture of the two compounds on the basis of a first-order reaction. The graph in Figure 2—obtained by plotting the value of $(\ln[\mathbf{3a}]_0 - \ln[\mathbf{3a}]_t)/(\ln[d\text{-}\mathbf{3a}]_0 - \ln[d\text{-}\mathbf{3a}]_t)$, which should correspond to k_H/k_D for reactions of first order *vs* the reaction time—reveals not only the isotope effect but, again, also demonstrates that, after an initial reaction period of approximately 50 min ($k_H/k_D \approx 0.6$), the mechanism of the reaction changes ("k_H/k_D" ≈ 1.2). The kinetic isotope effect obtained for the second period of the transformation can, of course, only

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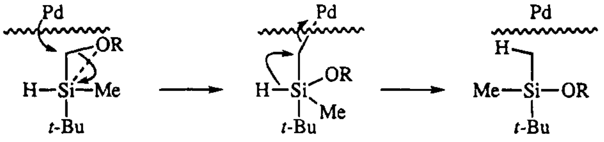
[25] Similar results, concerning the reaction rate and the chemical yields, were obtained by the utilization of different concentrations of palladium catalysts on charcoal (the reaction rate was approximately proportional to the palladium content of the catalyst). On the other hand, the application of the transition metal on carriers others than carbon (SiO_2 $CaCO_3$), of the homogeneous catalysts $(Ph_3P)_4Pd$, or of other transition-metal catalysts based on nickel or platinum, gave rise to no or only negligible transformation. To show that the reaction is not catalyzed by charcoal (the carrier material of the palladium catalyst), the hydrosilanes were treated with transition-metal-free activated charcoal, and no reaction was observed.

be acknowledged as a qualitative measure. It demonstrates, however, that a "normal" kinetic deuterium isotope effect would be obtained for the pure intermolecular portion of the reaction.

Inverse kinetic isotope effects are rather rare, and several attempts for their rationalization have been undertaken.[26-37] Davis et al. have explained such effects for heterogeneously catalyzed reactions[30] by the contribution of an inverse thermodynamic isotope effect, originating in a preferred adsorption of the deuteron-labeled substrate to the catalyst, to the overall kinetic rate expression of the multistep reaction consisting of diffusion of the reactant ot the catalyst, adsorption on the catalyst surface, chemical transformation, desorption from the catalyst surface, and, finally, diffusion of the product away from the catalyst. A similar explanation might be applicable for the intramolecular palladium-catalyzed rearrangement of compounds of type **3** as well. That the rate or the degree of adsorption to the catalyst is important for the overall rate of the rearrangement of **3** to **4** seems evident from the difference in the reaction rates observed with the compounds **3a** and **3b**, the latter reacting considerably faster, most probably due to the better adsorption at the surface of the catalyst because of the two oxygen atoms in the alkoxymethyl substituent.

Hence, the reaction of the "first-order" portion of the rearrangement, as deduced from the results described above, possibly consists of a fast and reversible adsorption of the substrate to the catalyst, on the surface of which intramolecular [1,2][1,2]-shifts of the alkoxy and the hydrogen groups occur. The manner by which the rearrangement is accelerated by the transition metal is still unclear. However, the intermediary complete cleavage of the H−Si bond by dissociative chemisorption of the hydrosilane to the metal, as proposed as a possibility for the transition-metal-catalyzed formation of silyl ethers from hydrosilanes and alcohols,[38] can be excluded: *e.g.*, the transformation of **3a** in presence of deuteron-saturated catalyst did not lead to incorporation of deuterium in the rearrangement product. A plausible mechanism could involve the formation of an intermediary pentacoordinated species of type **5** by a palladium-assisted [1,2]-shift of the alkoxy group to the silicon center, followed by a [1,2]-hydride shift to the α-position and simultaneous reductive elimination of the transition metal (Scheme 2). Independent of the exact mechanism, because of the purely intramolecular character of the reaction, this palladium-catalyzed conversion of alkoxymethyl-substituted silanes of type **3** to alkyl silyl ethers of type **4** represents an example, and to the best of our knowledge the first example, of a transition-metal-catalyzed dyotropic rearrangement of type I.

Scheme 2



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The mechanism of the dominant reaction in the second period of the transformations remains equivocal and is still under investigation: the results of the kinetic investigations obtained so far suggest a autocatalyzed intermolecular reaction course, where in the rate-determining step the H−Si bond is cleaved. The intermolecular mechanism and the reaction kinetics of higher order do not allow us to classify such a transformation as a dyotropic rearrangement.

Experimental Section

General Considerations. All organic sulvents were distilled prior to use, and the solvents used for reactions were additionally dried according to standard procedures. All reactions were carried out under an argon atmosphere. Column chromatography was performed on Merck 60 silica gel (40−63 μm). IR spectra were measured on a Perkin-Elmer 792; the samples were taken as neat liquid films between sodium chloride plates, and data are given in $\tilde{\nu}$ (cm^{-1}) with vs (very strong), s (strong), m (middle), w (weak), and vw (very weak) with respect to the most intense absorption. ^1H NMR spectra were measured at 300 MHz in $CDCl_3$ on a Bruker AC 300; δ (ppm) values are relative to $CHCl_3$ (δ 7.26) with J in Hz, and multiplicities are denoted as s = singlet, d = doublet, t = triplet, and m = multiplet. ^{13}C NMR spectra were measured at 50.4 MHz in $CDCl_3$ on a Varian XL 200; δ (ppm) values are relative to $CDCl_3$ (δ 77.0). Multiplicities were obtained from DEPT experiments. MS data were measured on a Finnigan MAT SSQ 700 in the chemical ionization (CI) mode with NH_3 as the reactant gas; data are given in *m/z* (relative abundance in percent).

[(Benzyloxy)methyl]-*tert*-butylmethyldeuteriosilane (*d*-3a). A solution of 348 mg (1.57 mmol) of [(benzyloxy)methyl]-*tert*-butylmethylsilane (**3a**)[23] in 5 mL of CCl_4 was cooled to −25 °C and treated with Cl_2 until the color persisted. The excess Cl_2 was immediately removed with a stream of N_2 and the solvent completely evaporated *in vacuo*. After the residue was dissolved in 5 mL of THF, 96 mg (2.29 mmol) of $LiAlD_4$ (99% isotopically pure) was added at 0 °C; then the mixture was stirred at 25 °C for 24 h. It was quenched at 0 °C with 3 N HCl solution and extracted with Et_2O to give after chromatography (hexane) 280 mg (80%) of *d*-**3a** as a colorless oil. IR: 3084 w, 3060 w, 3025 m, 2945 vs, 2922 vs, 2878 s, 2850 vs, 2810 m, 2000−1700 vw, 1532 s (Si−D), 1492 w, 1458 s, 1430 m, 1376 m, 1360 m, 1300 w, 1248 m, 1200 w, 1105 s, 1090 s, 1071 s, 1027 m, 1007 m, 980 w, 936 m, 902 w, 831 vs, 800 s, 777 s, 732 vs, 715 s, 695 vs. ^1H NMR: 7.37−7.26 (m, 5 arom H), 4.49 (s, $PhCH_2O$), 3.32, 3.29 (AB, J = 13.0, $SiCH_2O$), 0.96 (s, $(CH_3)_3CSi$), 0.10 (*s*, CH_3Si). ^{13}C NMR: 138.7 (s, arom C), 128.3, 127.6, 127.4 (3d, arom CH), 77.0 (t, $PhCH_2O$), 60.0 (t, $SiCH_2O$), 27.2 (*q*, $(CH_3)_3CSi$), 15.9 (s, $(CH_3)_3CSi$), −10.0 (q, CH_3Si). MS: 241 (100, $[M + NH_4]^+$, 223 (5), 183 (10), 148 (89), 108 (24). Anal. Calcd for $C_{13}H_{21}DOSi$ (M_r = 223.394): C, 69.90; H, 9.98 (corrected for D content). Found: C, 69.94; H, 10.19.

***tert*-Butyl[(2-methoxyethoxy)methyl]methyldeuteriosilane (*d*-3b).** To a solution of 2.01 g (7.12 mmol) of bis-

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(2-methoxyethoxy)[(2-methoxyethoxy)methyl]methylsilane[23] in 25 mL of Et_2O at 0 °C was added 5.7 mL of a *t*-BuLi solution (*ca.* 1.5 M in pentane, corresponding to *ca.* 8.6 mmol), and, after 10 min, 360 mg (8.59 mmol) of $LiAlD_4$ (99% isotopically pure). After 2 h, the mixture was poured on 10% HCl/ice and extracted with Et_2O to give after chromatography (pentane/Et_2O 40:1) 608 mg (45%) of *d*-**3b** as a colorless oil. IR: 2949 vs, 2927 vs, 2880 vs, 2853 vs, 2812 s, 1535 s (Si−D), 1461 s, 1433 m, 1390 w, 1362 s, 1336 w, 1300 w, 1249 s, 1197 m, 1133 vs, 1107 vs, 1025 m, 1008 m, 982 w, 939 w, 868 w, 832 vs, 802 vs, 780 vs, 716 s, 688 s. ^{1}H NMR: 3.58−3.50 (m, OCH_2CH_2O), 3.37 (s, CH_3O), 3.37, 3.31 (AB, J = 13.1, $SiCH_2O$), 0.95 (s, $(CH_3)_3CSi$), 0.08 (s, CH_3Si). ^{13}C NMR: 74.4 (t, $SiCH_2OCH_2CH_2$), 71.8 (t, $SiCH_2OCH_2$), 61.2 (t, $SiCH_2O$), 59.0 (q, CH_3O), 27.1 (q, $(CH_3)_3CSi$, 15.8 (s, $(CH_3)_3CSi$), −10.1 (q, CH_3Si). MS: 209 ($[M + NH_4]^+$). Anal. Calcd for $C_9H_{21}DO_2Si$ (M_r = 191.349): C, 56.49; H, 11.65 (corrected for D content). Found: C, 56.73; H, 10.63.

Standard Conditions for the Rearrangement Reaction. To a stirred 0.064 M solution of hydro- and deuteriosilane in dry pentane at 25 °C was added catalyst (10% by weight). After completion of the reaction, which was controlled by TLC or GC, the catalyst was filtered off, the solvent was evaporated, and the product was chromatographed with the eluent system specified below.

(Benzyloxy)-*tert*-butyldimethylsilane (4a). The rearrangement of 108 mg (0.49 mmol) of **3a**[23] afforded, after chromatography (pentane), 75 mg (70%) of **4a** as a colorless oil. This compound was identical with a sample obtained by treatment of 503 mg (3.34 mmol) of *tert*-butylchlorodimethylsilane with 144 mg (1.33 mmol) of benzyl alcohol and 487 mg (4.81 mmol) of NEt_3 in 5 mL of Et_2O, giving rise to 113 mg (38%) of **4a**, after acidification of the mixture with $AcOH/H_2O$, extraction with Et_2O, and chromatography of the crude product. IR: 3085 w, 3063 w, 3028 w, 2955 vs, 2928 vs, 2885 s, 2855 vs, 2000−1700 vw, 1494 w, 1460 s, 1387 m, 1374 m, 1358 m, 1303 w, 1252 vs, 1206 s, 1108 vs, 1096 vs, 1068 vs, 1026 s, 1005 s, 937 w, 898 w, 837 vs, 812 s, 774 vs, 726 vs, 695 vs, 665 s. ^{1}H NMR: 7.37−7.21 (m, 5 arom H), 4.76 (s, $PhCH_2O$), 0.95 (s, $(CH_3)_3CSi$), 0.11 (s, $(CH_3)_2Si$). ^{13}C NMR: 141.4 (s, arom C), 128.2, 126.9, 126.0 (3d, arom CH), 65.0 (t, OCH_2Ph), 26.0 (q, $(CH_3)_3CSi$), 18.4 (s, $(CH_3)_3CSi$), −5.2 (q, $(CH_3)_2Si$). MS: 240 (75, $[M + NH_4]^+$), 223 (8, $[M + H]^+$), 132 (14), 108 (100). Anal. Calcd for $C_{13}H_{22}OSi$ (M_r = 222.402): C, 70.21; H, 9.97. Found: C, 70.23; H, 9.89.

(Benzyloxy)-*tert*-butyl(deuteriomethyl)methylsilane (*d*-4a). The rearrangement of 87.9 mg (0.39 mmol) of *d*-**3a** afforded, after chromatography (pentane), 61.5 mg (70%) of a mixture of *d*-**4a** and **4a** (ratio 1.3:1) as a colorless oil. IR, ^{1}H NMR, and ^{13}C NMR spectra of the mixture are almost identical with those of **4a**. IR: additional signal at 1163 m. ^{1}H NMR: additional signal at 0.09 (t, J = 2.2, DCH_2Si). MS: 241 (100), 240 (66), 224 (12), 223 (7).

***tert*-Butyl(2-methoxyethoxy)dimethylsilane (4b).** The rearrangement of 71 mg (0.37 mmol) of **3b**[23] afforded, after chromatography (pentane/Et_2O 25:1), 42 mg (59%) of **4b** as a colorless oil. This compound was identical with a sample obtained by treatment of 490 mg (3.25 mmol) of *tert*-butylchlorodimethylsilane with 131 mg (1.72 mmol) of 2-methoxyethanol and 513 mg (5.07 mmol) of NEt_3 in 5 mL of Et_2O, giving rise to 174 mg (53%) of **4b**, after acidification of the mixture with $AcOH/H_2O$, extraction with Et_2O, chromatography of the crude product, and bulb-to-bulb distillation (100 °C (air bath temperature)/25 mbar). IR: 2955 vs, 2928 vs, 2883 s, 2856 vs, 2817 w, 1461 m, 1386 vw, 1360 w, 1294 vw, 1255 s, 1199 m, 1144 s, 1108 vs, 1026 w, 1005 w, 950 m, 937 m, 834 vs, 810 m, 775 vs, 715 w, 660 m; ^{1}H NMR 3.76 (t, J = 5.2, $SiOCH_2$), 3.46 (t, J = 5.2, $SiOCH_2CH_2$), 3.38 (s, CH_3O), 0.90 (s, $(CH_3)_3CSi$), 0.07 (s, $(CH_3)_2Si$). ^{13}C NMR: 74.1 (t, $SiOCH_2CH_2$), 62.6 (t, $SiOCH_2$), 59.0 (q, CH_3O), 25.9 (q, $(CH_3)_3CSi$), 18.4 (s, $(CH_3)_3CSi$), −5.3 (*q*, $(CH_3)_2Si$). MS: 208 (100, $[M + NH_4]^+$), 191 (27, $[M + H]^+$), 132 (15). Anal. Calcd for $C_9H_{22}O_2Si$ (M_r = 190.357): C, 56.79; H, 11.65. Found: C, 56.85; H, 11.91.

***tert*-Butyl(deuteriomethyl)(2-methoxyethoxy)methylsilane (*d*-4b).** The rearrangement of 100 mg (0.52 mmol) of *d*-**3b** afforded, after chromatography (pentane/Et_2O 30:1), 60.3 mg (60%) of a mixture of *d*-**4b** and **4b** (ratio ~1.6:1) as a colorless oil. IR, ^{1}H NMR, and ^{13}C NMR spectra of the mixture are almost identical with those of **4b**. IR: additional signal at 1164 m. ^{1}H NMR: additional signal at 0.05 (t, J = 2.2, DCH_2Si). MS: 209 (100), 208 (56).

Kinetic Measurements. The reactions were carried out in the presence of undecane or tetradecane as an internal standard for quantitative GC analysis. The samples taken from the reaction mixture were filtered through a plug of cotton and analyzed by quantitative GC (Carlo Erba Strumentazione Serie 4160; column DB-1 (J & W), length 15 m, diameter 0.25 mm, film 0.25 μm, $p(H_2)$ = 0.8 kg/cm^2, p(air) = 1.2 kg/cm^2, p(carrier) = 0.4 kg/cm^2). Retention times: isothermal condition at 110 °C, **3a**/*d*-**3a** (9.35 min), **4a**/*d*-**4a** (6.96 min), tetradecane (8.63 min); at 70 °C, **3b**/*d*-**3b** (6.58 min), **4b**/*d*-**4b** (4.41 min), undecane (7.16 min). The samples were also analyzed by GC−MS (Varian GC, column DB-5 (J & W), length 30 m, diameter 0.25 mm, film 0.25 μm, p(He) = 14.5 psi). Retention times: temperature program (100 °C for 2 min followed by gradient 10 °C/min up to 200 °C), **3a**/*d*-**3a** (8.10 min), **4a**/*d*-**4a** (7.20 min); isothermal conditions at 100 °C, **4a**/*d*-**4a** (8.18 min), **4b**/*d*-**4b** (2.80 min). The results of the kinetic experiments are shown graphically in Figures 1 and 2.

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