

NEW ONE CARBON HOMOLOGATION REAGENTS UTILIZING ELECTROCHEMICAL OXIDATION OF ORGANOSILICON COMPOUNDS¹

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Abstract: Phenylthio(trimethylsilyl)methane, phenylthiobis(trimethylsilyl)methane, methoxy(trimethylsilyl)methane, and methoxybis(trimethylsilyl)methane are deprotonated and the resulting anions are alkylated with electrophiles such as organic halides. The alkylation products are readily converted into the corresponding dimethyl acetals or methyl esters by electrochemical oxidation in methanol.

Organosilicon compounds are widely utilized as useful intermediates in organic synthesis.² One of the most important concepts in organosilicon chemistry is so called " β -effects", the ability of silyl groups to promote the formation or development of carbocations β to silicon.³ Recent studies on electron transfer reactions of organosilicon compounds indicate that silyl groups also promote the formation of β cation radical species of heteroatoms.⁴ Most recently we have disclosed that β -silicon effect for electron transfer reactions is mainly ascribed to the rise of the HOMO level by the interaction of the carbon-silicon bonding orbital and the nonbonding p orbital of the heteroatom.⁵ On the basis of this concept we have developed electrochemical oxidation reactions of organosilicon compounds containing a heteroatom such as oxygen⁶ and sulfur⁷ β to silicon. Anodic oxidation of such compounds results in selective cleavage of the carbon-silicon bond and introduction of an oxygen nucleophile onto the carbon.

Another important property of silicon is stabilization of carbanion α to silicon. Various types of carbanions stabilized by the adjacent silicon atom have been developed and utilized in organic synthesis.⁸

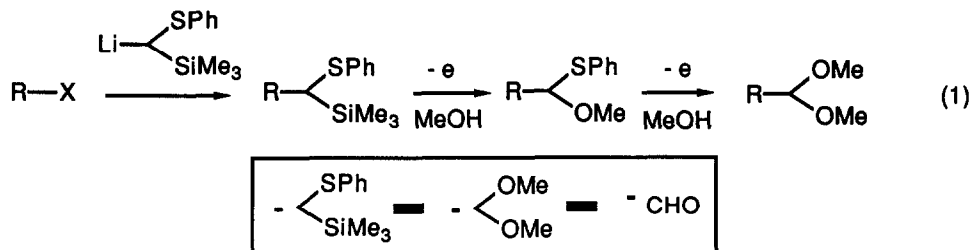
In this paper we wish to describe new one carbon homologation reagents based upon the concepts of both β -silicon effect for electron transfer reactions and silicon stabilization of α carbanion.

Results and Discussion

Phenylthio(trimethylsilyl)methane.

Phenylthio(trimethylsilyl)methane is known to be readily deprotonated with n-butyllithium and the resulting carbanion α to silicon reacts with various electrophiles such as organic halides to give the corresponding alkylation products.⁹ We found that the resulting 1-phenylthio-1-trimethylsilylalkanes were oxidized effectively by the electrochemical method in methanol to give the corresponding dimethyl acetals which are protected form of aldehydes (eq 1). Thus phenylthio(trimethylsilyl)methane provides a synthon¹⁰ of 1,1-dialkoxymethyl anion. Since acetals are readily hydrolyzed to aldehydes, it also provides a synthon of formyl anion.

Although silyl substitution causes rather small decrease in oxidation potentials of sulfides (about 0.1 V), the fate of the initially formed cation radical species seems to be controlled by the facile cleavage of the carbon-silicon bond. The radical thus obtained is further oxidized on the anode to give the carbocation which is trapped by methanol producing the 1-methoxy-1-phenylthioalkane. The carbon-sulfur bond is then cleaved by further electrolysis to give dimethyl acetals as the final products.¹¹ As a matter of fact, 1-methoxy-1-phenylthio-



alkane was obtained as a major product together with a small amount of 1,1-dimethoxyalkane after electricity of 2.0 F/mol was consumed.

Applications of the present method to some electrophiles are listed in Table 1. Alkyl halides, allyl halides, and epoxides are effective as the electrophile. Functional groups such as free hydroxyl and alkoxycarbonyl groups, and carbon-carbon double bonds tolerate under the electrolytic conditions. The electrochemical oxidation in the presence of a diol such as 1,2-dihydroxyethane and 1,3-dihydroxypropane in acetonitrile afforded the corresponding cyclic acetals.

Conversion of 1-phenylthio-1-trimethylsilylalkanes into the corresponding aldehydes can also be accomplished by chemical oxidizing agents such as MCPBA.⁹ The reaction probably proceeds via initial formation of thermally unstable sulfoxide which undergoes a facile sila-Pummerer rearrangement. Although this chemical reaction is quite useful for the synthesis of aldehydes, the present electrochemical reaction provides a direct access to the protected form of aldehydes under neutral conditions. Closely related one carbon homologation reagent, methoxy(phenylthio)(trimethylsilyl)methane has also been reported.¹² After the alkylation chemical oxidation of this synthon gives aldehydes, carboxylic acids, and acylsilanes.

Phenylthiobis(trimethylsilyl)methane.

Phenylthiobis(trimethylsilyl)methane, which has an additional silyl group was also found to be a useful reagent for homologation. Phenylthiobis(trimethylsilyl)methane was readily prepared by lithiation of phenylthio(trimethylsilyl)methane followed by the treatment with chlorotrimethylsilane.

The alkylation of phenylthiobis(trimethylsilyl)methane was accomplished by deprotonation with *n*-butyllithium / TMEDA in hexane or *n*-butyllithium in THF followed by the treatment with alkyl halides (eq 2, Table 1). The electrochemical oxidation of the alkylation products, 1-phenylthio-1,1-bis(trimethylsilyl)alkanes proceeded smoothly in methanol to give the corresponding methyl esters. Therefore phenylthiobis(trimethylsilyl)methane provides a synthon of alkoxycarbonyl anion.

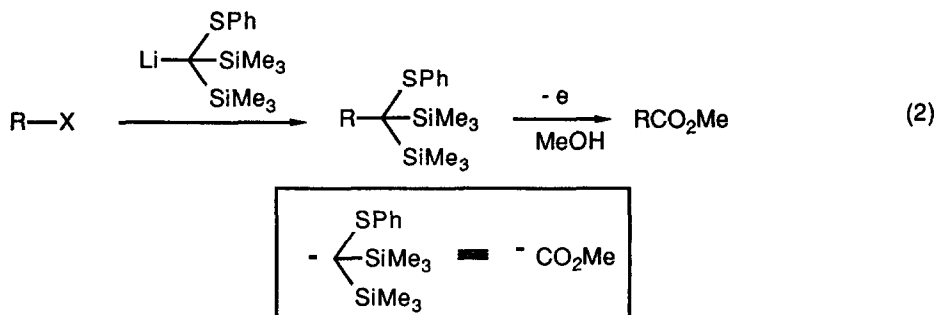

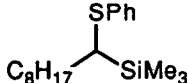
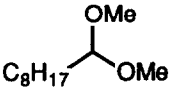
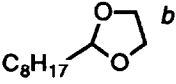
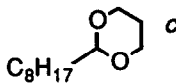


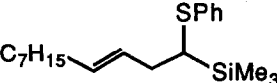
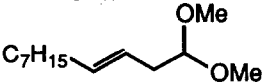
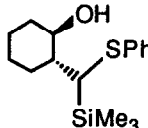
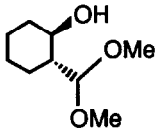
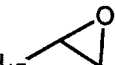
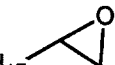
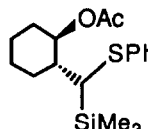
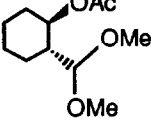
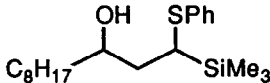
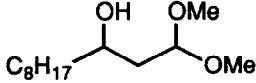

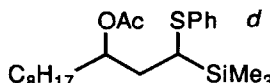
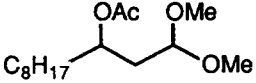
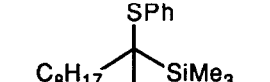

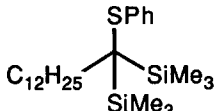
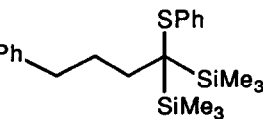


Table 1. One Carbon Homologation Reagents Containing Sulfur as Heteroatom

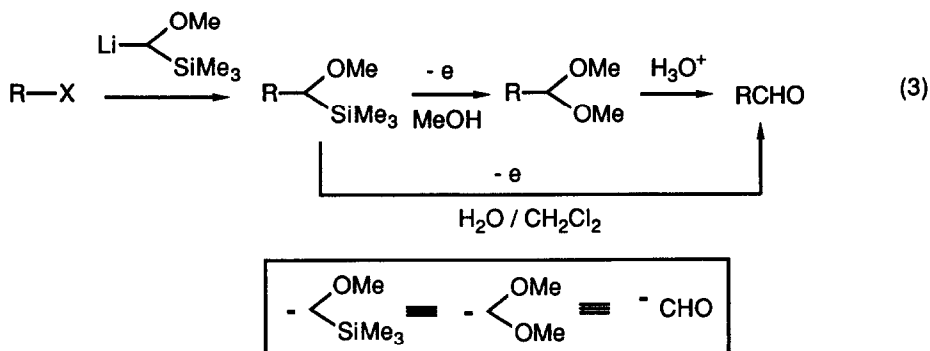
reagent	electrophile	alkylation product	%yield	acetal ^a	electricity F/mol	%yield
	C ₈ H ₁₇ Br		87		4.13	84
		 ^b	4.16	60		
		 ^c	4.61	46		
			98		4.21	64
			74		3.96	81
		 ^d			3.59	81
			91		4.15	65
	C ₈ H ₁₇ Br	 ^d			3.98	72
			73	C ₈ H ₁₇ CO ₂ Me	9.83	72
	C ₁₂ H ₂₅ Br		55	C ₁₂ H ₂₅ CO ₂ Me	11.5	81
			98	Ph-CH ₂ -CH ₂ -CH ₂ -CO ₂ Me	11.0	66

^a Anodic oxidation was carried out in methanol unless otherwise stated. ^b Carried out in the presence of 1,2-dihydroxyethane (18.5 equiv) in acetonitrile. ^c Carried out in the presence of 1,3-dihydroxypropane (14.2 equiv) in acetonitrile. ^d Synthesized by acetylation of the corresponding hydroxyl compound.

The following point is noteworthy. If the reaction proceed by a similar mechanism as that for 1-phenylthio-1-trimethylsilylalkanes, the orthoesters should be formed. However, such products were not detected at all in the electrochemical oxidation. A separate experiment revealed that orthoesters are rapidly hydrolyzed to the corresponding methyl esters in the medium that is used for the electrochemical reaction. Presumably a small amount of water in methanol and a significant amount of ionic species such as tetraethylammonium tosylate play important roles for the rapid hydrolysis. Therefore the initially formed orthoesters seem to be hydrolyzed almost spontaneously to the methyl esters under the electrochemical conditions.

Methoxy(trimethylsilyl)methane.

The organosilicon compounds having oxygen instead of sulfur as the heteroatom were also found to be effective homologation reagents. For example, methoxy(trimethylsilyl)methane was deprotonated by sec-butyllithium in THF¹³ and the resulting carbanion α to silicon was allowed to react with organic halides to give the alkylated products (eq 3, Table 2). The electrochemical oxidation in methanol resulted in facile cleavage of the carbon-silicon bond and the formation of dimethyl acetals which can be readily hydrolyzed to aldehydes by the treatment with acid. Direct conversion to aldehydes was also accomplished by the electrolysis in the presence of water in dichloromethane as solvent under neutral conditions. Thus methoxy(trimethylsilyl)methane provides a synthon of the dimethoxymethyl anion or the formyl anion.



The anion of methoxy(trimethylsilyl)methane also reacted smoothly with carbonyl compounds as reported by Magnus.¹⁴ It should be noted that the resulting 2-hydroxy-1-methoxy-1-trimethylsilylalkanes do not undergo Peterson elimination under the alkylation conditions, although the reaction of phenylthio(trimethylsilyl)methane and phenylthiobis(trimethylsilyl)methane with carbonyl compounds give olefinic products via Peterson elimination. 2-Hydroxy-1-methoxy-1-trimethylsilylalkanes were oxidized electrochemically in methanol without affecting the free hydroxyl group to give the corresponding dimethyl acetals. After protection of the hydroxyl group acid-catalyzed hydrolysis afforded α -benzyloxy aldehydes in high yields (eq 4). Methoxy-(dimethylphenylsilyl)methane can also be utilized in a similar fashion (Table 2).

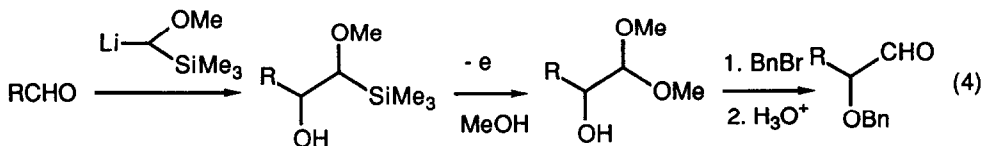


Table 2. One Carbon Homologation Agents Containing Oxygen as Heteroatom.

reagent	electrophile	alkylation product	%yield	acetal ^a	electricity F/mol	%yield
	C ₁₂ H ₂₅ Br		74		2.13	79
	C ₇ H ₁₅ CHO		78		2.95	87
	C ₇ H ₁₅ CHO		82		2.49	74
			^b		2.64	84
	C ₁₂ H ₂₅ Br		78	C ₁₂ H ₂₅ CO ₂ Me	4.00	92
	Ph-CH ₂ -CH ₂ -CH ₂ -Br		99	Ph-CH ₂ -CH ₂ -CH ₂ -CO ₂ Me	4.00	91
	Ph-CH ₂ -CH ₂ -Cl		98			
	CH ₂ =CH-(CH ₂) ₉ -Br		92	CH ₂ =CH-(CH ₂) ₉ -CO ₂ Me	4.00	75
	THPO(CH ₂) ₃ I		89	THPO(CH ₂) ₃ CO ₂ Me ^c	4.90	58
	Ph-CH ₂ -Br		67	Ph-CH ₂ -CO ₂ Me	4.00	80
	C ₈ H ₁₇ -epoxide		98	C ₈ H ₁₇ -CH(OH)-CO ₂ Me	4.00	92

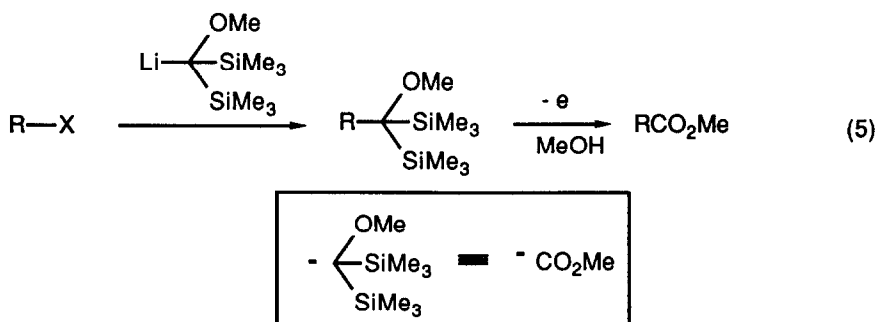
^a Anodic oxidation was carried in methanol. ^b Synthesized from the corresponding hydroxyl compound. ^c The anodic oxidation was carried out in the presence of a small amount of pyridine.

Conversion of 2-hydroxy-1-methoxy-1-trimethylsilylalkanes into the corresponding aldehydes via Peterson elimination has been developed by Magnus.^{13a} The present method provides, however, a direct method for the conversion to the aldehydes having a hydroxyl group at α position.

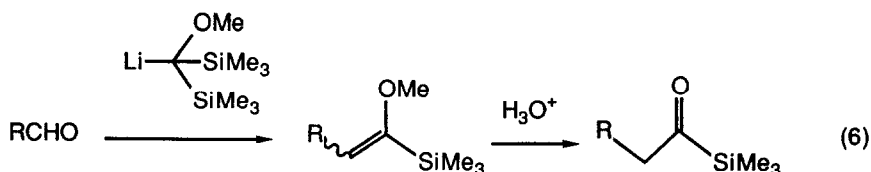
Methoxybis(trimethylsilyl)methane.

Methoxybis(trimethylsilyl)methane was readily prepared by the treatment of methoxy(trimethylsilyl)methylithium with chlorotrimethylsilane. It should be noted that methoxybis(trimethylsilyl)methane is more easily oxidized than methoxy(trimethylsilyl)methane. Difference in oxidation potential is about 0.3 V.

Deprotonation of methoxybis(trimethylsilyl)methane was readily accomplished by the treatment with *n*-butyllithium which is a less strong base than *sec*-butyllithium. Higher acidity of the methine proton due to the additional α silyl group seems to be responsible for easier deprotonation. The resulting anion was allowed to react with alkyl halides to obtain the alkylation products in high yields (eq 5, Table 2). Although alkyl iodides and bromides reacted smoothly at -78 °C, the reaction with alkyl chlorides were extremely slow at this temperature and required much higher temperature (0 °C to room temperature). Thus 1-bromo-3-chloropropane was selectively converted into 4-chloro-1-methoxy-1,1-bis(trimethylsilyl)butane without affecting chloride moiety (92%). Methoxybis(trimethylsilyl)methylithium also reacted with terminal epoxides to give 3-hydroxy-1-methoxy-1,1-bis(trimethylsilyl)alkanes. Cyclic epoxides such as cyclohexene oxide, however, were inactive under similar conditions.



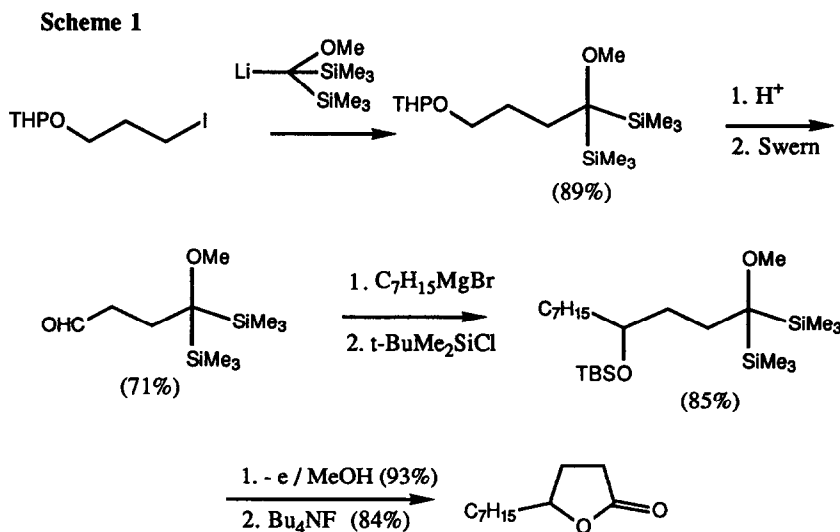
The reaction of methoxybis(trimethylsilyl)methylithium with aldehydes did not give the desired 2-hydroxy-1-methoxy-1,1-trimethylsilylalkanes, but gave 1-methoxy-1-trimethylsilyl-1-alkenes which can be readily converted into the corresponding acylsilanes (eq 4).¹⁴ Probably an additional silyl group promotes the Peterson elimination.



The electrochemical oxidation of 1-methoxy-1,1-bis(trimethylsilyl)alkanes took place smoothly in methanol to give the corresponding methyl esters in high yields (eq 5). Presumably the initially formed orthoesters were hydrolyzed to the corresponding esters under the conditions. Since most of the starting material was usually

consumed after electricity of 4 F/mol (theoretical value) was passed, the current efficiency is very high. Thus methoxybis(trimethylsilyl)methane provides an effective synthon of the alkoxy carbonyl anion (eq 5).

The potentiality of the present methodology is demonstrated by the synthesis of γ -undecalactone (Scheme 1). The treatment of THP protected 1-hydroxy-3-iodopropane with methoxybis(trimethylsilyl)methyl lithium produced the corresponding alkylation product. Acidic removal of THP group followed by Swern oxidation gave the aldehyde which was allowed to react with hexylmagnesium bromide and the resulting alcohol was protected as tert-butyl dimethylsilyl ether. The electrochemical oxidation in methanol followed by the treatment with fluoride ion afforded γ -undecalactone. Compatibility of α -alkoxysilane moiety ($-C(Y)(OMe)SiMe_3$, Y = H or $SiMe_3$) toward acidic conditions such as removal of THP, basic conditions such as Grignard reactions, and chemical oxidations such as Swern oxidation should be noteworthy. Such compatibility together with its thermal stability allows synthetic reactions employing α -alkoxysilane moiety to be run under wide range of conditions. Mild reaction conditions (neutral, room temperature) and easy separation of the product from the volatile silicon containing byproduct are also advantageous. Therefore present methodology provides a powerful tool in organic synthesis.



Experimental

General. Glass-support precoated (Merck silica gel 60 F254, 0.25 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu gas chromatograph equipped with 2 m x 3 mm column packed with Silicone OV-1 (2%) on Chromosorb WAW DMCS. Proton NMR spectra were determined on a Hitachi R-90H spectrometer (90 MHz) unless otherwise stated. JEOL GX-400 (400 MHz) was also used. Infrared (IR) spectra were determined on a JASCO A-102 diffraction grating spectrophotometer. Mass spectra were determined on a JEOL JMS-D-300 or JMS-AX500 mass spectrometer. Ionization voltage was 70 eV.

Preparative electrolysis was carried out by using Kikusui Model PAB-32-0.5 or PAB 32-1.2A regulated DC power supply under constant current condition.

Phenylthio(trimethylsilyl)methane was prepared according to the literature.^{9b} Methoxy(trimethylsilyl)methane was used as obtained commercially (Shinetsu).

Alkylation of Phenylthio(trimethylsilyl)methane. Typical Procedure.⁹ To a solution of *n*-butyllithium / hexane (1.6M, 3.0 ml, 4.8 mmol) and TMEDA (0.6 ml, 4.0 mmol) in 5.0 ml of hexane was added phenylthio(trimethylsilyl)methane (504 mg, 2.57 mmol) at 0 °C. After being stirred at 0 °C for 5 h, 1-decene oxide (565 mg, 3.62 mmol) was added at this temperature. The mixture was stirred at 0 °C for 2 h and at room temperature for 1 h. Water was added and the organic layer was separated and dried over Na₂SO₄. After evaporation of the solvent the residue was purified via flash chromatography (hexane / ethyl acetate 19 : 1 to 9 : 1) to obtain 3-hydroxy-1-phenylthio-1-trimethylsilylundecane (827 mg, 91% yield). ¹H NMR spectrum indicated that the product was obtained as a mixture of two diastereomers (1 : 1) and they were characterized as the mixture. TLC Rf 0.46 (hexane / ethyl acetate 9 : 1); ¹H NMR (CDCl₃) δ 0.135 (s), 0.144 (s) total 9 H, 0.8 - 1.1 (m, 3 H), 1.1 - 1.6 (m, 17 H), 1.6 - 2.0 (m, 3 H), 2.5 - 2.9 (m, 1 H), 3.6 - 4.0 (m, 1 H), 7.1 - 7.6 (m, 5 H); IR (neat) 3400 (m, br), 3050 (w), 2950 (sh), 2920 (s), 2850 (m), 1580 (w), 1480 (m), 1460 (m), 1435 (m), 1245 (s), 840 (s), 740 (m), 690 (m) cm⁻¹; Low resolution MS m/e (%) 355 (M+3, 0.4), 354 (M+2, 2), 353 (M+1, 4), 352 (M, 13), 337 (6), 262 (32), 209 (34), 182 (20), 167 (20), 149 (36), 144 (26), 110 (32), 73 (100); High resolution MS Calcd for C₂₀H₃₆OSi: 352.2254. Found: 352.2247.

Electrochemical Oxidation of 1-Phenylthio-1-trimethylsilylalkanes. Typical Procedure. 3-Hydroxy-1-phenylthio-1-trimethylsilylundecane (72 mg, 0.204 mmol) and Et₄NOTs/MeOH (0.2 M, 1.0 ml) was placed in an undivided cell equipped with a carbon rod anode and a carbon rod cathode (i.d. 2 mm). Constant current (10 mA) was passed through the cell. After the electricity of 4.15 F/mol was passed the mixture was partitioned between NaHCO₃ and ether. The ether layer was separated and dried over Na₂SO₄. After evaporation of the solvent, the residue was purified via flash chromatography (hexane / ethyl acetate = 9 : 1 to 4 : 1) to obtain 3-hydroxy-1,1-dimethoxyundecane (31 mg, 65% yield). TLC Rf 0.17 (hexane / ethyl acetate = 9 : 1); ¹H NMR δ 0.75 - 1.0 (m, 3 H), 1.0 - 1.6 (m, 17 H), 1.6 - 1.85 (m, 2 H), 2.65 - 2.9 (br, 1 H), 3.35 (s, 3 H), 3.38 (s, 3 H), 3.55 - 3.9 (m, 1 H), 4.58 (t, *J* = 5.5 Hz, 1 H); IR (neat) 3420 (s, br), 2920 (s), 2850 (m), 1460 (m), 1380 (m), 1190 (m), 1110 (s), 1050 (s), 815 (m) cm⁻¹; Low resolution MS m/e (%) 231 (M-1, 0.2), 201 (3), 182 (8), 119 (11), 97 (15), 87 (29), 75 (100); High resolution MS Calcd for C₁₂H₂₅O₂ (M-MeO): 201.1855. Found: 201.1863.

Phenylthiobis(trimethylsilyl)methane. To a solution of *n*-butyllithium / hexane (1.6 M, 3.5 ml, 5.6 mmol) and TMEDA (1.0 ml, 6.6 mmol) in 5.0 ml of hexane was added phenylthio(trimethylsilyl)methane (756 mg, 3.85 mmol) at 0 °C. After being stirred at 0 °C for 1 h and 45 min chlorotrimethylsilane (0.76 ml, 5.99 mmol) was added at this temperature. After being stirred at 0 °C for 1 h and 45 min the mixture was partitioned between pentane and water. The organic layer was separated and dried over Na₂SO₄. After evaporation of the solvent, bulb-to-bulb distillation (about 200 °C/ 5 mmHg) afforded the title compound (970 mg, 94% yield). ¹H NMR (CDCl₃) δ 0.12 (s, 18 H), 1.51 (2, 1 H), 6.95 - 7.45 (m, 5 H); IR (neat) 3060 (w), 2950 (m), 2900 (w), 1580 (m), 1480 (m), 1250 (s), 1000 (m), 840 (s), 735 (m), 685 (m) cm⁻¹; Low resolution MS 271 (M+3,3), 270 (M+2, 15), 269 (M+1, 27), 268 (M, 100), 256 (2.5), 255 (11), 254 (19), 253 (76), 181 (17), 180 (21), 177 (27), 167 (33), 165 (76), 135 (28), 118 (28), 73 (92); High resolution MS Calcd for C₁₃H₂₄SSi₂: 268.1138. Found: 268.1149; Anal. Calcd for C₁₃H₂₄SSi₂ C: 58.14, H:9.01. Found C: 58.06, H: 9.05.

Alkylation of Phenylthiobis(trimethylsilyl)methane. Typical Procedure. Lithiation of phenylthiobis(trimethylsilyl)methane can be accomplished by the treatment with *n*-BuLi / TMEDA in hexane, but the following procedure seems to be more convenient. To a solution of phenylthiobis(trimethylsilyl)methane (358 mg, 1.33 mmol) in 5.0 ml of THF was added *n*-butyllithium / hexane (1.6 M, 0.75 ml, 1.20 mmol) at -78 °C. After being stirred at 0 °C for 15 min and at 0 °C for 0.5 h, 1-bromo-3-phenylpropane (193 mg, 0.969 mmol) was added at -78 °C. The mixture was warmed to room temperature and stirred at this temperature overnight. Water was added and the organic materials were extracted with ether and dried over Na₂SO₄. After evaporation of the solvent, the excess phenylthiobis(trimethylsilyl)methane was removed by bulb-to-bulb distillation (about 150 °C/1 mmHg). The residue was purified via flash chromatography (hexane / ethyl acetate 39 : 1) to obtain 1-phenylthio-1,1-bis(trimethylsilyl)-3-phenylpropane (368 mg, 98% yield). ¹H NMR (CDCl₃, 400 MHz) δ 0.01 (s, 18 H), 1.75 - 1.85 (m, 2 H), 2.1 - 2.25 (m, 2 H), 2.70 (t, *J* = 7.2 Hz, 2 H), 7.15 - 7.4 (m, 5 H); IR (neat) 3060 (w), 3025 (w), 2930 (m), 2900 (w), 2860 (w), 1450 (m), 1440 (m), 1250 (s), 860 (s), 830 (s), 740 (s), 695 (s) cm⁻¹; Low resolution MS m/e (%) 388 (M+2, 4), 387 (M+1, 9), 386 (M, 14), 313 (8), 281 (10), 182 (34), 167 (26), 131 (54), 73 (100); High resolution MS Calcd for C₂₂H₃₄SSi₂: 386.1920. Found 386.1935.

Electrochemical Oxidation of 1-Phenylthio-1,1-bis(trimethylsilyl)alkanes. Typical Procedure. 1-Phenylthio-1,1-bis(trimethylsilyl)-3-phenylpropane (195 mg, 0.504 mmol) and Et₄NOTs/MeOH

(0.2 M, 10 ml) were placed in an undivided cell equipped with a carbon rod anode and a carbon rod cathode (i.d. 6 mm). Constant current (10 mA) was passed at room temperature (11.0 F/mol). After removal of methanol under reduced pressure the residue was partitioned between ether and brine. The ether layer was separated and dried over Na_2SO_4 . After evaporation of the solvent the residue was purified via flash chromatography (hexane / ethyl acetate 19 : 1) to obtain methyl 4-phenylpropanoate (59 mg, 66% yield).

Alkylation of Methoxy(trimethylsilyl)methane. Typical Procedure.¹⁴ To a solution of methoxy(trimethylsilyl)methane (359 mg, 3.0 mmol) in 5.0 ml of THF was added *sec*-butyllithium / hexane (1.3 M, 2.0 ml, 2.6 mmol) at -78°C . The mixture was stirred at -25°C for 30 min and recooled to -78°C . 1-Bromoundecane (498 mg, 20 mmol) was added and the mixture was stirred at this temperature for 5 min and at room temperature for 1 h. Saturated aq NH_4Cl was added and organic materials were extracted with ether and dried over MgSO_4 . After evaporation of the solvent 1-methoxy-1-trimethylsilyltridecane was isolated via flash chromatography (hexane / ethyl acetate = 39 : 1) (430 mg, 75% yield). ^1H NMR (CDCl_3) δ 0.03 (s, 9 H), 0.7 - 1.0 (m, 3 H), 1.0 - 1.65 (m, 22 H), 2.62 - 2.85 (m, 1 H), 3.35 (s, 3 H); IR (neat) 2925 (s), 2850 (s), 1460 (w), 1245 (m), 1095 (m), 835 (s) cm^{-1} ; Low resolution MS m/e (%) 271 (M- CH_3 , 50), 129 (4), 111 (8), 103 (34), 97 (20), 89 (47), 83 (30), 73 (100), 69 (24), 54 (7.5); High resolution MS Calcd for $\text{C}_{16}\text{H}_{35}\text{OSi}$ (M- CH_3): 271.2357. Found: 271.2460.

Electrochemical Oxidation of 1-Methoxy-1-trimethylsilylalkanes. Typical Procedure. 2-Hydroxy-1-methoxy-1-trimethylsilylnonane (295 mg, 1.2 mmol) and 0.2 M $\text{Et}_4\text{NOTs}/\text{MeOH}$ (10 ml) were placed in an undivided cell equipped with a carbon rod anode and a carbon rod cathode (i.d. 6 mm). Constant current (10 mA) was passed at room temperature. After the electricity of 2.95 F/mol was consumed, the reaction mixture was partitioned between brine and ether. The ether layer was separated and dried over MgSO_4 . After evaporation of the solvent, the crude product was purified via flash chromatography (hexane / ethyl acetate 19 : 1 containing a trace amount of triethylamine) to obtain 2-Hydroxyl-1,1-dimethoxynonane (196 mg, 80% yield). ^1H NMR (CDCl_3) δ 0.75 - 1.00 (m, 3 H), 1.10 - 1.60 (m, 12 H), 2.0 - 2.2 (br, 1 H), 3.42 (s, 3 H), 3.45 (s, 3 H), 3.45 - 3.65 (m, 1 H), 4.11 (d, $J = 5.9$ Hz, 1 H); IR (neat) 3450 (br), 2900 (s), 2850 (s), 1450 (m), 1370 (w), 1180 (m), 1110 (m), 1060 (m), 960 (m) cm^{-1} ; Low resolution MS m/e (%) 173 (3), 172 (1), 127 (40), 75 (100); High resolution MS Calcd for $\text{C}_{10}\text{H}_{21}\text{O}_2$ (M-OMe): 173.1540. Found 173.1524.

Electrochemical Oxidation of 1-Methoxy-1-trimethylsilylalkanes in the Presence of Water. Typical Procedure. 1-Methoxy-1-trimethylsilyltridecane (150 mg, 0.523 mmol), tetrabutylammonium fluoroborate (69 mg), dichloromethane (1.0 ml), and water (45 μl) were placed in an undivided cell equipped with a carbon rod anode (i.d. 6 mm) and a platinum plate cathode (20 x 30 mm). Constant current (10 mA) was passed at room temperature. After the electricity of 3.00 F/mol was consumed, the reaction mixture was partitioned between ether and water. The ether layer was separated and dried over Na_2SO_4 . After evaporation of the solvent, the residue was purified via flash chromatography (hexane / ethyl acetate = 39 : 1) to obtain tridecanal (84 mg, 81% yield).

Methoxybis(trimethylsilyl)methane. To a solution of methoxy(trimethylsilyl)methane (6.00 g, 49.7 mmol) in 50 ml of THF was added *sec*-butyllithium / cyclohexane (65 ml, 84.5 mmol) at -78°C . The mixture was warmed to -25°C and stirred at this temperature for 40 min. The mixture was recooled to -78°C and chlorotrimethylsilane (9.838 g, 90.6 mmol) was added. The mixture was warmed to room temperature and stirred at this temperature for 1 h. Brine was added and the organic materials were extracted with ether and dried over MgSO_4 . After evaporation of the solvent, the residue was purified via distillation (65 - $70^\circ\text{C}/15$ mmHg) to obtain the title product (9.128 g, 96% yield): VPC tR 1.75 min (100 - 230°C , $20^\circ\text{C}/\text{min}$); ^1H NMR (CDCl_3) δ 0.06 (s, 18 H), 2.46(s, 1 H), 3.32 (s, 3 H); IR (neat) 2950 (s), 2800 (m), 1443 (m), 1245 (s), 1085 (s), 1025 (m), 860 (s), 840 (s), 752 (m), 690 (m) cm^{-1} ; Low resolution MS m/e (%) 190 (11), 175 (26), 147 (100), 133 (14), 102 (9), 89 (19), 73 (30), 59 (10); Anal. Calcd for $\text{C}_5\text{H}_{14}\text{OSi}$: C: 50.46%, H: 11.64%. Found: C: 50.68%, H: 11.73%.

Alkylation of Methoxybis(trimethylsilyl)methane. Typical Procedure. To a solution of methoxybis(trimethylsilyl)methane (280 mg, 1.47 mmol) in 5 ml of THF was added *n*-butyllithium / hexane (1.6 M, 1.0 ml 1.6 mmol) at -78°C . The mixture was warmed to 0°C and stirred at this temperature for 20 min to obtain a clear yellow solution. The solution was recooled to -78°C and 11-bromo-1-undecene (349 mg, 1.5 mmol) was added. After being stirred at this temperature for 5 min, the mixture was stirred at 0°C for 1 h. Brine was added and organic materials were extracted with ether and dried over MgSO_4 . After evaporation of the solvent the residue was purified via flash chromatography to obtain 12-methoxy-12,12-bis(trimethylsilyl)-1-dodecene. ^1H NMR (CDCl_3) δ 0.10 (s, 18 H), 1.10 - 1.80 (m, 22 H), 3.25 (s, 3 H); 4.75 - 5.1 (m, 2 H), 5.5 -

6.0 (m, 1 H); IR (neat) 3050 (w), 2900 (s), 2850 (s), 1640 (w), 1450 (w), 1245 (s), 1060 (s), 990 (w), 900 (m), 835 (s, br), 750 (m), 675 (m) cm^{-1} ; Low resolution MS m/e (%) 342 (0.3), 327 (44), 269 (6), 253 (24), 239 (9), 147 (8), 89 (21), 73 (100); High resolution MS Calcd for $\text{C}_{19}\text{H}_{42}\text{OSi}_2$: 342.2774. Found: 342.2774.

Electrochemical Oxidation of 1-Methoxy-1,1-bis(trimethylsilyl)alkanes. The reactions were carried out essentially in the same manner as those for 1-methoxy-1-trimethylsilylalkanes.

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References and Notes

1. Electrochemical oxidation of organosilicon compounds. Part 8. For part 7, ref 5.
2. For example, (a) Colvin, E. W. *Silicon in Organic Synthesis*, Butterworths: London, 1981; (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*, Springer-Verlag, Berlin, 1983.
3. For example, Wierschke, S. G; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496 - 1500.
4. (a) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6855 - 6856; (b) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U.-C.; Kim, J.-U. *Ibid.*, **1988**, *110*, 8099 - 8111; (c) Xu, W.; Jeon, Y. T.; Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *Ibid.*, **1989**, *111*, 406 - 408; (d) Block E.; Yench, A. J.; Aslam, M.; Eswarakrishnan, V.; Luo, J.; Sano, A. *J. Am. Chem. Soc.* **1988**, *110*, 4748 - 4753; (e) Kira, M.; Nakazawa, H.; Sakurai, H. *Chem. Lett.* **1986**, 497 - 500. For cation radicals of organosilicon compounds, see (f) Bock, H. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1627 - 1649; (g) Bock, H.; Kaim, W. *Acc. Chem. Res.*, **1982**, *1*, 9 - 17.
5. Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.*, **1990**, *112*, 1962.
6. (a) Yoshida, J.; Murata, T.; Isoe, S. *J. Organometal. Chem.* **1988**, *345*, C23 - C27. See also (b) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Bull. Chem. Soc., Jpn.*, **1989**, *62*, 219 - 225.
7. Yoshida, J.; Isoe, S. *Chem. Lett.*, **1987**, 631 - 634. See also Koizumi, T.; Fuchigami, T.; Nonaka, T. *Chem. Lett.*, **1987**, 1095 - 1096.
8. For example: (a) Brobel, B. -T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852 - 866; (b) Magnus, P. *Aldrichimica Acta*, **1980**, *13*, 238 - 246; (c) Chan, T.-H. *Acc. Chem. Res.*, **1977**, *10*, 442 - 448. See also ref (2).
9. (a) Kocienski, P. J. *Tetrahedron Lett.* **1980**, *21*, 1559 - 1562; (b) Ager, D. J.; Cookson, R. C. *Tetrahedron Lett.* **1980**, *21*, 1677 - 1680; (c) Ager, D. J. *Tetrahedron Lett.*, **1981**, *22*, 2803 - 2806, 2923 - 2926; (d) Ager, D. J.; East, M. B. *J. Org. Chem.*, **1986**, *51*, 3983 - 3992.
10. For example, (a) Hase, T. A. Ed., *Umposed Synthons*, Wiley: New York, 1987; (b) Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239 - 336.
11. Uneyama, K.; Torii, S. *Tetrahedron Lett.* **1971**, 329 - 332.
12. (a) Otera, J.; Niibo, Y.; Nozaki, H. *J. Org. Chem.* **1989**, *54*, 5003 - 5007; (b) Mandai, T.; Yamaguchi, M.; Nakayama, Y.; Otera, J.; Kawada, M. *Tetrahedron Lett.* **1985**, *26*, 2675 - 2676. See also Sato, T.; Okazaki, H.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* **1988**, *11*, 5209 - 5211.
13. (a) Magnus, P.; Roy, G. *Organometallics*, **1982**, *1*, 553 - 559; See also (b) Kanemasa, S.; Tanaka, J.; Nagahama, H.; Tsuge, O. *Chem. Lett.* **1985**, 1223 - 1226; (c) Tsuge, O.; Kanemasa, S.; Nagahama, H.; Tanaka, J. *Chem. Lett.* **1984**, 1803 - 1806. Alkylation of the anion of epoxysilanes has been reported: (d) Molander, G. A.; Mautner, K. *J. Org. Chem.* **1989**, *54*, 4042 - 4050.
14. Yoshida, J.; Matsunaga, S.; Isoe, S. *Tetrahedron Lett.* **1989**, *30*, 5293 - 5296.