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Novel Water-Soluble Organosilane Compounds as a Radical Reducing Agent in Aqueous Media

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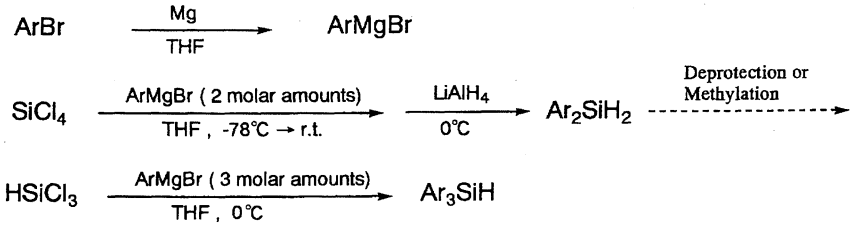
The development of novel water-soluble organosilane compounds and their application to radical reactions in water medium have been studied. A series of novel organosilane compounds having hydrophilic groups, such as an ether group and a hydroxy group in the side chain to bear hydrophilicity, were synthesized by the reaction of trichlorosilane or tetrachlorosilane and Grignard reagents. The reactivities of these organosilane compounds were studied in the radical reduction of 2-bromoethyl phenyl ether in ethanol in the presence of triethylborane under aerobic conditions. The results showed that diarylsilane was the most effective among them. The radical reduction of alkyl and aryl halides with diarylsilane was applied to a reaction in aqueous media, which gave the corresponding reduction product in good yields. Thus, the present organosilanes are very useful for the reduction of water-soluble substrates, such as halo sugars in water.

Recently, organic reactions in water and water-promoted organic reactions have attracted much attention because there are specific effects produced in water, such as a hydrogen-bonding network; many biological processes occur in the presence of water.[1] Furthermore, the reactions in water media are much better than those in general organic media from an environmental point of view. Hitherto, some organic reactions in water, mainly initiated by Breslow, were carried out: the Diels–Alder reaction, the Aldol reaction, the Barbier-type reaction, etc.[1] On the other hand, the use of radical reactions has dramatically increased since the 1980's.[2] Most of these radical reactions in principle proceed under neutral conditions; therefore, the formation and reaction of radicals are not affected by the presence of water. Thus, if radical reactions could be carried out in water media, they would be extremely useful in sugar, nucleoside, and peptide chemistry, since the high ability of functional-group transformations with radical reactions in general organic media is well known. Studies on radical reagents in an aqueous solvent have so far been extremely limited. Breslow[3] and Collum[4] have reported on water-soluble stannanes, i.e., tris[3-(2-methoxyethoxy)-propyl]stannane and a dialkylstannane derivative. However, organotin compounds are highly toxic and incur work-up and purification problems. Generally, it is well known that organosilanes have a strong affinity to halogen atoms, and can be used for the reduction of halides in the presence of an initiator, such as peroxide.[5] Accordingly, novel organosilanes were prepared and their reactivities for the reduction of halides in aqueous media were investigated.

Results and Discussion

Novel organosilanes were synthesized by the Grignard reaction with aryl bromides. Here, aryl bromides bearing ether, onium, and hydroxy groups were prepared by the Williamson ether synthesis. After these aryl bromides were converted into Grignard reagents, the reactions of trichlorosilane or tetrachlorosilane with 2 or 3 molar amounts of these Grignard reagents followed by a treatment with lithium aluminum hydride gave diarylsilanes or triarylsilanes, as shown in Scheme 1. These silane compounds were purified from the reaction mixture by column chromatography. The yields of organosilane are shown in Table 1. Next, the radical reactivity of these organosilane compounds in ethanol, as a protic solvent, was studied. The radical reduction of 2-bromoethyl phenyl ether to phenetole, initiated by triethylborane[6] in ethanol under aerobic conditions at room temperature, was investigated as a model reaction (Table 2). This reaction was scarcely initiated by AIBN, which is widely used as a radical initiator in organic tin compounds under refluxing conditions. These results show that the reactivity of aryl-



Scheme 1.

Table 1. Yields of Novel Organosilanes

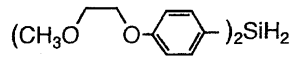
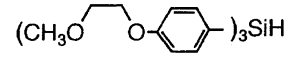
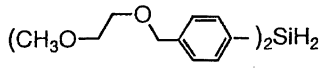
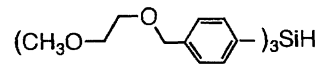
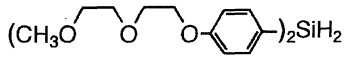
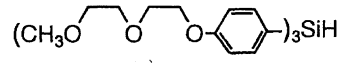
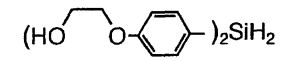
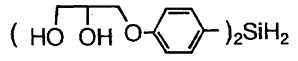
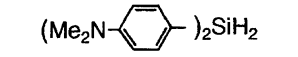
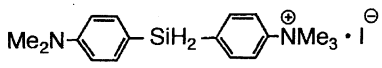
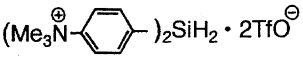
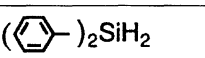
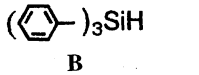
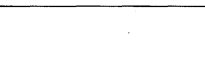
Entry	$(Ar)_nSiH_{4-n}$		Yield/%
1		(**A**)	52
2		(**B**)	59
3		(**C**)	30
4		(**D**)	37
5		(**E**)	40
6		(**F**)	28
7		(**G**)	35
8		(**H**)	41
9		(**I**)	54
10		(**J**)	38
11		(**K**)	54

Table 2. Reduction of 2-Bromoethyl Phenyl Ether with Organosilane Compounds in Ethanol

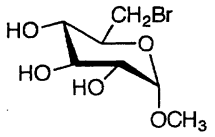
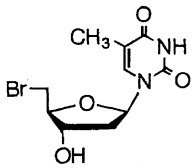
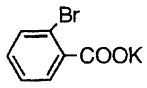
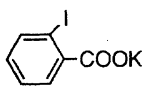
Entry	"Si" reagent	Yield/%
1		73
2	**A**	67
3	**C**	60
4	**E**	62
5	**G**	60
6	**H**	30
7	**I**	49
8	**J**	12
9	**K**	8
10	$(C_2H_5)_2SiH_2$	17
11		48
12	**B**	2
13	**D**	21
14	**F**	36
15	$(C_2H_5)_3SiH$	8
16		52

silanes is much higher than that of alkylsilanes (Entries 1, 10, 11, and 15); the reactivity of diarylsilanes was higher than those of monoarylsilanes and triarylsilanes (Entries 1, 11, and 16). Moreover, an extension of the ether linkage did not affect the reactivity of diarylsilanes (Entries 2, 3, and 4). Organosilanes having an onium group showed lower reactivity (Entries 8 and 9). This was apparently caused by the instability of these organosilanes in the presence of water. Then, a radical reduction of 2-chloroethyl phenyl ether and 2-iodoethyl phenyl ether with bis[4-(2-methoxyethoxy)-phenyl]silane (**A**) under the same conditions was carried out to give reduction products in 6 and 81% yields, respectively.

The solubility of novel diarylsilanes in water was roughly determined from the integral ratio of the ^1H NMR of organosilane with dioxane as an internal standard in deuterium oxide. Thus, the solubilities of bis[4-(2-methoxyethoxy)phenyl]silane (**A**) and bis{4-[2-(2-methoxyethoxy)ethoxy]phenyl}silane (**E**) are about 1.0×10^{-2} M (1 M=1 mol dm^{-3}) and 1.5×10^{-2} M, respectively; these silanes are stable for about several days at room temperature in deuterium oxide. From these results, these novel organosilanes are thought to be applicable to radical reactions in a water medium. The radical reduction of 2-bromoethyl phenyl ether with bis{4-[2-(2-methoxyethoxy)ethoxy]phenyl}silane (**E**), which showed the highest solubility to water among the present novel diarylsilanes, was carried out in mixed-solvent systems of ethanol and water. The yield of the reduction product (60—70%) hardly varied with increasing the ratio of water. This result again suggested that radical reduction with the present organosilanes in the presence of water proceeds similarly to radical reduction in organic media. Thus, the reduction of other substrates with bis{4-[2-(2-methoxyethoxy)-ethoxy]phenyl}silane (**E**), bis[4-(2-hydroxyethoxy)phenyl]-silane (**G**), and bis[4-(2,3-dihydroxypropoxy)phenyl]silane (**H**) in aqueous media was studied; the results are given in Table 3.

The radical reduction of potassium 6-bromohexanoate and potassium 2-bromohexanoate gave the reduction product in good yields (Entries 1, 2). The reduction of methyl 6-bromo-6-deoxy-α-D-glucopyranoside also afforded the reduction

Table 3. Radical Reduction in Aqueous Media

Entry	Substrate	Yields/%			
		"Si" reagent	**E**	**G**	**H**
1	$Br(CH_2)_5COOK$		99	99	92
2	$CH_3(CH_2)_3CHBrCOOK$		92	97	74
3			66	84	88
4			37	42	18
5			23	—	—
6			71	99	80

product in good yield (Entry 3). However, the reduction of 5′-bromo-5′-deoxythymidine gave the reduction product in low yields (Entry 4), since a decomposition of the nucleoside under the present reaction conditions occurred. The reduction of potassium *o*-bromobenzoate and potassium *o*-iodobenzoate, which form the sp^2 carbon radical, was carried out. The results show that it is difficult to abstract the bromine atom bonding to the sp^2 carbon, while the iodine atom of potassium *o*-iodobenzoate is easily abstracted by the silyl radical.[7] From these results, it can be seen that the present organosilanes can promote the radical reduction of alkyl bromides, alkyl iodides, and aryl iodides, initiated by triethylborane, in aqueous media under aerobic conditions.

Radical cyclization using the present organosilanes in an aqueous medium was studied. The radical cyclization of potassium 7-bromo-2-heptenoate with bis{4-[2-(2-methoxyethoxy)ethoxy]phenyl}silane (**E**) and bis[4-(2-hydroxyethoxy)phenyl]silane (**G**) was carried out to give 48 and 82% yields of cyclopentylacetic acid, respectively; no direct reduction product, 2-heptenoic acid, was formed.

In conclusion, the radical reduction of alkyl bromides, alkyl iodides, and aryl iodides using the present novel water-soluble diarylsilanes proceeded to give the corresponding reduction products in good yields. The present organosilane compounds are very useful for the reduction of water-soluble substrates, such as halo sugars, in water under mild conditions (aerobic conditions at room temperature). The utilization of the present water-soluble organosilanes makes it possible to extend the scope of organic chemistry in water.

Experimental

General. ^{1}H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-FX270, JEOL-JNM-GSX400, and JEOL-JNM-GSX500 spectrometers. ^{29}Si NMR spectra were obtained with a Bruker AC300 spectrometer. The chemical shifts are expressed in ppm downfield from TMS in δ units. The mass spectra were recorded on Hitachi M-60, JEOL-HX-110, and JEOL-JMS-ATII-15 spectrometers. IR spectra were measured with Hitachi 215 and JASCO FT/IR-200 spectrometers. A microanalysis was performed with a Perkin–Elmer 240 elemental analyzer at the Chemical Analysis Center of Chiba University. The melting points were determined on a Yamato Melting Points Apparatus Model MP-21. Wakogel C-200 and Silica Gel 60 (Merck) were used for column chromatography, Kieselgel 60 F_{254} (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Materials. Most of the alkyl halides and simple organosilanes are commercially available. The following compounds were prepared according to procedures described in the literatures: methyl 6-bromo-6-deoxy-α-D-glucopyranoside,[8] 5′-bromo-5′-deoxythymidine,[9] 7-bromo-2-heptenoic acid.[10]

General Procedure for the Preparation of Starting Material.

1-Bromo-4-(2-methoxyethoxy)benzene: A solution of 4-bromophenol (0.15 mol), 2-bromoethyl methyl ether (0.33 mol), and K_2CO_3 (0.3 mol) in dry acetone (150 ml) was heated to 60 °C and stirred for 3 d. The solution was filtered and evaporated. The residual oil was distilled (97—107 °C/1.0 mmHg, 1 mmHg = 133.322 Pa) to give 1-bromo-4-(2-methoxyethoxy)benzene. IR (Neat) 2930, 2880, 1590, 1490, 1245, 1130, 1060, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.45 (3H, s, CH_3–), 3.74 (2H, t, J = 4.6 Hz, –CH_2–), 4.08 (2H, t, J = 4.6 Hz, –CH_2–), 6.81 (2H, d, J = 6.8 Hz, Ar), 7.36 (2H, d, J = 6.8 Hz, Ar). HRMS (EI) Found: *m/z* 229.9940 (^{79}Br), 231.9908 (^{81}Br). Calcd for $C_9H_{11}O_2$ ^{79}Br: M^+, 229.9942; $C_9H_{11}O_2$ ^{81}Br: M^+, 231.9923.

1-Bromo-4-[2-(2-methoxyethoxy)ethoxy]benzene: Oil; bp 135—160 °C/1.0 mmHg (lit,[11] bp 103—112 °C/0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ = 3.38 (3H, s, CH_3–), 3.57 (2H, t, J = 4.5 Hz, –CH_2–), 3.71 (2H, t, J = 4.5 Hz, –CH_2–), 3.84 (2H, t, J = 4.9 Hz, –CH_2–), 4.09 (2H, t, J = 4.9 Hz, –CH_2–), 6.79 (2H, d, J = 6.8 Hz, Ar), 7.35 (2H, d, J = 6.8 Hz, Ar). HRMS (EI) Found: *m/z* 274.0181 (^{79}Br), 276.0201 (^{81}Br). Calcd for $C_{11}H_{15}O_3$ ^{79}Br: M^+, 274.0205, $C_{11}H_{15}O_3$ ^{81}Br: M^+, 276.0185.

1-Bromo-4-[(2-methoxyethoxy)methyl]benzene: Sodium hydride (0.152 mol) was added to a solution of 4-bromobenzyl alcohol (0.113 mol) and 2-bromoethyl methyl ether (0.171 mol) in THF (25 ml) at −50 °C. After the solution was slowly warmed up to room temperature, it was heated to 50 °C and stirred for 4 d, and then filtered and evaporated. The residue was purified by column chromatography to give 1-bromo-4-[(2-methoxyethoxy)-methyl]benzene. IR (Neat) 2880, 1590, 1490, 1200, 1100, 1010, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.39 (3H, s, CH_3–), 3.56—3.61 (4H, m, –CH_2–), 4.52 (2H, s, ArCH_2–), 7.22 (2H, d, J = 8.2 Hz, Ar), 7.46 (2H, d, J = 8.2 Hz, Ar). HRMS (EI) Found: *m/z* 244.0108 (^{79}Br), 246.0079 (^{81}Br). Calcd for $C_{10}H_{13}O_2$ ^{79}Br: M^+, 244.0099, $C_{10}H_{13}O_2$ ^{81}Br: M^+, 246.0079.

1-Bromo-4-[2-(2-tetrahydropyranyloxy)ethoxy]benzene: A solution of 2-bromoethanol (0.6 mol), 3,4-dihydro-2*H*-pyran (0.78 mol), and *p*-toluenesulfonic acid monohydrate (cat. amount) in dry THF (100 ml) was heated to 60 °C and stirred for 2 h. After being neutralized by K_2CO_3 (3 g) and evaporated, the residue, 4-bromophenol (0.48 mol), and K_2CO_3 (0.9 mol) were dissolved in dry acetone (450 ml). The solution was heated to 60 °C and stirred for 4 d, then filtered and evaporated. The residue was distilled (150 °C/2.0 mmHg) to give 1-bromo-4-[2-(2-tetrahydropyranyloxy)ethoxy]benzene. IR (Neat) 2940, 2880, 1590, 1490, 1245, 1125, 1040, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.52—1.88 (6H, m, THP –CH_2–), 3.51—3.55 (1H, m, –CH_2–), 3.77—3.82 (1H, m, –CH_2–), 3.86—3.92 (1H, m, –CH_2–), 4.01—4.06 (1H, m, –CH_2–), 4.10—4.13 (2H, m, THP 6-H), 4.69 (1H, t, J = 3.5 Hz, THP 2-H), 6.81 (2H, dd, J = 6.8, 2.2 Hz, Ar), 7.36 (2H, dd, J = 6.8, 2.2 Hz, Ar). HRMS (EI) Found: *m/z* 300.0364 (^{79}Br), 302.0338 (^{81}Br). Calcd for $C_{13}H_{17}O_3$ ^{79}Br: M^+, 300.0361, $C_{13}H_{17}O_3$ ^{81}Br: M^+, 302.0341.

1-Bromo-4-(2,3-isopropylidenedioxypropoxy)benzene: 2,3-Epoxy-1-propanol (0.3 mol) was added dropwise to a solution of 4-bromophenol (0.15 mol) and K_2CO_3 (0.3 mol) in dry acetone (200 ml). After the solution was heated to 60 °C and stirred for 2 d, the reaction mixture was filtered and evaporated. The residue was purified by column chromatography to give 1-bromo-4-(2,3-dihydroxypropoxy)benzene. This compound was treated with concd H_2SO_4 (1.0 ml) in dry acetone (250 ml). The solution was then neutralized by $Ca(OH)_2$ and filtered through a Celite pad. After reducing the solvent under reduced pressure, the residue was purified by column chromatography to afford 1-bromo-4-(2,3-isopropylidenedioxypropoxy)benzene. IR (neat) 2980, 2930, 1590, 1490, 1240, 1160, 1060, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.40 (3H, s, CH_3–), 1.46 (3H, s, CH_3–), 3.89 (1H, dd, J = 8.4, 5.9 Hz, –CH_2–), 3.91 (1H, dd, J = 9.2, 5.9 Hz, –CH_2–), 4.02 (1H, dd, J = 9.2, 5.9 Hz, –CH_2–), 4.16 (1H, dd, J = 8.4, 5.9 Hz, –CH_2–), 6.80 (2H, d, J = 6.8 Hz, Ar), 7.37 (2H, dd, J = 6.8 Hz, Ar). HRMS (EI) Found: *m/z* 286.0195 (^{79}Br), 288.0189 (^{81}Br). Calcd for $C_{12}H_{15}O_3$ ^{79}Br: M^+, 286.0205, $C_{12}H_{15}O_3$ ^{81}Br: M^+, 288.0185.

General Procedure for the Synthesis of Organosilane Com-

pounds. The Grignard reagent was prepared by a conventional procedure from aryl bromide (60 mmol) and magnesium (72 mmol) in dry THF (50 ml). A solution of the Grignard reagent in THF was added dropwise to trichlorosilane (20 mmol) or tetrachlorosilane (30 mmol) in THF (10 ml) at −78 °C. The solution was slowly warmed to room temperature, and stirred for one hour. To this solution, lithium aluminum hydride (30 mmol) was added at 0 °C. After 30 min, the resulting solution was quenched with small amounts of 1 M HCl aq and ice, and then extracted with chloroform. The chloroform layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography to give the organosilane compound.

Deprotection of Organosilane Compounds: Trifluoroacetic acid (1 ml) was added to a solution of bis{4-[2-(2-tetrahydropyranyloxy)ethoxy]phenyl}silane (crude) or bis[4-(2,3-isopropylidenedioxypropoxy)phenyl]silane (crude) in methanol (100 ml). After removing the solvent under reduced pressure, the product was purified by column chromatography.

Methylation of Organosilane Compounds: Methyl iodide (0.4 mmol) was added to a solution of bis[4-(dimethylamino)phenyl]silane (0.4 mmol) in dry THF (10 ml). After the solution was stirred for 1 d at room temperature, the precipitated trimethylammonium salt was collected by filtration.

Bis[4-(2-methoxyethoxy)phenyl]silane (A): Oil; IR (neat) 2900, 2135, 1600, 1260, 1130, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.44 (6H, s, CH_3–), 3.75 (4H, t, J = 4.7 Hz, –CH_2–), 4.13 (4H, t, J = 4.7 Hz, –CH_2–), 4.87 (2H, s, SiH_2), 6.94 (4H, d, J = 8.6 Hz, Ar), 7.49 (4H, d, J = 8.6 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 59.19 (q, CH_3–), 66.99 (t, –CH_2–), 70.93 (t, –CH_2–), 114.53 (d, Ar), 122.81 (s, Ar), 137.08 (d, Ar) 160.24 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −34.49. HRMS (EI) Found: *m/z* 332.1434. Calcd for $C_{18}H_{24}O_4Si$: M^+, 332.1442.

Tris[4-(2-methoxyethoxy)phenyl]silane (B): Mp 116.8—118.0 °C; IR (KBr) 2900, 2100, 1600, 1250, 1120, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.44 (9H, s, CH_3–), 3.75 (6H, t, J = 4.8 Hz, –CH_2–), 4.13 (6H, t, J = 4.8 Hz, –CH_2–), 5.39 (1H, s, SiH), 6.93 (6H, d, J = 8.3 Hz, Ar), 7.45 (6H, d, J = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 59.18 (q, CH_3–), 66.95 (t, –CH_2–), 70.95 (t, –CH_2–), 114.39 (d, Ar), 125.10 (s, Ar), 137.15 (d, Ar), 160.10 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −19.36. HRMS (EI) Found: *m/z* 482.2098. Calcd for $C_{27}H_{34}O_6Si$: M^+, 482.2122.

Bis{4-[(2-methoxyethoxy)methyl]phenyl}silane (C): Oil; IR (neat) 2840, 2120, 1600, 1100, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.39 (6H, s, CH_3–), 3.54—3.65 (8H, m, –CH_2CH_2–), 4.58 (4H, s, $ArCH_2$), 4.90 (2H, s, SiH_2), 7.36 (4H, d, J = 7.7 Hz, Ar), 7.57 (4H, d, J = 7.7 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 59.09 (q, CH_3–), 69.45 (t, –CH_2–), 71.98 (t, –CH_2–), 73.12 (t, –CH_2–Ar), 127.38 (d, Ar), 130.64 (s, Ar), 135.78 (d, Ar), 140.07 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −33.92. HRMS (EI) Found: *m/z* 360.1744. Calcd for $C_{20}H_{28}O_4Si$: M^+, 360.1755.

Tris{4-[(2-methoxyethoxy)methyl]phenyl}silane (D): Oil; IR (neat) 2850, 2130, 1600, 1110, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.39 (9H, s, CH_3–), 3.55—3.65 (12H, m, –CH_2CH_2–), 4.58 (6H, s, $ArCH_2$), 5.44 (1H, s, SiH), 7.35 (6H, d, J = 7.9 Hz, Ar), 7.53 (6H, d, J = 7.9 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 59.09 (q, CH_3–), 66.50 (t, –CH_2–), 71.98 (t, –CH_2–), 73.19 (t, –CH_2–Ar), 127.34 (d, Ar), 132.52 (s, Ar), 135.90 (d, Ar), 139.95 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −18.65. Found: C, 68.51; H, 7.73%. Calcd for $C_{30}H_{40}O_6Si$: C, 68.67; H, 7.68%.

Bis{4-[2-(2-methoxyethoxy)ethoxy]phenyl}silane (E): Oil; IR (neat) 2860, 2140, 1590, 1250, 1120, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.39 (6H, s, CH_3–), 3.58 (4H, t, J = 4.6 Hz, –CH_2–), 3.72 (4H, t, J = 4.6 Hz, –CH_2–), 3.86 (4H, t, J = 5.0 Hz, –CH_2–), 4.15 (4H, t, J = 5.0 Hz, –CH_2–), 4.86 (2H, s, SiH_2), 6.93 (4H, d, J = 8.6 Hz, Ar), 7.48 (4H, d, J = 8.6 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 59.08 (q, CH_3–), 67.15 (t, –CH_2–), 69.67 (t, –CH_2–), 70.75 (t, –CH_2–), 71.94 (t, –CH_2–), 114.54 (d, Ar), 122.77 (s, Ar), 137.09 (d, Ar), 160.24 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −34.46. HRMS (EI) Found: *m/z* 420.1965. Calcd for $C_{22}H_{32}O_6Si$: M^+, 420.1966.

Tris{4-[2-(2-methoxyethoxy)ethoxy]phenyl}silane (F): Oil; IR (neat) 2840, 2090, 1580, 1240, 1100, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.39 (9H, s, CH_3–), 3.57 (6H, t, J = 4.6 Hz, –CH_2–), 3.72 (6H, t, J = 4.6 Hz, –CH_2–), 3.86 (6H, t, J = 5.0 Hz, –CH_2–), 4.15 (6H, t, J = 5.0 Hz, –CH_2–), 5.39 (1H, s, SiH), 6.92 (6H, d, J = 8.4 Hz, Ar), 7.44 (6H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 59.11 (q, CH_3–), 67.11 (t, –CH_2–), 69.71 (t, –CH_2–), 70.77 (t, –CH_2–), 71.95 (t, –CH_2–), 114.41 (d, Ar), 125.05 (s, Ar), 137.18 (d, Ar), 160.12 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −19.39. HRMS (FAB+) Found: *m/z* 614.2903. Calcd for $C_{33}H_{46}O_9Si$: M^+, 614.2908.

Bis[4-(2-hydroxyethoxy)phenyl]silane (G): Mp 91.5—93.5 °C; IR (KBr) 3350, 2900, 2110, 1575, 1485, 1235, 1164, 902, 860, and 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.88 (2H, s, OH), 3.97 (4H, t, J = 4.4 Hz, –CH_2–), 4.10 (4H, t, J = 4.4 Hz, –CH_2–), 4.88 (2H, s, SiH_2), 6.94 (4H, d, J = 8.4 Hz, Ar), 7.51 (4H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 61.4 (t, –CH_2–), 68.9 (t, –CH_2–), 114.5 (d, Ar), 123.1 (s, Ar), 137.2 (d, Ar), 160.1 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −34.45. HRMS (EI) Found: *m/z* 304.1118. Calcd for $C_{16}H_{20}O_4Si$: M^+, 304.1130.

Bis[4-(2,3-isopropylidenedioxypropoxy)phenyl]silane: Mp 100.0—113.5 °C; IR (KBr) 2950, 2130, 1590, 1250, 1120, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.40 (6H, s, CH_3–), 1.46 (6H, s, CH_3–), 3.89 (2H, dd, J = 8.5, 5.9 Hz, –CH_2–), 3.94 (2H, dd, J = 9.6, 5.9 Hz, –CH_2–), 4.06 (2H, dd, J = 9.6, 5.9 Hz, –CH_2–), 4.16 (2H, dd, J = 8.5, 5.9 Hz, –CH_2–) 4.47 (2H, quint, J = 5.9 Hz, CH), 4.87 (2H, s, SiH_2), 6.92 (4H, d, J = 8.5 Hz, Ar), 7.49 (4H, d, J = 8.5 Hz, Ar). HRMS (FAB+) Found: *m/z* 444.1979. Calcd for $C_{20}H_{28}O_4Si$: M^+, 444.1966.

Bis[4-(2,3-dihydroxypropoxy)phenyl]silane (H): Mp 149.5—156.5 °C; IR (KBr) 3300, 2920, 2100, 1600, 1260, 1130, 890 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 3.43 (4H, t, J = 5.7 Hz, –CH_2–), 3.78 (2H, m, CH), 3.87 (2H, dd, J = 9.8, 6.2 Hz, –CH_2–), 4.01 (2H, dd, J = 9.8, 5.4 Hz, –CH_2–), 4.68 (2H, t, J = 5.7 Hz, Pr 3-OH), 4.81 (2H, s, SiH_2), 4.97 (2H, d, J = 5.1 Hz, Pr 2-OH), 6.98 (4H, d, J = 8.5 Hz, Ar), 7.47 (4H, d, J = 8.5 Hz, Ar); ^{13}C NMR (DMSO-d_6) δ = 62.65 (t, propoxy), 69.42 (t, propoxy), 69.87 (d, propoxy), 114.68 (d, Ar), 121.41 (s, Ar), 136.92 (d, Ar), 160.44 (s, Ar); ^{29}Si NMR (DMSO-d_6) δ = −30.26. HRMS (FAB+) Found: *m/z* 364.1323. Calcd for $C_{20}H_{28}O_4Si$: M^+, 364.1340.

Bis[4-(dimethylamino)phenyl]silane (I): Mp 78.5—79.5 °C; IR (KBr) 2850, 2100, 1585, 1500, 1360, 1115, 842, and 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.96 (12H, s, CH_3–), 4.85 (2H, s, SiH_2), 6.72 (4H, d, J = 7.9 Hz, Ar), 7.45 (4H, d, J = 7.9 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 40.13 (q, CH_3–), 112.01 (d, Ar), 117.08 (s, Ar), 136.74 (d, Ar), 151.38 (s, Ar); ^{29}Si NMR ($CDCl_3$) δ = −34.98. HRMS (EI) Found: *m/z* 270.1556. Calcd for $C_{16}H_{22}N_2Si$: M^+, 270.1552.

4-{[4-(Dimethylamino)phenyl]silyl}-*N*,*N*,*N*-trimethylanilinium Iodide (J): Mp 138.0—140.0 °C (decomp); IR (KBr) 3440, 2990, 2140, 1595, 1505, 1360, 1235, 1120, 935, 860, and 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.97 (6H, s, NCH_3), 3.99 (9H, s, N^+CH_3), 4.89 (2H, s, SiH_2), 6.72 (2H, d, J = 8.6 Hz, Ar), 7.41 (2H, d, J = 8.6 Hz, Ar), 7.80 (2H, d, J = 8.8 Hz, Ar), 7.93 (2H, d, J = 8.8 Hz, Ar); ^{29}Si NMR ($CDCl_3$) δ = −34.67. HRMS (FAB+) Found: *m/z* 285.1778. Calcd for $C_{17}H_{25}N_2Si$: M^+, 285.1785.

4,4′-Silanediylbis(*N*,*N*,*N*-trimethylanilinium) Bis(trifluoro-

methanesulfonate) (K): Mp 60.0—63.0 °C; IR (KBr) 3150, 2125, 2140, 1450, 1245, 1140, 1015, 940, and 805 cm^{-1}; ^1H NMR (D_2O) $\delta = 3.64$ (18H, s, CH_3–), 4.97 (2H, s, SiH_2), 7.86 (4H, d, $J = 9.0$ Hz, Ar), 7.89 (4H, d, $J = 9.0$ Hz, Ar); ^{13}C NMR (D_2O) $\delta = 59.59$ (q, CH_3), 122.05 (d, Ar), 137.29 (s, Ar), 140.48 (d, Ar), 150.95 (s, Ar); ^{29}Si NMR (D_2O) $\delta = -17.60$. HRMS (FAB+) Found: *m/z* 285.1771. Calcd for $C_{17}H_{25}N_2Si$: M^+, 285.1785.

General Procedure for the Determination of the Solubility of Organosilanes in Water. A mixture of organosilane (3—17 mg) and dioxane (3—6 mg) as an internal standard in D_2O (0.6 ml) was prepared in a sealed NMR tube. After 1 d, the ^1H NMR spectrum was measured, and the amount of organosilane dissolved in D_2O was determined from the integral ratio based on dioxane.

General Procedure for the Radical Reduction with Organosilanes. Triethylborane (1.2 ml) in THP (1 mol dm^{-3}) was added into a mixture of the substrate (0.5 mmol) and organosilane (1.2 mmol) in a solvent (2.5 ml of ethanol or dist. water) under aerobic conditions at room temperature. After stirring for 4 h, the same amount of triethylborane was added again, and the obtained mixture was stirred overnight. Phenetole, hexanoic acid, benzoic acid, and cyclopentylacetic acid were identical with commercial compounds.

Methyl 6-Deoxy-α-D-glucopyranoside: Mp 79—84 °C; $[\alpha]_D^{28}$ 143.45° ($c = 0.307$, MeOH); IR (neat) 3300, 2900, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.28$ (3H, d, $J = 6.2$ Hz, 6-H), 3.13 (1H, td, $J = 9.2$, 4.5 Hz, 4-H), 3.41 (3H, s, CH_3O–), 3.51—3.72 (3H, m, 2-H, 3-H, 5-H), 4.38 (1H, d, $J = 8.1$ Hz, 2-OH), 4.66 (1H, d, $J = 4.5$ Hz, 4-OH), 4.69 (1H, d, $J = 3.7$ Hz, 1-H), 5.33 (1H, d, $J = 4.0$ Hz, 3-OH). MS (EI) Found: $M - CH_3O = 147$.

5′-Deoxythymidine: ^1H NMR (DMSO-d_6) $\delta = 1.23$ (3H, d, $J = 6.6$ Hz, 5′-H), 1.79 (3H, d, $J = 1.1$ Hz, 5-CH_3), 2.00—2.25 (2H, m, 2′-H), 3.95 (1H, m, 3′-H), 4.20 (1H, m, 4′-H), 5.24 (1H, d, $J = 4.4$ Hz, 3′-OH), 6.09 (1H, t, $J = 7.0$ Hz, 1′-H), 7.39 (1H, d, $J = 1.1$ Hz, 6-H), 11.27 (1H, s, 3-H). HRMS (FAB+) Found: *m/z* 227.1021. Calcd for $C_{10}H_{15}N_2O_4$: $(M+H)^+$, 227.1031.

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