Inorganica Chimica Acta, 220 (1994) 129–135

Synthesis, properties and reactions of sila-functional α-heteroatom-substituted organosilicon compounds

Jun-ichi Yoshida*, Hidekazu Tsujishima, Kazunori Nakano** and Sachihiko Isoe*
Department of Material Science, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi, Osaka 558 (Japan)

(Received January 5, 1994)

Abstract

Several types of sila-functional α-heteroatom-substituted organosilicon compounds were synthesized. α-Heteroatom-substituted hydrosilanes were prepared by the reaction of the corresponding α-heteroatom-substituted carbanions with chlorodiorganosilanes. α-Heteroatom-substituted alkoxysilanes were synthesized by chlorination of α-heteroatom-substituted hydrosilanes with $PdCl_2/CCl_4$ followed by reaction with alcohols in the presence of triethylamine. α-Heteroatom-substituted fluorosilanes were obtained by direct $CuF_2 \cdot 2H_2O/CCl_4$ promoted fluorination of the corresponding hydrosilanes. Electrochemical oxidation potentials of sila-functional α-heteroatom-substituted organosilicon compounds were determined. The introduction of a hydrogen or a fluorine substituent on the silicon caused a small increase in the oxidation potentials, which is consistent with the results of molecular orbital calculations. Preparative anodic oxidation of α-heteroatom-substituted hydro- and fluorosilanes in methanol resulted in the cleavage of the carbon–silicon bond and introduction of the methoxyl group onto the carbon. Hydrosilylation of olefins with α-heteroatom-substituted hydrosilanes proceeded smoothly providing a useful method for the preparation of α-heteroatom-substituted organosilicon compounds.

Key words: Organosilicon compounds; Heteroatom; Oxidation potential; Anodic oxidation

Introduction

Recently, electron-transfer reactions of α-heteroatom-substituted organosilicon compounds have received considerable research interest [1]. Silyl groups facilitate electron transfer from a β-heteroatom such as oxygen, nitrogen and sulfur. Based on this concept, a variety of electrochemical oxidation reactions of α-heteroatom-substituted organosilicon compounds have been developed [2]. The β-effect of silicon for electron-transfer reaction is ascribed to the rise of the HOMO energy by the interaction of the C–Si σ orbital and the p orbital of the heteroatom [3]. The nature of the heteroatom has significant effects on the magnitude of the interaction. For example, the silicon effect for oxygen is much larger than that for sulfur. The energy level of non-bonding p orbital of oxygen is close to that of the C–Si σ orbital and their energy match is good. Therefore, they can interact with each other effectively to cause a significant increase in the HOMO level. The energy level of the non-bonding p orbital of sulfur is, however, much higher than that of the C–Si σ orbital and their energy match is not good. Therefore, they interact only weakly causing a small increase in the HOMO level. Since such effects are expected to depend upon the nature of the substituents on the silicon atom, we investigated the synthesis, electrochemical properties and reactions of sila-functional α-heteroatom-substituted organosilicon compounds.

Experimental

General remarks

Glass-support precoated (Merck silica gel 60 F_{254}, 0.25 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu gas chromatograph equipped with a 2 m × 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) or a Jeol JNM-GX-400 spectrometer (400 MHz). Carbon NMR spectra were determined on a Jeol JNM-GX-400 spectrometer. IR spectra were determined on a Jasco A-102 diffraction grating spectrophotometer. Mass

---

*Authors to whom correspondence should be addressed.

**Undergraduate Research Participant, Osaka Institute of Technology.

SSDI 0020-1693(94)03864-K

spectra were obtained on a Jeol JMS-AX500 spectrometer; the ionization potential was 70 eV.

Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from the ketyl radical before use. Hexamethylphosphoramide (HMPA) was distilled from CaH_2 before use. 1,2-Dimethoxyethane (DME) and carbon tetrachloride (CCl_4) was dried over molecular sieves 4 Å.

Rotating-disk electrode voltammetry

Rotating-disk electrode voltammetry was carried out using a Hokuto HB104 function generator, a Nikko Keisoku DPGS-1 potentiostat, a Graphtech WX1000 plotter, and a Nikko Keisoku RRDE-1 rotating disk electrode with Nikko Keisoku SC-4 controller. The voltammetry was carried out in 0.1 M $LiClO_4/CH_3CN$ using a glassy carbon disk working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode (−0.04 V versus SCE) with sweep rate of 10 mV/s at 1000 rpm.

Syntheses

(Menthyloxymethyl)tributylstannane

To a suspension of potassium hydride (35 wt.% in mineral oil, 5.975 g, 52.1 mmol) in THF (60 ml) a solution of L-menthol (6.384 g, 40.9 mmol) in THF (40 ml) was added dropwise. After being stirred at room temperature for 1.2 h, (iodomethyl)tributylstannane [4] (17.374 g, 40.3 mmol) was added and the mixture was stirred for 3 h at room temperature. The reaction mixture was partitioned between brine and ether. The organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified via flash chromatography (hexane:ethyl acetate = 99:1) to obtain 13.746 g (29.9 mmol, 74%) of the title compound. TLC: R_f 0.72 (hexane:ethyl acetate = 39:1). VPC: t_R 14.9 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^1H NMR (90 MHz, $CDCl_3$): δ 0.45–0.90 (m, 43H), 2.00–2.40 (m, 2H), 2.60–3.00 (m, 1H), 3.43 (d, $J = 9$ Hz, 1H), 3.91 (d, $J = 9$ Hz, 1H). IR (neat): 2970(s), 2900(s), 2850(s), 1455(m), 1375(w), 1100(w), 1080(m), 1060(m), 1050(m) cm^{-1}. Low resolution MS (EI) *m/e* (%): 403 (28), 347 (2), 321 (2), 291 (100), 265 (4), 235 (62), 209 (3), 179 (41), 151 (3), 139 (3), 121 (4), 97 (6), 83 (46), 69 (12), 55 (11). High resolution MS ($M^+ - Bu$): calc. for $C_{19}H_{39}OSn$: 403.2023; found: 403.1998.

(Menthyloxymethyl)dimethylsilane

To a solution of BuLi (1.6 N in hexane, 1.3 ml, 2.1 mmol) in DME (3 ml) and THF (2 ml) was added (menthyloxymethyl)tributylstannane (0.497 g, 1.08 mmol) at −78 °C. After being stirred at −78 °C for 30 min, dimethylchlorosilane (2.6 ml, 2.3 mmol) was added dropwise. The mixture was warmed to room temperature and stirred at this temperature for 1.5 h. The reaction mixture was partitioned between brine and ether, and the organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent the residue was purified via flash chromatography (hexane:ethyl acetate = 99:1) to obtain 0.172 g (0.753 mmol, 69%) of the title compound. TLC: R_f 0.49 (hexane:ethyl acetate = 19:1). VPC: t_R 7.4 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^1H NMR (90 MHz, $CDCl_3$): δ 0.10 (d, $J = 0.9$ Hz, 3H), 0.18 (d, $J = 0.9$ Hz, 3H), 0.54–1.86 (m, 16H), 1.90–2.36 (m, 2H), 2.75–2.95 (m, 1H), 2.95 (dd, $J = 3$ and 12 Hz, 1H), 3.46 (dd, $J = 3$ and 12 Hz, 1H), 3.78–4.03 (m, 1H). IR (neat): 2950(s), 2910(s), 2860(s), 2800(m), 2110(s), 1455(m), 1370(m), 1345(w), 1250(s), 1105(s), 1085(s), 1070(s), 890(s), 840(s), 715(w) cm^{-1}. Low resolution MS (CI) *m/e* (%): 227 (23), 213 (10), 151 (4), 139 (100), 123 (5), 107 (3), 89 (45), 83 (23), 75 (21), 69 (4), 61 (7). High resolution MS (CI) ($M^+ - H$): calc. for $C_{13}H_{27}OSi$: 227.1831; found: 227.1814.

(Menthyloxymethyl)diphenylsilane

To a solution of BuLi (1.6 N in hexane, 10.8 ml, 17.7 mmol) in DME (18 ml) and THF (18 ml) was added (menthyloxymethyl)tributylstannane (3.505 g, 7.63 mmol) at −78 °C. After being stirred at −78 °C for 30 min, diphenylchlorosilane (18 ml, 9.2 mmol) was added dropwise. The mixture was warmed to room temperature and stirred at this temperature for 3 h. The reaction mixture was partitioned between brine and ether, and the organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent the residue was purified via flash chromatography (hexane:ethyl acetate = 99:1 to 79:1) to obtain 2.47 g (7.01 mmol, 92%) of the title compound. TLC: R_f 0.47 (hexane:ethyl acetate = 19:1). VPC: t_R 16.5 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^1H NMR (90 MHz, $CDCl_3$): δ 0.50–1.80 (m, 16H), 1.90–2.35 (m, 2H), 2.80–3.15 (m, 1H), 3.30–3.60 (m, 1H), 3.80–4.10 (m, 1H), 4.90–5.00 (t, $J = 3$ Hz, 1H), 7.05–7.43 (m, 6H), 7.43–7.60 (m, 4H). IR (neat): 3050(w), 2950(s), 2920(s), 2850(s), 2800(w), 2125(m), 1450(m), 1430(s), 1370(m), 1345(w), 1105(s), 1080(s), 1070(s), 970(w), 915(w), 850(m), 825(m), 795(m), 730(s), 695(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 351 (0.14), 309 (0.18), 274 (2.9), 259 (0.2), 231 (2), 213 (52), 197 (10), 183 (79), 167 (3), 150 (8), 138 (45), 123 (16), 105 (30), 95 (39), 83 (100), 69 (42), 55 (42). High resolution MS ($M^+ - C_6H_5$): calc. for $C_{17}H_{27}OSi$: 275.1832; found: 275.1815.

(Phenylthiomethyl)dimethylsilane

To a solution of thioanisole (4.232 g, 34.1 mmol) in 60 ml of ether, was added BuLi (1.6 N in hexane, 28 ml, 45 mmol) at 0 °C. The mixture was heated to reflux overnight. Dimethylchlorosilane (6.0 ml, 54 mmol) was added at 0 °C and the mixture was refluxed for 5 h. The reaction mixture was partitioned between aq. $NaHCO_3$ and ether. The organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified via bulb-to-bulb distillation (140 °C/20 mmHg) to obtain the title compound (5.530 g, 30.3 mmol, 89%). TLC: R_f 0.42 (hexane:ethyl acetate = 39:1). VPC: t_R 4.2 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^1H NMR (90 MHz, $CDCl_3$): δ 0.23 (d, $J = 3$ Hz, 6H), 2.25 (d, $J = 3$ Hz, 2H), 3.95–4.20 (m, 1H), 6.90–7.50 (m, 5H). IR (neat): 3100(m), 3000(m), 2925(m), 2160(s), 1590(s), 1490(s), 1450(s), 1400(m), 1260(s), 1140(m), 1090(m), 1035(m), 890(s), 850(s), 810(s), 790(s), 745(s), 695(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 182 (100), 167 (90), 151 (19), 135 (18), 121 (20), 109 (7), 105 (13), 91 (46), 77 (17), 73 (85), 65 (8), 59 (56), 51 (5). High resolution MS (M^+): calc. for $C_9H_{14}SiS$: 182.0585; found: 182.0561.

Phenylthiobis(dimethylsilyl)methane

To a solution of diisopropylamine (0.620 ml, 4.42 mmol) in 10 ml of THF was added BuLi (1.6 N in hexane, 2.6 ml, 4.3 mmol) at −78 °C. The mixture was stirred at 0 °C for 0.5 h. (Phenylthiomethyl)-dimethylsilane (0.438 g, 2.40 mmol) was added at −78 °C. The mixture was warmed to −10 °C. HMPA (0.75 ml, 4.3 mmol) was added at −78 °C and the mixture was added to dimethylchlorosilane (0.50 ml, 4.5 mmol) at the same temperature. The mixture was warmed to room temperature. The reaction mixture was partitioned between brine and hexane. The organic phase was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified via flash chromatography (hexane) to obtain the title compound (0.237 g, 0.99 mmol, 41%). TLC: R_f 0.53 (hexane:ethyl acetate = 19:1). VPC: t_R 6.4 min (OV-1 2%, 2m, 100–240 °C, 10 °C/min). ^1H NMR (400 MHz, $CDCl_3$): δ 0.173 (d, $J = 3.66$ Hz, 6H), 0.188 (d, $J = 3.66$ Hz, 6H), 1.678–1.755 (m, 1H), 4.043–4.086 (m, 2H), 7.103–7.332 (m, 5H). IR (neat): 3100(m), 2970(s), 2920(m), 2125(s), 1590(s), 1485(s), 1445(s), 1255(s), 1090(m), 1070(m), 1010(s), 890(br, s), 780(s), 740(s), 690(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 240 (48), 223 (16), 209 (5), 195 (2), 180 (30), 165 (100), 151 (16), 135 (60), 121 (5), 115 (20), 104 (11), 91 (21), 85 (2), 73 (40), 59 (26). High resolution MS (M^+): calc. for $C_{11}H_{20}Si_2S$: 240.0824; found: 240.0841.

Conversion of hydrosilanes to alkoxysilanes

(Menthyloxymethyl)dimethyl(2-octyloxy)silane

To a mixture of $PdCl_2$ (0.030 g, 0.17 mmol) in 1.5 ml of CCl_4 was added (menthyloxymethyl)dimethylsilane (0.297 g, 1.30 mmol) dropwise. 2-Octanol (0.16 ml, 1.0 mmol) was added and the mixture was stirred at room temperature for 0.5 h. Triethylamine (0.18 ml, 1.3 mmol) was added and the mixture was stirred at room temperature for 2 h. The reaction mixture was partitioned between brine and ether. The organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified via flash chromatography (hexane:ethyl acetate = 99:1) to obtain the title compound (0.353 g, 0.990 mmol, 99%). TLC: R_f 0.56 (hexane:ethyl acetate = 19:1). VPC: t_R 11.2 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^1H NMR (90 MHz, $CDCl_3$): δ 0.16 (s, 6H), 0.40–1.80 (m, 32H), 1.90–2.40 (m, 2H), 2.66–3.10 (m, 1H), 2.80 (d, $J = 12$ Hz, 1H), 3.40 (d, $J = 12$ Hz, 1H), 3.60–4.10 (m, 1H). IR (neat): 2950(s), 2920(s), 2850(s), 1455(m), 1370(m), 1345(w), 1250(s), 1085(br, s), 840(s), 795(m) cm^{-1}. Low resolution MS (CI) *m/e* (%): 357 (38), 341 (6), 271 (3), 245 (3), 219 (26), 203 (1), 177 (3), 155 (9), 139 (100), 129 (17), 113 (56). High resolution MS ($M^+ - CH_3$): calc. for $C_{20}H_{41}O_2Si$: 341.2876; found: 341.2861.

(Menthyloxymethyl)diphenyl(2-octyloxy)silane

Yield 99%. TLC: R_f 0.49 (hexane:ethyl acetate = 39:1). VPC: t_R 27.3 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^1H NMR (90 MHz, $CDCl_3$): δ 0.46–1.83 (m, 33H), 1.90–2.16 (m, 2H), 2.75–3.10 (m, 1H), 3.26–3.56 (m, 1H), 3.75–4.30 (m, 1H), 7.20–7.46 (m, 6H), 7.46–7.83 (m, 4H). IR (neat): 3050(w), 2950(s), 2920(s), 2850(s), 2800(w), 1590(w), 1450(m), 1430(s), 1370(m), 1345(w), 1110(s), 1080(s), 1070(s), 965(w), 915(w), 845(w), 790(m), 730(s), 695(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 465 (0.1), 437 (0.1), 395 (3.45), 351 (2.3), 341 (12), 311 (45), 257 (8), 231 (16), 213 (24), 199 (100), 183 (8), 167 (2), 151 (10), 138 (33), 123 (7), 95 (18), 83 (28), 69 (13). High resolution MS (CI) ($M^+ + H$): calc. for $C_{31}H_{49}O_2Si$: 481.3502; found: 481.3483.

(Phenylthiomethyl)dimethyl(2-octyloxy)silane

Yield 73%. TLC: R_f 0.38 (hexane:ethyl acetate = 19:1). VPC: t_R 11.4 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^1H NMR (90 MHz, $CDCl_3$): δ 0.25 (s, 6H), 0.70–1.70 (m, 16H), 2.23 (s, 2H), 3.70–4.10 (m, 1H), 6.90–7.40 (m, 5H). IR (neat): 3075(w), 2960(s), 2940(s), 2860(m), 1585(m), 1485(s), 1440(m), 1380(m), 1255(s), 1130(m), 1070(br, s), 835(s), 735(s), 690(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 310 (16), 225 (5), 198 (3), 187 (39), 165 (7), 124 (22), 116 (4), 75 (100). High resolution MS (M^+): calc. for $C_{17}H_{30}OSiS$: 310.1786; found: 310.1785.

Conversion of hydrosilanes to fluorosilanes

A general procedure for the CuF_2 promoted conversion of hydrosilanes to fluorosilanes is as follows. To a stirred mixture of $CuF_2 \cdot 2H_2O$ (15 mmol) and CCl_4 (15 ml) was added hydrosilane (5.0 mmol) at room temperature. The mixture was refluxed overnight. Solid materials were separated by filtration and the solvent was removed by evaporation. The residue was purified by bulb-to-bulb distillation.

(Menthyloxymethyl)dimethylfluorosilane
Yield 75% (bulb-to-bulb distillation 105–125 °C/30 mmHg). VPC: t_R 6.6 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.24 (d, $J = 3.67$ Hz, 3H), 0.25 (d, $J = 3.05$ Hz, 3H), 0.69–1.00 (m, 12H), 1.13–1.24 (m, 1H), 1.24–1.38 (m, 1H), 1.51–1.67 (m, 2H), 2.05–2.21 (m, 2H), 2.82–2.94 (m, 1H), 2.90 (dd, $J = 5.49$ and 13.43 Hz, 1H), 3.45 (dd, $J = 3.67$ and 13.43 Hz, 1H). IR ($CDCl_3$): 2960(s), 2920(s), 2870(s), 1451(w), 1370(w), 1349(w), 1260(s), 1108(m), 1088(m), 1073(m), 852(s), 810(m), 708(br) cm^{-1}. Low resolution MS (CI) *m/e* (%): 231 (12), 245 (34), 227 (22), 197 (8), 168 (3), 161 (9), 149 (6), 140 (100), 139 (100), 137 (78), 123 (23), 109 (21). High resolution MS (M+H): calc. for $C_{13}H_{28}OSiF$: 247.1893; found: 247.1882.

(Phenylthiomethyl)dimethylfluorosilane
Yield 70% (bulb-to-bulb distillation 120–140 °C/20 mmHg). TLC: R_f 0.40 (hexane:ethyl acetate = 39:1). VPC: t_R 4.0 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.35 (d, $J = 7.5$ Hz, 6H), 2.35 (d, $J = 4.5$ Hz, 2H), 7.00–7.50 (m, 5H). IR (neat): 3060(w), 2960(m), 2890(w), 1585(s), 1485(s), 1440(s), 1390(m), 1225(s), 1135(m), 1090(m), 1070(w), 1025(m), 840(br, s), 735(s), 685(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 200 (97), 185 (26), 165 (13), 154 (15), 139 (50), 123 (25), 109 (12), 91 (93), 77 (100), 65 (6), 51 (4). High resolution MS (M^+): calc. for $C_9H_{13}SiSF$: 200.0492; found: 200.0482.

Phenylthiobis(dimethylfluorosilyl)methane
Yield 63% (bulb-to-bulb distillation 123 °C/15 mmHg). VPC: t_R 9.2 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^{1}H NMR ($CDCl_3$): δ 0.27 (d, 5.4 Hz, 6H), 0.38 (d, 5.4 Hz, 6H), 1.82 (t, 4.5 Hz, 1H), 6.93–7.63 (m, 5H). IR (neat): 3100(w), 3000(m), 2930(w), 1595(s), 1490(s), 1450(m), 1410(w), 1270(s), 1100(m), 1035(m), 1020(m), 870(br), 765(s), 750(s), 700(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 276 (49), 261 (9), 245 (4), 217 (2), 199 (30), 180 (26), 165 (100), 151 (11), 135 (53), 122 (5), 103 (4), 91 (6), 77 (24), 59 (6). High resolution MS (M^+): calc. for $C_{11}H_{18}SSi_2F_2$: 276.0636; found: 276.0648.

Anodic oxidation of (menthyloxymethyl)dimethylsilane and (menthyloxymethyl)dimethylfluorosilane
In an undivided cell equipped with a carbon rod anode and a platinum plate cathode was placed a solution of (menthyloxymethyl)dimethylsilane (54 mg, 0.24 mmol) in 0.2 M Et_4NOTs/MeOH (5 ml). Constant current electrolysis (10 mA) was carried out at room temperature (20.6 F/mol). The reaction mixture was partitioned between ether and aq. $NaHCO_3$. The organic phase was separated, dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by bulb-to-bulb distillation to obtain menthyloxymethyl methyl ether (28 mg, 59%) which was identified by comparison of its spectral data with an authentic sample [5].

Anodic oxidation of (menthyloxymethyl)dimethylfluorosilane was carried out in a similar fashion to obtain menthyloxymethyl methyl ether (62%, 3.4 F/mol).

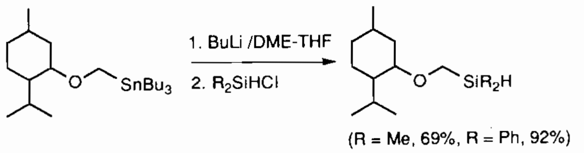
Hydrosilylation of 1-decene with (phenylthiomethyl)dimethylsilane
A mixture of 1-decene (0.095 ml, 0.50 mmol), (phenylthiomethyl)dimethylsilane (0.161 g, 0.883 mmol) and a solution of H_2PtCl_6 in 2-propanol (0.005 ml, 5×10^{-5} mmol) was heated in a sealed tube at 120 °C overnight. The volatile materials were removed by bulb-to-bulb distillation (140 °C/10 mmHg), and the residue was purified via flash chromatography (hexane) to obtain (phenylthiomethyl)(1-decyl)dimethylsilane (0.123 g, 0.381 mmol, 76%). TLC: R_f 0.36 (hexane). VPC: t_R 13.9 min (OV-1 2%, 2 m, 100–240 °C, 10 °C/min). ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.15 (s, 6H), 0.40–1.80 (m, 21H), 2.20 (s, 2H), 7.00–7.50 (m, 5H). IR (neat): 3060(w), 2920(s), 2850(s), 1585(m), 1485(s), 1470(m), 1440(m), 1390(m), 1250(s), 1125(w), 1090(w), 1025(m), 840(br, s), 735(s), 690(s) cm^{-1}. Low resolution MS (EI) *m/e* (%): 322 (33), 307 (3), 274 (2), 199 (17), 181 (100), 167 (29), 151 (4), 135 (19), 124 (34), 99 (12), 87 (14), 73 (22), 59 (64). High resolution MS (M^+): calc. for $C_{19}H_{34}SiS$: 322.2151; found: 322.2150.

Results and discussion

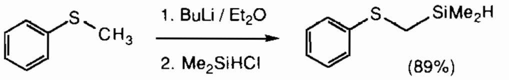
Synthesis of α-heteroatom-substituted hydrosilanes

Since it is well known that hydrosilanes can be readily converted into other sila-functional organosilicon compounds, we synthesized α-heteroatom-substituted hydrosilanes ($RYCH_2SiR'_2H$, Y = O, S). (α-Alkoxyalkyl)hydrosilanes were readily prepared by the reaction of α-alkoxycarbanions with chlorosilanes having a Si–H bond. For example, the transmetallation of (menthyloxymethyl)tributylstannane with BuLi [6] followed by the treatment with chlorodimethylsilane afforded (menthyloxymethyl)dimethylsilane (eqn. (1)). (Menthyloxymethyl)diphenylsilane was also prepared similarly.

(Phenylthiomethyl)dimethylsilane was prepared by the lithiation of thioanisole with BuLi in refluxing ether [7] followed by the treatment with chlorodimethylsilane (eqn. (2)).

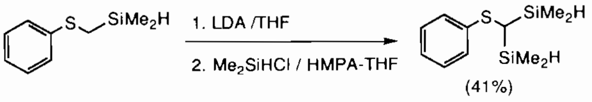


(1)



(2)

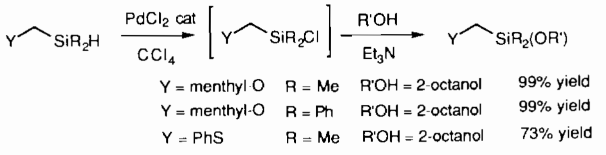
(Phenylthiomethyl)dimethylsilane was readily deprotonated with lithium diisopropylamide (LDA) in THF and the resulting anion was allowed to react with chlorodimethylsilane to obtain phenylthiobis(dimethylsilyl)methane (eqn. (3)).



(3)

Conversion of hydrosilanes to alkoxysilanes

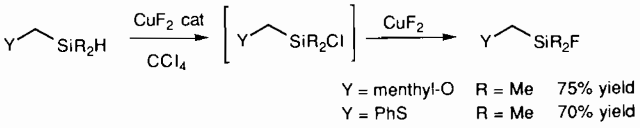
Direct conversion of hydrosilanes to alkoxysilanes was carried out by a one-pot process involving the PdCl$_2$-catalyzed chlorination in CCl$_4$ [8] followed by the reaction with an alcohol in the presence of triethylamine. Thus (menthyloxymethyl)dimethylsilane, (menthyloxymethyl)diphenylsilane and (phenylthiomethyl)dimethylsilane were converted into (menthyloxymethyl)dimethyl(2-octyloxy)silane, (menthyloxymethyl)diphenyl(2-octyloxy)silane, and (phenylthiomethyl)dimethyl(2-octyloxy)silane, respectively (eqn. (4)).



(4)

Conversion of hydrosilanes to fluorosilanes

Because of the unique properties of organofluorosilanes, there is a rich literature on the chemistry of organofluorosilanes [9]. We were interested in the effect of fluorine substituents on electrochemical redox properties of α-heteroatom-substituted organosilicon compounds. Since we have already developed a new direct method for the conversion of hydrosilanes to fluorosilanes using CuF$_2\cdot$2H$_2$O in CCl$_4$, α-heteroatom-substituted fluorosilanes were synthesized by using this method (eqn. (5)). The reaction was simple to perform. A mixture of a hydrosilane and CuF$_2\cdot$2H$_2$O was refluxed in CCl$_4$ overnight. After filtration followed by distillation the corresponding fluorosilane was obtained in fair to good yield. The reaction seemed to proceed by the initial CuF$_2$-catalyzed radical chlorination with CCl$_4$ followed by the conversion of the resulting chlorosilane to the fluorosilane with CuF$_2$ [10]. This method provides a convenient access to fluorosilanes under very mild conditions. The detailed mechanism and the scope of the reaction will be reported elsewhere.



(5)

Properties of sila-functional α-heteroatom-substituted organosilicon compounds

Electrochemical oxidation potentials

With α-heteroatom-substituted hydrosilanes, alkoxysilanes and fluorosilanes thus prepared in hand we have studied their electrochemical properties. Electro-

TABLE 1. Oxidation potentials of sila-functional α-heteroatom-substituted organosilicon compounds[a]

Compound	Oxidation potential	
	E_d (V)	$E_{1/2}$ (V)
$\mathrm{MenO{\wedge}SiMe_3}$[b]	1.65	1.83
$\mathrm{MenO{\wedge}SiMe_2H}$	1.73	1.87
$\mathrm{MenO{\wedge}SiMe_2OCH(CH_3)C_6H_{13}}$	—[c]	—
$\mathrm{MenO{\wedge}SiMe_2F}$	1.81	—
$\mathrm{MenO{\wedge}SiPh_2H}$	1.64	—
$\mathrm{MenO{\wedge}SiPh_2OCH(CH_3)C_6H_{13}}$	1.66	—
$\mathrm{PhS{\wedge}SiMe_3}$	1.17	1.29
$\mathrm{PhS{\wedge}SiMe_2H}$	1.17	—
$\mathrm{PhS{\wedge}SiMe_2OCH(CH_3)C_6H_{13}}$	1.10	1.25
$\mathrm{PhS{\wedge}SiMe_2C_{10}H_{21}}$	1.18	1.29
$\mathrm{PhS{\wedge}SiMe_2F}$	1.27	1.39
$\mathrm{PhS{-}\!<^{SiMe_3}_{SiMe_3}}$	1.09	1.18
$\mathrm{PhS{-}\!<^{SiMe_2H}_{SiMe_2H}}$	1.10	—
$\mathrm{PhS{-}\!<^{SiMe_2F}_{SiMe_2F}}$	1.26	1.41

[a] E_d (decomposition potential) and $E_{1/2}$ (half wave potential) were determined by rotating disk electrode voltammetry using a glassy carbon electrode in 0.1 M LiClO$_4$/CH$_3$CN with an Ag/AgCl reference electrode. [b] Men = menthyl. [c] A reproducible wave was not obtained probably because of hydrolysis of the alkoxysilane during the measurement.

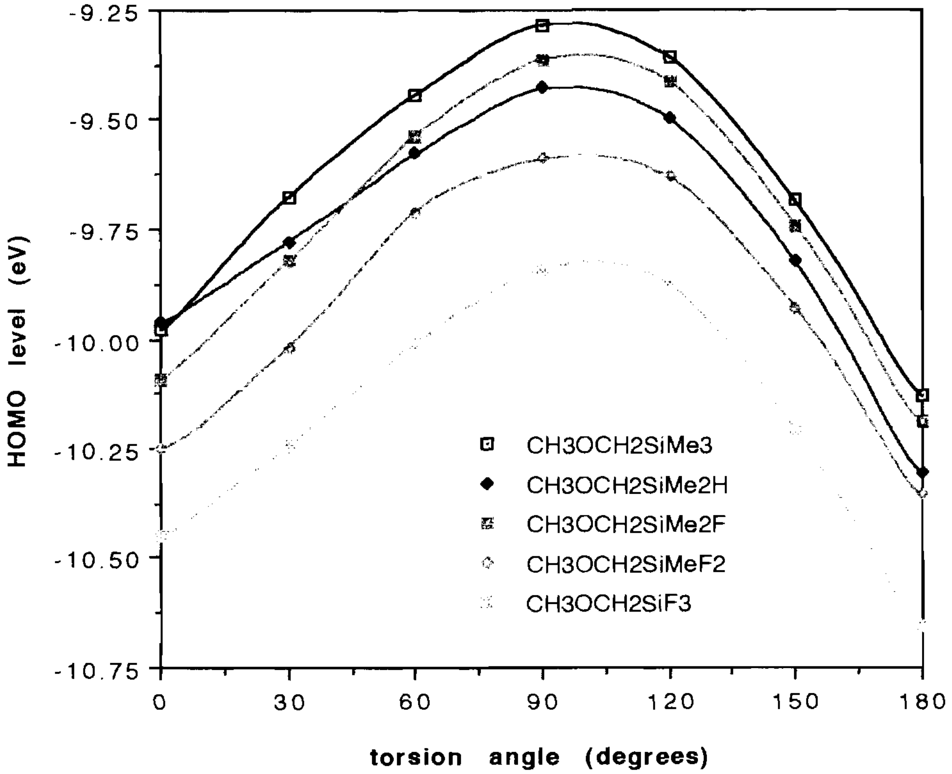


Fig. 1. Variation of HOMO levels of $CH_3OCH_2SiMe_nX_{3-n}$.

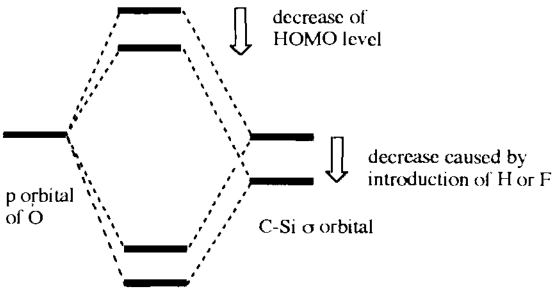


Fig. 2. Energy level diagram of interaction of the C–Si σ orbital and 2p orbital of the oxygen atom.

chemical oxidation potentials of sila-functional α-heteroatom-substituted organosilicon compounds were determined using rotating disk electrode voltammetry in $LiClO_4/CH_3CN$, and the results are summarized in Table 1. Oxidation potentials of α-heteroatom-substituted dimethylhydrosilanes were slightly more anodic than the corresponding trimethylsilanes. Oxidation potentials of alkoxysilanes were quite similar to those of hydrosilanes. The introduction of a fluorine substituent on the silicon atom caused further anodic shift of the oxidation wave.

The effect of the substituent on the silicon for (menthyloxymethyl)silanes is greater than that for (phenylthiomethyl)silanes. This observation is in accord with better overlap of the non-bonding p orbital of oxygen with the C–Si σ orbital than that of the orbital of sulfur. The oxidation potentials of sulfides having two silyl groups were also examined. Replacement of the methyl group by hydrogen caused little increase in the oxidation potential, but fluorine substitution caused an increase in the oxidation potential. The following points should be noted. The oxidation potentials of sulfides having two $SiMe_3$ groups or two $SiMe_2H$ groups were lower than those having one silyl group. Two silyl groups work cooperatively to reduce the oxidation potential. In the case of $SiMe_2F$, however, the oxidation potential of the compound having two silyl groups was quite similar to that having one silyl group. Therefore, two $SiMe_2F$ groups do not work cooperatively. This is probably because the energy level of the C–$SiMe_2F$ σ orbital is quite low and it cannot interact with the high sulfur p orbital effectively.

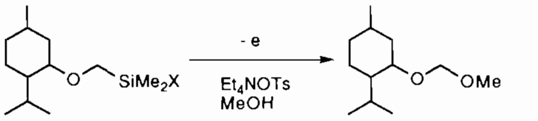
HOMO levels of α-alkoxysilanes having a hydrogen or a fluorine substituent on the silicon were determined by PM3 calculations [11], and plotted against the torsion angle of Si–C–O–C (Fig. 1). The results obtained by the calculations were consistent with the experimental oxidation potentials. The anodic shift caused by the replacement of the methyl group on the silicon atom by a hydrogen or fluorine atom is ascribed to the decrease in the energy level of the carbon–silicon σ orbital, which in turn lowers the HOMO level (Fig. 2). It is interesting that the shape of the curve of

HOMO level is not affected by the substituents on the silicon appreciably, indicating that the geometrical requirement does not depend upon the nature of the substituents.

Reactions of α-heteroatom-substituted hydrosilanes

Preparative anodic oxidation

Since we have shown that electrochemical oxidation of α-heteroatom-substituted trialkylsilanes gave rise to the cleavage of the C–Si bond and the introduction of a nucleophile onto the carbon [2], preparative anodic oxidation of sila-functional α-heteroatom-substituted organosilicon compounds was investigated. Constant current anodic oxidation of (menthyloxymethyl)-dimethylfluorosilane in methanol in an undivided cell gave menthyloxymethyl methyl ether although the yield of the product was not high (eqn. (6)) indicating that cleavage of the C–Si bond took place smoothly. Anodic oxidation of (menthyloxymethyl)dimethylsilane in methanol also resulted in the formation of the same product (59%), although the reaction required a large amount of electricity. Presumably the Si–H bond was also oxidized electrochemically during the reaction.

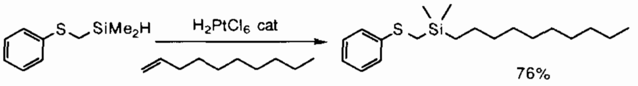


X = F: 62% (3.4 F/mol)
X = H: 59% (20.6 F/mol)

(6)

Hydrosilylation of olefins

Hydrosilylation of olefins [12] is one of the most important methods for the synthesis of organosilicon compounds. Therefore, we have examined the hydrosilylation of olefins with α-heteroatom-substituted hydrosilanes. The reaction of 1-decene with (phenylthiomethyl)dimethylsilane in the presence of a catalytic amount of H_2PtCl_6 proceeded smoothly at 120 °C in a sealed tube to give (phenylthiomethyl)dimethyldecylsilane in good yield (eqn. (7)). The presence of a sulfur atom in the hydrosilane did not interfere with the catalytic cycle. Thus hydrosilylation of α-heteroatom-substituted hydrosilanes provides a useful method for preparation of α-heteroatom-substituted organosilicon compounds.



(7)

Acknowledgements

We thank the Ministry of Education, Science and Culture, Japan for a Grant-in-Aid for Scientific Research for financial support.

References

1 J. Yoshida, T. Murata, S. Matsunaga, T. Maekawa, S. Shiozawa and S. Isoe, *Rev. Heteroatom. Chem., 5* (1991) 193.
2 (a) J. Yoshida and S. Isoe, *Chem. Lett.,* (1987) 631; (b) J. Yoshida and S. Isoe, *Tetrahedron Lett., 28* (1987) 6621; (c) J. Yoshida, T. Murata and S. Isoe, *J. Organomet. Chem., 345* (1988) C23; (d) J. Yoshida, S. Matsunaga and S. Isoe, *Tetrahedron Lett., 30* (1989) 219; (e) J. Yoshida, S. Matsunaga, T. Murata and S. Isoe, *Tetrahedron, 47* (1991) 615.
3 J. Yoshida, T. Maekawa, T. Murata, S. Matsunaga and S. Isoe, *J. Am. Chem. Soc., 112* (1990) 1962.
4 D. Seyferth and S.B. Andrews, *J. Organomet. Chem., 30* (1971) 151.
5 J. Yoshida, Y. Ishichi, K. Nishiwaki, S. Shiozawa and S. Isoe, *Tetrahedron Lett., 33* (1992) 2599.
6 W.C. Still, *J. Am. Chem. Soc., 100* (1978) 1481.
7 (a) D.J. Ager and R.C. Cookson, *Tetrahedron Lett., 21* (1980) 1677; (b) P.J. Kocienski, *Tetrahedron Lett., 21* (1980) 1559.
8 (a) J.P. Banovetz, Y.-L. Hsiao and R.M. Waymouth, *J. Am. Chem. Soc., 115* (1993) 2540; (b) Y. Nagai, H. Matsumoto, T. Yagihara and K. Morishita, *Kogyo Kagaku Zasshi, 71* (1968) 1112; (c) Y. Nagai, K. Yamazaki, I. Shiojima, N. Kobori and M. Hayashi, *J. Organomet. Chem., 9* (1967) P21.
9 R.M. Pike and K.A. Koziski, *J. Organomet. Chem. Library, 9* (1980) 41.
10 K. Tamao, J. Yoshida, H. Yamamoto, T. Kakui, H. Matsumoto, M. Takahashi, A. Kurita, M. Murata and M. Kumada, *Organometallics, 1* (1982) 355.
11 MOPAC Version 5, J.J.P. Stewart, *QCPE,* No. 455 (Revised as Version 5.01 by T. Hiranao, for HITAC and Unix machines; *JCPE Newslett., 1* (1989) 36) (revised as Version 5.02 by J. Yoshida, for NDP Fortran).
12 I. Ojima, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds,* Wiley, New York, 1989, Ch. 25.