Electrochemistry of Organosilicon Compounds. 2. Synthesis of Polysilane Oligomers by a Copper Electrode System[1]

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Electrochemical synthesis of some lower homologues of polysilanes has been reported. Disilanes, trisilanes, tetrasilanes, and pentasilanes were readily obtained in high yields by the use of a copper electrode system.

Introduction

Recently, considerable attention has been focused in the synthesis of the polymers that have silicon–silicon bonds in the polymer backbone, because these polymers are expected to be used as functional materials. However, the methods for the formation of the Si–Si bond reported to date are restricted to the alkali-[2,3] and alkali-earth[4] metal condensation, transition-metal-catalyzed reaction of hydrosilanes,[5–8] electrochemical reduction of chlorosilanes,[1,9–13] and redistribution reaction of disilane fractions of the residue of the direct method of methylchlorosilanes.[14,15] Moreover, there are some limitations for all of these methods.

Recently, we have demonstrated that the electrochemical reduction of chlorosilanes using platinum as the cathode and mercury as the anode in an undivided cell results in the formation of di- and trisilanes in high yields and also found that silver can be effectively used as the anode instead of mercury.[1] In order to find a much more effective electrode system for the Si–Si bond formation, we have investigated the use of the copper electrode system and found that polysilane oligomers are obtained in high yields by using this system.

Results and Discussion

As described in the previous paper,[1] the use of mercury as the anode material in an undivided cell affords high yields of disilanes. For example, the electrochemical reduction of chloromethyldiphenylsilane in 1,2-dimethoxyethane gave 1,2-dimethyltetraphenyldisilane (1) in 89% yield. However, when the reaction was carried out in the absence of mercury anode, the disilane 1 was produced only in low yield. Consequently, mercury serves as a good "sacrificed" anode and is oxidized to monovalent Hg ions during the electrolysis. Therefore, the stoichiometric amounts of mercury(I) chloride are produced as a byproduct upon the electrolysis. We thought it desirable to achieve the reaction with the use of nontoxic electrodes.

We have found that silver is an effective anode material for the formation of the Si–Si bond.[1] In this reaction, silver is oxidized to form insoluble silver chloride, and the surface of the silver electrode is covered with a growing layer of silver chloride, but both the anode and cathode do not become passive. Consequently, the electrolysis of chlorosilanes with the use of the silver anode proceeds smoothly to give disilanes in high yields. However, the silver electrode is not appropriate for the large-scale synthesis of polysilanes in the economic sense. We have found that copper metal can be used as the anode. In this case, the anode surface is also covered with a layer of insoluble copper(I) chloride, but again, the electrodes do not become passive.

The electrochemical synthesis of polysilane oligomers was carried out in 1,2-dimethoxyethane (20 mL), using a platinum plate (6 cm^2) as the cathode and a copper wire as the anode (28 cm^2) under controlled-current conditions (30 mA). When chloromethyldiphenylsilane (4.74 mmol) was electrolyzed, 1,2-dimethyltetraphenyldisilane (1) was obtained in 83% yield (eq 1), while the reduction of the

$$2Ph_2MeSiCl \xrightarrow{+2e} \underset{1\ (83\%)}{Ph_2MeSi\text{–}SiMePh_2} \qquad (1)$$

same chlorosilane in the presence of 2.6 mol equiv of chlorotrimethylsilane gave 1,1-diphenyltetramethyldisilane (2) in 77% yield (eq 2).

$$Ph_2MeSiCl + Me_3SiCl \xrightarrow{+2e} \underset{2\ (77\%)}{Ph_2MeSi\text{–}SiMe_3} + 1(\text{trace}) \qquad (2)$$

The Pt–Cu electrode system is also applicable to the synthesis of trisilanes. The reaction of dichloromethylphenylsilane with 10.3 mol equiv of chlorotrimethylsilane gave 2-phenylheptamethyltrisilane (3) and 2,3-diphenyloctamethyltetrasilane (4) in 61% and 23% yields, respectively (eq 3). When 1-chloro-1-phenyltetramethyldisilane was electrolyzed in the presence of 2.1 mol equiv

$$PhMeSiCl_2 + 2Me_3SiCl \xrightarrow{+4e} \underset{3\ (61\%)}{Me_3Si\text{–}PhMeSi\text{–}SiMe_3} + \underset{4\ (23\%)}{Me_3Si\text{–}PhMeSi\text{–}PhMeSi\text{–}SiMe_3} \qquad (3)$$

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of chlorotrimethylsilane, the trisilane **3** was obtained in 74% yield, together with 14% yield of the tetrasilane **4** (eq 4).

$$Me_3Si\text{-}PhMeSiCl + Me_3SiCl \xrightarrow{+2e} \mathbf{3}\ (74\%) + \mathbf{4}\ (4\%) \quad (4)$$

Furthermore, it was shown that the Pt–Cu electrode system can be extended to the synthesis of polysilane oligomers such as tetra- and pentasilanes. Thus, the electrolysis of 1-chloro-1-phenyltetramethyldisilane gave the tetrasilane **4** in 90% yield (eq 5), while similar treatment of chloropentamethyldisilane gave decamethyltetrasilane (**5**) in 89% yield (eq 6). The electrolysis of a 1:4 mixture of dichloromethylphenylsilane and chloropentamethyldisilane gave 3-phenylundecamethylpentasilane (**6**) in 79% yield (eq 7).

$$2Me_3Si\text{-}PhMeSiCl \xrightarrow{+2e} \mathbf{4}\ (90\%) \quad (5)$$

$$2Me_3Si\text{-}Me_2SiCl \xrightarrow{+2e} \underset{\mathbf{5}\ (89\%)}{Me_3Si\text{-}Me_2Si\text{-}Me_2Si\text{-}SiMe_3} \quad (6)$$

$$PhMeSiCl_2 + 2Me_3Si\text{-}Me_2SiCl \xrightarrow{+4e} \underset{\mathbf{6}\ (79\%)}{Me_3Si\text{-}Me_2Si\text{-}PhMeSi\text{-}Me_2Si\text{-}SiMe_3} \quad (7)$$

We have also found that copper can be used for the cathode material instead of platinum. When the electrolysis of chloromethyldiphenylsilane was carried out with copper as both the anode and cathode, the disilane **1** was obtained in 78% yield.

Thus, with the use of the Pt–Cu or Cu–Cu electrode system, a wide variety of polysilane oligomers, disilanes through pentasilanes, were obtained selectively in high yields. In the electrochemical formation of the Si–Si bond reported to date, a large amount of siloxanes are always produced. However, in the present system, the formation of siloxanes was found to be less than a few percent in all cases.[16]

The advantage of the present system is that the synthesis of the polysilane oligomers can be readily performed at room temperature and no special workup is required for isolation of the products. Moreover, the use of the copper anode is suitable for large-scale synthesis because copper is much cheaper than silver and much less toxic than mercury. Thus, we carried out the electrolysis of chloromethyldiphenylsilane (104 mmol) using copper nets of 60 mesh ASTM for both the cathode (95 cm^2) and the anode (400 cm^2) in 1,2-dimethoxyethane (200 mL) containing tetrabutylammonium perchlorate (10 g) (see Figure 1) and obtained 15.11 g (74% yield) of pure disilane **1** after recrystallization from ethanol–benzene (9:1). Similarly, 10.68 g (80%) of disilane **2** was obtained by the electrolysis of a mixture of chloromethyldiphenylsilane (49.3 mmol) and chlorotrimethylsilane (124 mmol), while 5.09 g (65%) of trisilane **3** and 1.62 g (28%) of tetrasilane **4** were obtained by the electrolysis of a mixture of dichloromethylphenylsilane (29.5 mmol) and chlorotrimethylsilane (181 mmol), followed by treatment of the resulting mixture with MPLC on silica gel. Similarly, electrolysis of 1-chloro-1-phenyltetramethyldisilane (74.5 mmol) gave 12.0 g (83%) of tetrasilane **4**. Pentasilane **5** (12.9 g, 74%) was also obtained by the electrolysis of dichloromethylphenylsilane (46.0 mmol) and chloropentamethyldisilane (305 mmol), followed by dilution of the concentrated reaction mixture with hexane, removal of tetrabutylammonium perchlorate by filtration, and then distillation of the resulting solution.

(16) The formation of siloxanes can be avoided by careful drying of the electrolytic system including the solvent and supporting electrolyte as well as by exhaustive electrolysis of chlorosilanes. Particular precautions are noted in the previous work.[1]

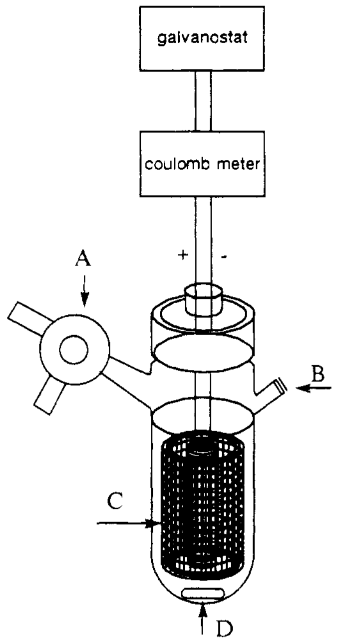

Figure 1. Electrolytic apparatus with copper–copper electrodes for large-scale synthesis: (A) three-way cock attached to vacuum/nitrogen lines; (B) rubber septum for sampling; (C) copper nets; (D) magnetic spin bar.

Experimental Section

General Considerations. The electrolysis of chlorosilanes for a small scale was carried out in a 25-mL undivided cell equipped with a platinum plate (6 cm^2) as the cathode and a coiled copper wire (28 cm^2) 1 mm in diameter as the anode. Into the cell was placed 1.25 g of tetrabutylammonium perchlorate, and the cell was dried at 50 °C in vacuo for 3 h. Chlorosilane and 20 mL of 1,2-dimethoxyethane were then added to the cell under a dry nitrogen atmosphere. Electrolysis was carried out in a manner of controlled current (30 mA). The progress of the reaction was monitored by GPC, and the electrolysis was continued until the starting material disappeared.[17] The resulting solution was concentrated under a reduced pressure. Products were isolated by MPLC (silica gel 40–63 μm), eluting with hexane or a mixture of hexane and dichloromethane (9:1).

For the purpose of the large-scale synthesis of disilanes through tetrasilanes, electrolysis was performed by using copper nets (60 mesh ASTM) for both the cathode (95 cm^2) and the anode (400 cm^2) in 1,2-dimethoxyethane (200 mL) containing tetrabutylammonium perchlorate (10 g) with a constant current of 200 mA. The copper nets were washed with diluted hydrochloric acid and then with water and dried before use. The copper net used as the anode was installed cylindrically in the reaction vessel, and the cathode was set up in the middle of the anode, as shown in Figure 1. In the case of the pentasilane synthesis, the amounts of the solvent and supporting electrolyte used were 15 g and 400 mL, respectively, and the surface area for the cathode and the anode was set up to be 213 and 850 cm^2, respectively.

The structures of the polysilanes obtained were characterized by spectroscopic methods, as well as by elemental analysis. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. ^1H NMR (90 MHz) and ^{13}C NMR (22.5 MHz) spectra were determined on a JEOL Model JNM-FX-90A spectrometer. All spectral data obtained for the polysilanes were identical with those reported previously. In the reaction consisting of two different chlorosilanes, the yields were calculated on the basis

(17) During the electrolysis, the solution turned pale yellow at the initial stage and then became colorless.

of the chlorosilanes which were used in a smaller amount. Current efficiency (ce) was calculated by an equation: [mol of product × number of electrons concerned/quantity of electricity in Faradays] × 100.

Materials. Chloromethyldiphenylsilane, chlorodimethylphenylsilane, dichloromethylphenylsilane, and chlorotrimethylsilane were supplied by Shin-Etsu Chemical Co. Ltd. and were used after distillation. Chloropentamethyldisilane[18] and 1-chloro-1-phenyltetramethyldisilane[19] were synthesized by the method reported in the literature. 1,2-Dimethoxyethane and tetrabutylammonium perchlorate were purified and dried in the manner described in the previous paper.[1]

Reduction of Chloromethyldiphenylsilane. Chloromethyldiphenylsilane (4.74 mmol) was electrolyzed for 5.0 h (5.57 mF) to give 1,2-dimethyltetraphenyldisilane[20] (1) (0.780 g, 1.98 mmol, 83% yield, 71% ce). When the same reaction was carried out with copper as both anode and cathode material, the disilane 1 was obtained in 78% yield. All spectral data obtained for 1 were identical with those obtained in the previous work.[1]

Reduction of a Mixture of Chloromethyldiphenylsilane and Chlorotrimethylsilane. A mixture of chloromethyldiphenylsilane (4.06 mmol) and chlorotrimethylsilane (10.6 mmol) was electrolyzed for 9.8 h (11.0 mF) to give 1,1-diphenyltetramethyldisilane[21] (2) (0.842 g, 3.11 mmol, 77% yield, 57% ce). Spectral data obtained for 2 were identical with those obtained in the previous work.[1]

Reduction of a Mixture of Dichloromethylphenylsilane and Chlorotrimethylsilane. Dichloromethylphenylsilane (2.76 mmol) and chlorotrimethylsilane (28.5 mmol) were electrolyzed for 17.4 h (19.5 mF) to give 2-phenylheptamethyltrisilane[22] (3) (0.451 g, 1.69 mmol, 61% yield, 35% ce) and 2,3-diphenyloctamethyltetrasilane (4) (0.125 g, 0.323 mmol, 23% yield, 10% ce). Spectral data obtained for 3 were identical with those obtained in the previous work.[1] The tetrasilane 4 was identical with that obtained below.[23]

Reduction of a Mixture of 1-Chloro-1-phenyltetramethyldisilane and Chlorotrimethylsilane. 1-Chloro-1-phenyltetramethyldisilane (4.10 mmol) and chlorotrimethylsilane (8.70 mmol) were electrolyzed for 7.9 h (8.84 mF) to give trisilane 3 (0.808 g, 3.03 mmol, 74% yield, 69% ce) and tetrasilane 4 (0.114 g, 0.29 mmol, 14% yield, 7% ce).

Reduction of 1-Chloro-1-phenyltetramethyldisilane. 1-Chloro-1-phenyltetramethyldisilane (4.05 mmol) was electrolyzed for 3.8 h (4.26 mF) to give tetrasilane[24] 4 (0.702 g, 1.81 mmol, 90% yield, 85% ce): ^1H NMR (δ in $CDCl_3$) −0.02 (s, 9 H, Me), 0.00 (s, 9 H, Me), 0.48 (s, 3 H, Me), 0.50 (s, 3 H, Me), 7.15–7.45 (m, 10 H, Ph); ^{13}C NMR (δ in $CDCl_3$) −7.45 (Me), −1.01 (Me_3), 127.60, 127.71, 127.92, 134.64, 134.80, 137.51, 137.62 (Ph); Mass m/e 386 (M^+), 371 (M^+ − Me), 313 ($M^+ - Me_3Si$), 193 ($Me_3SiPhMeSi^+$), 73 (Me_3Si^+).

Reduction of Chloropentamethyldisilane. Chloropentamethyldisilane (9.01 mmol) was electrolyzed for 7.9 h (8.80 mF) to give decamethyltetrasilane[25] (5) (1.051 g, 4.00 mmol, 89% yield, 91% ce): ^1H NMR (δ in $CDCl_3$) 0.10 (s, 18 H, Me), 0.12 (s, 12 H, Me); ^{13}C NMR (δ in $CDCl_3$) −5.88 (Me), −1.22 (Me); Mass m/e 262 (M^+), 247 (M^+ − Me), 189 ($M^+ - Me_3Si$), 131 ($Me_3SiMe_2Si^+$), 73 (Me_3Si^+).

Reduction of Dichloromethylphenylsilane and Chloropentamethyldisilane. Dichloromethylphenylsilane (3.60 mmol) and chloropentamethyldisilane (14.3 mmol) were electrolyzed for 13.9 h (15.6 mF) to give 3-phenylundecamethylpentasilane (6) (1.09 g, 2.85 mmol, 79% yield, 73% ce): ^1H NMR (δ in $CDCl_3$) −0.07 (s, 18 H, Me), 0.206 (s, 6 H, Me), 0.213 (s, 6 H, Me), 0.47 (s, 3 H, Me), 7.15–7.40 (m, 5 H, Ph); ^{13}C NMR (δ in $CDCl_3$) −7.02 (Me), −5.23 (Me_2), −4.91 (Me_2), −1.50 (Me_6), 127.60, 127.76, 134.37, 138.43 (Ph); Mass m/e 382 (M^+), 309 ($M^+ - Me_3Si$), 251 ($M^+ - Me_5Si_2$), 131 ($Me_3SiMe_2Si^+$), 73 (Me_3Si^+). Anal. Calcd for $C_{17}H_{38}Si_5$: C, 53.32; H, 10.00. Found: C, 53.20; H, 9.98.

Large-Scale Electrolysis with a Cu–Cu Electrode System. Chloromethyldiphenylsilane (104 mmol) was electrolyzed for 24.8 h (185 mF). The reaction mixture was concentrated, and the resultant was eluted through a short silica-gel column with benzene to remove tetrabutylammonium perchlorate. Recrystallization from ethanol–benzene (9:1) afforded disilane 1 (15.11 g, 38.3 mmol, 74% yield, 41% ce).

Chloromethyldiphenylsilane (49.3 mmol) and chlorotrimethylsilane (124 mmol) were electrolyzed for 13.8 h (103 mF). Disilane 2 (10.68 g, 39.5 mmol, 80% yield, 77% ce) was isolated by chromatographic techniques.

Dichloromethylphenylsilane (29.5 mmol) and chlorotrimethylsilane (181 mmol) were electrolyzed for 14.3 h (107 mF). Trisilane 3 (5.09 g, 19.1 mmol, 65% yield, 71% ce) and tetrasilane 4 (1.62 g, 4.19 mmol, 28% yield, 24% ce) were isolated by chromatographic techniques.

1-Chloro-1-phenyltetramethyldisilane (74.5 mmol) was electrolyzed for 14.2 h (106 mF). Tetrasilane 4 (11.97 g, 31.0 mmol, 83% yield, 58% ce) was isolated by chromatographic techniques.

Dichloromethylphenylsilane (46.0 mmol) and chloropentamethyldisilane (305 mmol) were electrolyzed for 35.0 h (261 mF). The reaction mixture was concentrated and diluted with hexane. Tetrabutylammonium perchlorate was filtered off. Pentasilane 6 (12.91 g, 33.7 mmol, 74% yield, 52% ce) was isolated by distillation of the filtrate (115–116 °C/2 Torr).

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