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Electrochemical Oxidation of Hydrosilanes. A Synthetic Approach to Halosilanes and Disilanes[1)]

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Electrolytic oxidation of dimethylphenylsilane (**1**) in the presence of $CuCl_2$ or CuCl afforded chlorodimethylphenylsilane in high yields (>90%), while similar electrolysis of **1** in the presence of BF_4^- ions afforded fluorodimethylphenylsilane in 90% yield. 1,2-Diphenyltetramethyldisilane was obtained from **1** in 48% yield by the electrolysis with a Pt–Cu electrode system. A "paired" electrolysis of methyldiphenylsilane on the anode and chloromethyldiphenylsilane on the cathode afforded 1,2-dimethyltetraphenyldisilane in 64% yield.

The silicon–silicon bond formation is of considerable importance for building up organopolysilane molecules. To date, many papers concerning the formation of Si–Si bonds have been published.[2)] In an effort to develop the method for the formation of an Si–Si bond which involves no alkali metal condensation, we have found that lower homologues of polysilanes such as disilanes, trisilanes, tetrasilanes, and pentasilanes, are readily synthesized in high yields by cathodic reduction of chlorosilanes in an undivided cell with the use of a copper anode.[3-5)] Therefore, if chlorosilanes can be produced electrochemically from hydrosilanes, successive electrolysis may lead to the formation of Si–Si bonds. In this connection, we studied on the electrochemical conversion of dimethylphenylsilane (**1**) to chlorodimethylphenylsilane (**2**) and then to 1,2-diphenyltetramethyldisilane (**3**).

$$\underset{\mathbf{1}}{Me_2PhSiH} \longrightarrow \underset{\mathbf{2}}{Me_2PhSiCl} \longrightarrow \underset{\mathbf{3}}{Me_2PhSiSiPhMe_2}$$

In a cyclic voltammogram of hydrosilane **1** measured by using glassy carbon as the working electrode in an acetonitrile–$LiClO_4$ solution, an irreversible oxidation peak was observed at 2.2 V (*vs.* SCE). In the cathodic direction, **1** exhibited no reduction waves up to the limit of the solvent system. In the voltammogram obtained with a Pt electrode, a broad peak was observed at 2.5 V, together with a small peak appearing at ca. 1.4 V.[6)]

The preparative electrolysis of **1** was performed with controlled current (30 mA) using tetrabutylammonium (TBA) perchlorate (1.0 g) as the supporting electrolyte and 1,2-dimethoxyethane (DME) (25 cm^3) as the solvent in a 30-cm^3 undivided cell under a dry nitrogen atmosphere.[7)] Products were identified by comparing their spectral data with those of authentic samples. Reaction conditions and yields of the products are summarized in Table 1.

First, we carried out the electrolysis of **1** (5 mmol) using Pt plates (6 cm^2) as the anode and cathode until all of **1** was consumed (4.4 F mol^{-1}) (F=96485 C). The electrolyzed solution was concentrated, and the resulting mixture was chromatographed on SiO_2 eluting with hexane to afford disilane **3** in 7% yield, together with 15% of 1,3-diphenyltetramethyldisiloxane (**4**). The formation of **3** and **4** indicates that the oxidation of **1** on the anode produces a product such as dimethylphenylsilyl perchlorate (**5**) which is then reduced on the cathode to give dimer **3** or decomposed to **4** (Scheme 1). The synthesis of silyl perchlorates, which are highly sensitive to moisture, has been reported.[8-11)]

Table 1. Electrolysis of hydrosilane in DME (25 cm^3) containing TBA salts (1.0 g) in an undivided cell

Substrate (*n* /mmol)		Electrolyte	Anode	Cathode	Electricity/F mol^{-1}	Product (Yield/%)		
1 (5.0)		Bu_4NClO_4	Pt	Pt	4.4	**3** (7)$^{a)}$	**4** (15)$^{a)}$	
1 (7.0)	$CuCl_2$ (8.1)	Bu_4NClO_4	Pt	Pt	1.7	**2** (88)$^{b)}$	**4** (tr.)$^{b)}$	
1 (4.3)	CuCl (9.4)	Bu_4NClO_4	Pt	Pt	2.1	**2** (93)$^{b)}$	**4** (tr.)$^{b)}$	
1 (4.7)	CuCl (6.1)	Bu_4NBF_4	Pt	Pt	2.2	**6** (90)$^{b)}$	**4** (tr.)$^{b)}$	
1 (5.9)	$CuCl_2$ (3.1)	Bu_4NClO_4	Pt	Pt	2.0	**2** (95)$^{b)}$	**4** (tr.)$^{b)}$	
1 (5.8)	CuCl (3.0)	Bu_4NClO_4	Pt	Pt	1.6	**2** (46)$^{b)}$	**4** (9)$^{b)}$	**1** (31)$^{b)}$
1 (6.0)	CuCl (3.1)	Bu_4NClO_4	Cu	Pt	6.4	**3** (48)$^{a)}$	**4** (36)$^{a)}$	
7 (9.9)	**8** (8.4)	Bu_4NClO_4	Cu	Pt	1.5	**9** (64)$^{a,c)}$	**10** (3)$^{a,c)}$	**7** (21)$^{a,c)}$

a) Yield of isolated products. b) Yield determined by GLC. c) Yield based on the sum of **7** and **8** used.

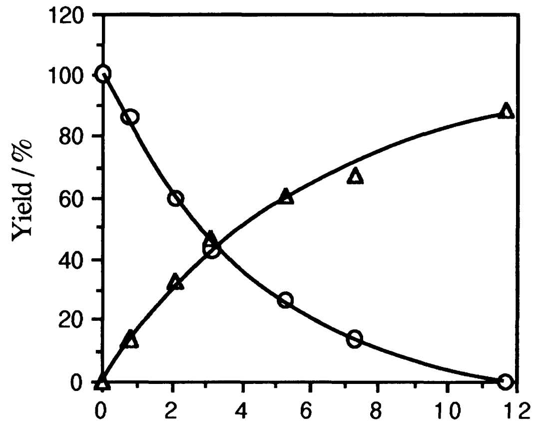
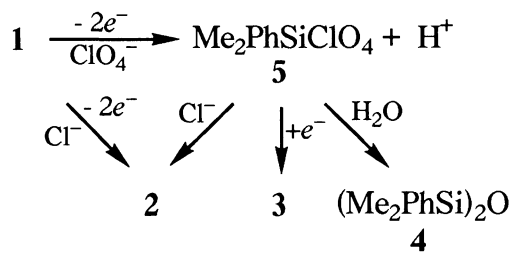


Fig. 1. Electrolysis of **1** (7.0 mmol) in the presence of $CuCl_2$ (8.1 mmol) on Pt–Pt electrodes in DME–Bu_4NClO_4 solution. Symbols stand for **1** (○) and **2** (△).



Scheme 1.

Suppose that chloride ions are present in the electrolytic solution, chlorosilane **2** should be produced either directly from **1** or indirectly *via* perchlorate **5** once formed (Scheme 1). We thus carried out the electrolysis of hydrosilane **1** in the presence of chloride ions and monitored the progress of the reaction by GLC using pentadecane as an internal standard. As expected, the oxidation of **1** in the presence of one molar equiv of $CuCl_2$ proceeded quite smoothly (Fig. 1) and afforded **2** in 88% yield at the point of passing 1.7 F mol^{-1} of the electricity. The oxidation of **1** was also effected well by the electrolysis (2.1 F mol^{-1}) in the presence of 2 molar equiv of CuCl to give **2** in 93% yield.[12] Disiloxane was formed only in trace amounts in these experiments. When the electrolysis of **1** in the presence of CuCl was performed using TBA tetrafluoroborate as the supporting electrolyte, fluorodimethylphenylsilane (**6**) was obtained in 90% yield. In this case, it seems likely that chlorosilane **2** once formed reacts with BF_4^- ions to give **6**. Such halogen–exchange reaction between chlorosilane and BF_4^- ions has been observed previously.[5] Thus, halosilanes can be obtained readily by the electrolysis of hydrosilane in the presence of halogen ions.[13]

$$\mathbf{1} \longrightarrow \mathbf{2} \xrightarrow{BF_4^-} \underset{\mathbf{6}}{Me_2PhSiF}$$

Next, we considered the possibility that silicon–silicon bonds are formed in one-pot reaction from **1**. In the electrolysis of **1** described above, reduction of Cu^{2+} or Cu^+ ions to metallic copper takes place as the cathodic reaction. If the electrolysis of **1** is performed with 0.5 molar equiv of $CuCl_2$ (Eqs. 1 and 2), chlorosilane **2** formed anodically might be reduced to disilane **3** on the cathode (Eq. 3) because of the charge balance. The electrochemical sequence should be summarized formally as Eq. 4.

$$\begin{array}{llcll}
\text{(anode)} & Me_2PhSiH + 1/2\ CuCl_2 & \longrightarrow & Me_2PhSiCl + H^+ + 1/2\ Cu^{2+} + 2e^- & (1) \\
\text{(cathode)} & 1/2\ Cu^{2+} + e^- & \longrightarrow & 1/2\ Cu^0 & (2) \\
 & Me_2PhSiCl + e^- & \longrightarrow & 1/2\ (Me_2PhSi)_2 + Cl^- & (3) \\
\hline
\text{(total)} & Me_2PhSiH + 1/2\ CuCl_2 & \longrightarrow & 1/2\ (Me_2PhSi)_2 + 1/2\ Cu^0 + HCl & (4)
\end{array}$$

In order to check this possibility, we tried the electrolysis of **1** in the presence of 0.5 molar equiv of $CuCl_2$ in a DME–TBA perchlorate solution. However, the electrolysis (2.0 F mol^{-1}) under these conditions afforded, again, chlorosilane **2** in 95% yield but not disilane **3**. Reduction of proton liberated from the oxidation of **1** may take place instead of the reduction of **2** (see Eq. 7). The electrolysis (1.6 F mol^{-1}) in the presence of 0.5 molar equiv of CuCl resulted in a mixture of **2** (46%), disiloxane **4** (9%), and starting compound **1** (31%). Prolonged electrolysis under these conditions would not afford **3** but led to the increase of the amount of **4**. The lack of chloride ions caused further oxidation of products once formed.

As reported previously,[4] the electrolytic reduction of chlorosilane **2** with the use of Cu anode affords disilane **3** in 83% yield. In this case, Cu anode acts as a "sacrificial anode" and thus suppresses the formation of undesirable oxidation products on the anode. We hence carried out the electrolysis of **1** in the presence of 0.5 molar equiv of CuCl using Cu anode (28 cm^2) and Pt cathode (6 cm^2). After passing 6.4 F mol^{-1} of the electricity, the reaction mixture was treated by MPLC to afford disilane **3** in 48% yield, together with 36% of **4**. Thus, disilane **3** is certainly produced from hydrosilane **1** in one–pot reaction under the present conditions, although more study is necessary for improving the yield of **3**.

Methyldiphenylsilane (**7**) is also electrode active. The cyclic voltammogram of **7** measured with the glassy carbon electrode in an acetonitrile–$LiClO_4$ solution shows an oxidation peak at 2.1 V. Interestingly, when a mixture of **7** (9.9 mmol) and chloromethyldiphenylsilane (**8**) (8.4 mmol) was electrolyzed in DME using the Cu anode and Pt cathode with supply of 1.5 F mol^{-1} of the electricity, 1,2-dimethyltetraphenyldisilane (**9**) was obtained in 64% yield on the basis of the sum of **7** and **8** used, together with 21% of starting hydrosilane **7**. Thus, the "paired" electrolysis of **7** on the anode and **8** on the cathode proceeds quite smoothly to give disilane **9** (see Eqs. 5–7). Only a small amount of 1,3-dimethyltetraphenyldisiloxane (**10**) (3%) was formed in the present electrolysis .

$$\text{(anode)} \quad MePh_2SiH + Cl^- \longrightarrow MePh_2SiCl + H^+ + 2e^- \qquad (5)$$

$$\text{(cathode)} \quad MePh_2SiCl + e^- \longrightarrow 1/2\,(MePh_2Si)_2 + Cl^- \qquad (6)$$

$$H^+ + e^- \longrightarrow 1/2\,H_2 \qquad (7)$$

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5) A. Kunai, E. Toyoda, T. Kawakami, and M. Ishikawa, *Organometallics*, **11**, 2899 (1992).
6) The peak currents at 2.2 V on C and 2.5 V on Pt increase linearly with increasing sweep rate (v) in the range of 10–50 mV sec^{-1} but not with $v^{1/2}$. Moreover, the currents are not proportional to the concentration of **1** (5–20 mmol dm^{-3}). At present time, we assume that these phenomena are related to some adsorbed species on the electrode surface.
7) Details for the electrolytic system are mentioned in our previous papers (Refs. 4 and 5).
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12) The present reaction can be also used for the chlorination of trialkylsilanes. The electrolysis of *t*-$BuMe_2SiH$ under the similar conditions afforded *t*-$BuMe_2SiCl$ (83%), while the reaction of Et_3SiH produced Et_3SiCl (>50%).
13) We have also reported the chlorination of hydrosilanes with a $CuCl_2$–CuI reagent: A. Kunai, T. Kawakami, E. Toyoda, and M. Ishikawa, *Organometallics*, **11**, 2708 (1992).

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