Electrochemical Reduction of Dichlorosilanes in the Presence of 2,3-Dimethylbutadiene[1)]

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Synopsis. Electrolytic reduction of dichloromethylphenyl-, dichlorodiphenyl-, dichlorodi-*o*-tolyl-, and dichlorodi-*p*-tolylsilanes in the presence of 2,3-dimethylbutadiene afforded 1-methyl-1-phenyl-, 1,1-diphenyl-, 1,1-di-*o*-tolyl-, and 1,1-di-*p*-tolyl-3,4-dimethyl-1-silacyclopent-3-ene, respectively, while the similar reaction of chloromethyldiphenylsilane with 2,3-dimethylbutadiene afforded 1-(methyldiphenylsilyl)- and 1,4-bis(methyldiphenylsilyl)-2,3-dimethyl-2-butene. A reaction mechanism leading to these products has been discussed.

There has been considerable interest in the electrochemistry of chlorosilanes as a synthetic tool for the polysilanes as well as carbosilanes, since the electrochemical silicon–silicon bond formation can be achieved by cathodic reduction of chlorosilanes using sacrificial counter electrodes such as Hg,[2,3)] Al,[4)] Mg,[5)] Ag,[3)] and Cu.[6,7)]

As reported previously, the cathodic reduction of chlorosilanes in an undivided cell with the use of a copper anode affords disilanes in high yields.[3,6)] The electrolysis is not restricted to the reaction of monochlorosilanes but can be applied to the reaction of dichlorosilanes. For example, the electrolysis of dichloromethylphenylsilane (**1a**) in the presence of chlorotrimethylsilane affords 2-phenylheptamethyltrisilane in 61% yield, while with chloropentamethyldisilane, **1a** produces 3-phenylundecamethylpentasilane in 79% yield (Scheme 1). In order to learn more about the electrochemical behavior of dichlorosilanes and to clarify their reactivity towards diene, we carried out the electrolysis of dichlorosilanes in the presence of 2,3-dimethylbutadiene.

Results and Discussion

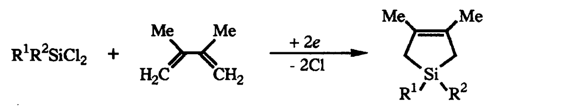
The electrolysis of dichlorosilanes was performed with a constant current using a Pt plate as the cathode, a copper coil as the anode, and tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium tetraphenylborate (TBATPB) as the supporting electrolyte in 1,2-dimethoxyethane (DME) in an undivided cell under dry nitrogen.[8)] Results are summarized in Table 1.

When a mixture of **1a** and 2.8 molar excess of 2,3-dimethylbutadiene was electrolyzed using TBAP as the supporting electrolyte until all of **1a** was consumed (1.7 F mol^{-1}) (F=96485 C), 1-methyl-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (**2a**) was formed in 10% yield (Scheme 2). No other volatile products were detected by GLC.[9)] The adduct **2a** was isolated by MPLC and its structure was verified by ^{1}H NMR, ^{13}C NMR, IR, and mass spectroscopic analysis, as well as by elemental analysis.

$MePhSiCl_2$ + Me_3SiCl $\xrightarrow{+e}$ $Me_3Si–SiMePh–SiMe_3$ (61%)
1a

1a + $Me_3Si–SiMe_2Cl$ $\xrightarrow{+e}$ $Me_3Si–SiMe_2–SiMePh–SiMe_2–SiMe_3$ (79%)

Scheme 1.



1a R^1=Me, R^2=Ph **1b** R^1=R^2=Ph **2a** R^1=Me, R^2=Ph **2b** R^1=R^2=Ph
1c R^1=R^2=*o*-Tol **1d** R^1=R^2=*p*-Tol **2c** R^1=R^2=*o*-Tol **2d** R^1=R^2=*p*-Tol

Scheme 2.

Silacyclopentene was obtained in higher yields from the reaction of dichlorodiphenylsilane (**1b**). Thus, the electrolysis of **1b** with TBAP in the presence of the diene afforded 1,1-diphenyl-3,4-dimethyl-1-silacyclopent-3-ene (**2b**) in 27% yield, while **2b** was obtained in 23% yield by the electrolysis of **1b** with TBATPB. The electrolysis of **1b** in tetrahydrofuran (THF) also afforded **2b** in 23% yield with TBAP and in 28% yield with TBATPB. It is worth noting that a copolymer consisting of diphenylsilylene and 2,3-dimethyl-2-butene-1,4-diyl units, $-[(Ph_2Si)_n(CH_2CMe{=}CMeCH_2)_m]-$, was also isolated. For example, when the electrolyzed solution of **1b** with the use of TBAP in DME was treated with a small amount of lithium aluminum hydride and the resultant products were reprecipitated from benzene–methanol, the polymer with molecular weight of M_w=1500 (M_w/M_n=1.4, n=1, m=0.6) was obtained in 41% yield. In IR spectrum of the polymer obtained from the reaction using TBAP as the supporting electrolyte, strong frequencies due to silicon–oxygen bonds were observed. The formation of Si–O bonds in the polymer chain may be ascribed to the use of perchlorate. On the other hand, no remarkable absorption bands due to a siloxy group were observed in IR spectrum of the polymer (38% yield, M_w=1700, M_w/M_n=1.4, n=1, m=1) obtained from the electrolysis of **1b** with TBATPB in DME.

The electrolysis of dichlorodi-*o*-tolylsilane (**1c**) with TBATPB in DME in the presence of an excess of the diene also afforded a similar adduct, 1,1-di-*o*-tolyl-3,4-dimethyl-1-silacyclopent-3-ene (**2c**) in 10% yield, together with a 4% yield of the polymer.[9)] Electrolysis of di-

Table 1. Electrochemical Reduction of Chlorosilanes in the Presence of 2,3-Dimethylbutadiene on Pt Cathode under Controlled Current Conditions.

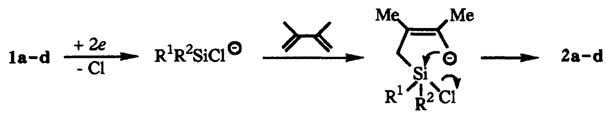
Chlorosilane (Amt./mmol)	Diene mmol	Electrolyte (Amt./g)	Solvent (Amt./cm^3)	Electricity F mol^{-1}	Product[a)] (Yield/%)
$MePhSiCl_2$ (5.8)	16.1	TBAP (1.0)	DME (25)	1.7	**2a** (10), polymer[c)] (9)[b)]
Ph_2SiCl_2 (4.9)	14.7	TBAP (1.0)	DME (25)	2.4	**2b** (27), polymer[d)] (41)
Ph_2SiCl_2 (5.0)	14.9	TBATPB (1.0)	DME (25)	3.5	**2b** (23), polymer[e)] (38)
Ph_2SiCl_2 (5.0)	15.8	TBAP (1.0)	THF (25)	3.0	**2b** (23), polymer[f)] (42)
Ph_2SiCl_2 (3.1)	9.9	TBATPB (0.4)	THF (25)	2.8	**2b** (28), polymer[g)] (44)
(*o*-Tol)$_2SiCl_2$ (5.2)	15.9	TBATPB (0.4)	DME (25)	7.0	**2c** (10), polymer[h)] (4)[b)]
(*p*-Tol)$_2SiCl_2$ (4.8)	16.0	TBAP (1.0)	DME (25)	1.6	**2d** (4), **3** (5)[b)]
$Ph_2MeSiCl$ (4.6)	16.0	TBAP (1.0)	DME (25)	3.0	**4** (35), **5** (6), **6** (15), **7** (5)
$Ph_2MeSiCl$ (3.4)	30.2	TBATPB (0.4)	DME (25)	2.9	**4** (19), **5** (3), **6** (5), **7** (1.5)
$Ph_2MeSiCl$ (4.74)	0	TBAP (1.3)	DME (25)	1.2	**4** (83)[i)]
$Ph_2MeSiCl$ (3.69)	0	TBATPB (0.4)	DME (25)	1.9	**4** (84)[i)]

a) Yields of all silacyclopentenes were determined by GLC. Polymers were isolated by reprecipitation from benzene–methanol, and the yields were calculated on the basis of their compositions estimated by ^{1}H NMR. b) Other products consisted of oligomers ($M_w < 1000$). c) $M_w = 1900$ ($M_w/M_n = 1.4$) d) $M_w = 1500$ ($M_w/M_n = 1.4$). e) $M_w = 1700$ ($M_w/M_n = 1.4$). f) $M_w = 4700$ ($M_w/M_n = 2.4$). g) $M_w = 1300$ ($M_w/M_n = 1.3$). h) $M_w = 1000$ ($M_w/M_n = 1.3$). i) Results of previous work (Ref. 7).

chlorodi-*p*-tolylsilane (**1d**) with TBAP resulted in the formation of 1,1-di-*p*-tolyl-3,4-dimethyl-1-silacyclopent-3-ene (**2d**) (4% yield) and octa-*p*-tolylcyclotetrasiloxane (**3**) (5% yield).[9)]

In order to obtain more information, we carried out the reaction of chloromethyldiphenylsilane (**1e**) in the presence of dimethylbutadiene. As reported previously,[6,7)] the electolysis of **1e** affords 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (**4**) in more than 80% yields. In contrast to these results, the electrolysis of **1e** with TBAP in the presence of 2,3-dimethylbutadiene produced 2,3-dimethyl-1-(methyldiphenylsilyl)-2-butene (**5**) and 2,3-dimethyl-1,4-bis(methyldiphenylsilyl)-2-butene (**6**) in 6% and 15% yields, along with 35% of **4** and 5% of 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane (**7**), while the same reaction with TBATPB afforded **5** and **6** in 3% and 5% yields, together with 19% of **4** and 1.5% of **7**.

We also measured reduction potentials of chlorosilanes by cyclic voltammetry using a glassy carbon disk as the electrode in an acetonitrile–TBAP solution. The voltammogram obtained for **1e** clearly shows a single reduction peak at the potential of $E_p = -2.65$ V vs. SCE, while the peak for **1b** appears at $E_p = -2.50$ V.[10)] In contrast to these, no peaks due to the reduction of 2,3-dimethylbutadiene were observed up to the limit of the solvent–electrolyte system (−2.9 V). Therefore, the formation of **5** and **6** as well as **4** can be understood by the reaction of methyldiphenylsilyl anion produced by two-electron reduction of **1e**. The reaction of the anion with the diene or **1e** leads to the formation of these products.[11)] Similarly, chlorodiorganosilyl anions generated from **1a**—**d** add to the diene to give 4-silyl-2-butenide anions (Scheme 3). Intra- and intermolecular nucleophilic substitution of the silyl-substituted 2-butenide anions affords **2a**—**d** and the copolymers,



Scheme 3.

respectively.[12)]

Experimental

General. DME, THF, TBAP, and TBATPB were purified and dried in a manner described in the previous paper.[8)] Chlorosilanes **1c**[13)] and **1d**[14)] were synthesized by the reaction of the Grignard reagents prepared from *o*- and *p*-bromotoluenes with tetrachlorosilane. ^{1}H NMR and ^{13}C NMR spectra were determined on a JEOL Model JNM EX-270 spectrometer. IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer. Molecular weights of polymers were determined by gel permeation chromatography using Shodex KF-806 and KF-804 as the column and THF as the eluent, relative to polystyrene standards. Cyclic voltammograms were measured referred to SCE at a sweep rate of 100 mV s^{-1} using a glassy carbon disk (4 mm in diameter) as the electrode in acetonitrile containing 0.1 mol dm^{-3} TBAP under dry nitrogen.

Electrolysis of 1a—e. The electrolysis of chlorosilanes was performed with a constant current (20 mA) using a Pt plate (6 cm^2) as the cathode, a copper coil (31 cm^2) as the anode, and TBAP or TBATPB as the supporting electrolyte in 25 cm^3 of DME in a 30-cm^3 undivided cell under dry nitrogen.[8)] Yields of **2a**—**d** and **3**—**7** were determined by GLC. Results are summarized in Table 1.

Products **2a**—**d** and **3**—**7** were isolated from the reaction mixtures by MPLC.

For **2a**:[15)] ^{1}H NMR ($CDCl_3$) $\delta = 0.41$ (s, 3H, SiMe), 1.11 (s, 6H, Me), 1.50 (d, 2H, HC*H*, $J = 18$ Hz), 1.63 (d, 2H, HC*H*, $J = 18$ Hz), 7.31—7.55 (m, 5H, ring H); ^{13}C NMR ($CDCl_3$) $\delta = -3.81$ (SiMe), 19.23, 25.05 (Me and CH_2), 127.76, 129.02, 133.66 (ring HC), 130.69, 138.76 (*ipso* and C=C). Found *m/z* 202.1124. Calcd for $C_{13}H_{18}Si$: M, 202.1178.

For 2b:[16] ^{1}H NMR ($CDCl_3$) δ=1.79 (s, 6H, Me), 1.88 (s, 4H, CH_2), 7.36—7.58 (m, 10H, ring H); ^{13}C NMR ($CDCl_3$) δ=19.30, 24.15 (Me and CH_2), 127.85, 129.33, 134.72 (ring HC), 130.69, 136.37 (*ipso* and C=C); MS *m/z* 264 (M^+). Found: C, 81.57; H, 7.52%. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62%.

For 2c: ^{1}H NMR ($CDCl_3$) δ=1.77 (s, 6H, Me), 1.97 (s, 4H, CH_2), 2.27 (s, 6H, Me), 7.14—7.54 (m, 8H, ring H); ^{13}C NMR ($CDCl_3$) δ=19.21, 22.78, 24.51 (Me and CH_2), 124.94, 129.51, 129.72, 135.36 (ring HC), 130.57, 144.22 (*ipso* and C=C); MS *m/z* 292 (M^+). Found: C, 82.13; H, 8.27%. Calcd for $C_{20}H_{24}Si$: C, 82.13; H, 8.27%.

For 2d: ^{1}H NMR ($CDCl_3$) δ=1.78 (s, 6H, Me), 1.85 (s, 4H, CH_2), 2.37 (s, 6H, Me), 7.20 (d, 4H, ring H, J=7.9 Hz), 7.47 (d, 4H, ring H, J=7.9 Hz); ^{13}C NMR ($CDCl_3$) δ=19.32, 21.49, 24.30 (Me and CH_2), 128.68, 134.75 (ring HC), 130.66, 132.85, 139.19 (*ipso* and C=C); MS *m/z* 292 (M^+). Found: C, 82.14; H, 8.24%. Calcd for $C_{20}H_{24}Si$: C, 82.13; H, 8.27%.

For 5:[17] ^{1}H NMR ($CDCl_3$) δ=0.55 (s, 3H, SiMe), 1.43 (s, 3H, Me), 1.47 (s, 3H, Me), 1.60 (s, 3H, Me), 2.09 (s, 2H, CH_2), 7.30—7.55 (m, 10H, ring H); ^{13}C NMR ($CDCl_3$) δ=−3.86 (SiMe), 20.40, 20.94, 21.08, 23.24 (Me and CH_2), 127.67, 129.06, 134.52 (ring HC), 122.25, 123.86, 137.65 (*ipso* and C=C); MS *m/z* 280 (M^+). Found: C, 81.30; H, 8.54%. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.62%.

For 6: ^{1}H NMR ($CDCl_3$) δ=0.50 (s, 6H, SiMe), 1.30 (s, 6H, Me), 2.06 (s, 4H, CH_2), 7.31—7.51 (m, 20H, ring H); ^{13}C NMR ($CDCl_3$) δ=−3.93 (SiMe), 21.64, 23.33 (Me and CH_2), 127.69, 129.04, 134.50 (ring HC), 122.80, 137.77 (*ipso* and C=C); MS *m/z* 476 (M^+). Found: C, 80.60; H, 7.56%. Calcd for $C_{32}H_{36}Si_2$: C, 80.61; H, 7.61%.

Isolation of Polymer. In a typical case, the electrolyzed solution of **1b** in the presence of 2,3-dimethylbutadiene was treated with a small amount of lithium aluminum hydride and the resultant products were reprecipitated from benzene–methanol to give a copolymer consisting of diphenylsilylene and 2,3-dimethyl-2-butene-1,4-diyl units, $-[(Ph_2Si)_n\ (CH_2CMe{=}CMeCH_2)_m]-$. The electrolysis with TBAP in DME afforded the polymer with molecular weight of M_w=1500 (M_w/M_n=1.4, n=1, m=0.6) in 41% yield: IR (film) 1060 (ν_{Si-O}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.8—2.2 (br m, Me and CH_2), 6.8—7.7 (br m, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ=20.5—23.5 (br m, Me and CH_2), 127.0—137.5 (br m, phenyl ring carbons).

Similar electrolysis with TBATPB in DME afforded the polymer with molecular weight of M_w=1700 (M_w/M_n=1.4, n=1, m=1) in 38% yield: ^{1}H NMR ($CDCl_3$) δ=0.8—2.2 (br m, Me and CH_2), 6.9—7.6 (br m, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ=20.4—21.6 (br m, Me and CH_2), 127.3—137.3 (br m, phenyl ring carbons).

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References

1) Electrochemistry of Organosilicon Compounds. Part IV. For Part III, see Ref. 7.

2) a) E. Hengge and G. Litscher, *Angew. Chem.*, **88**, 414 (1976); b) E. Hengge and G. Litscher, *Monatsh. Chem.*, **109**, 1217 (1978); c) E. Hengge and H. Firgo, *J. Organomet. Chem.*, **212**, 155 (1981).

3) A. Kunai, T. Kawakami, E. Toyoda, and M. Ishikawa, *Organometallics*, **10**, 893 (1991).

4) C. Biran, M. Bordeau, P. Pons, M. -P. Leger, and J. Dunogues, *J. Organomet. Chem.*, **382**, C17 (1990).

5) T. Shono, S. Kashimura, M. Ishifune, and R. Nishida, *J. Chem. Soc., Chem. Commun.*, **1990**, 1160.

6) A. Kunai, T. Kawakami, E. Toyoda, and M. Ishikawa, *Organometallics*, **10**, 2001 (1991).

7) A. Kunai, E. Toyoda, T. Kawakami, and M. Ishikawa, *Organometallics*, **11**, 2899 (1992).

8) Details for the electrolytic system are mentioned in our previous paper (Refs. 3 and 6).

9) Other products mainly consisted of nonvolatile oligomers with low molecular weights (M_w<1000).

10) Polarographic half-wave potentials for some aryl-substituted mono- and dichlorosilanes have been reported to be $E_{1/2}$=−2.8 to −3.2 V vs. Ag/$AgClO_4$ (−2.2 to −2.6 V vs. SCE): a) R. E. Dessy, W. Kitching, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 453 (1966); b) R. J. P. Corriu, G. Dabossi, and M. Martineau, *J. Organomet. Chem.*, **222**, 195 (1981); c) P. Boudjouk, B.-H. Han, and K. R. Anderson, *J. Am. Chem. Soc.*, **104**, 4992 (1982). See also Ref. 2c.

11) A similar reaction of 1,3-cyclohexadiene with chlorotrimethylsilane has been reported: T. Shono, S. Kashimura, and Y. Yamaguchi, "59th National Meeting of the Chemical Society of Japan," Yokohama, April 1990, Abstr., No. 3D712.

12) 1-Silacyclopent-3-enes are also obtained by the reaction of dichlorosilane, diene, and Mg. A different mechanism has been proposed for this reaction: a) J. Dunogues, R. Calas, J. Dedier, and F. Pisciotti, *J. Organomet. Chem.*, **25**, 51 (1970); b) R. D. Rieke and H. Xiong, *J. Org. Chem.*, **56**, 3109 (1991).

13) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

14) K. Kuroda and N. Ishikawa, *Nippon Kagaku Zasshi*, **90**, 322 (1969).

15) M. Ishikawa, F. Ohi, and M. Kumada, *J. Organomet. Chem.*, **86**, C32 (1975).

16) M. L. Filleux-Blanchard, N. -D. An, and G. Manuel, *J. Organomet. Chem.*, **137**, 11 (1977).

17) O. B. Afanasova, Y. E. Zabarev, T. M. Sokolava, and E. A. Chernyshev, *Zh. Obshch. Khim.*, **57**, 1909 (1987).