Electrolytic Behavior of Iodo- and Chlorosilanes. The Formation of Si-Si and Si-*sp*-C Bonds[1]

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Electrolysis of iodosilanes with Al/Pt electrodes in pivalonitrile results in the formation of the Si–Si bonds to give the corresponding disilanes. On the other hand, the electrolysis of various halosilanes such as iodo-, chloro-, and fluorosilanes with Pt/Pt electrodes in the presence of phenylacetylene leads to the formation of the Si–*sp*-carbon bonds to give phenylethynylated products.

It is well known that electrolytic reduction of allyl, benzyl, and aryl halides in the presence of chlorosilanes leads to the formation of the silicon–carbon bonds,[2a-f] which are produced by nucleophilic attack of an initially formed carbanion onto an Si–Cl bond. Electrochemical silylation of the unsaturated bonds in activated olefins, dienes, and hydroaromatics with chlorosilanes has also been reported.[3a,b,2f] More recently, it has been demonstrated that compounds with the Si–Si bonds are produced in good yields by the electrolytic reduction of chlorosilanes in an undivided cell using a sacrificed metal anode[4a-h] such as Hg, Al, Mg, Ag, and Cu, or using a hydrogen electrode.[4i]

The utilization of chlorosilanes in the field of electrochemistry is thus well developed to date but is limited to the formation of the silicon–sp^3- and sp^2-carbon bonds as well as the silicon–silicon bonds. Moreover, no report concerning the electrochemical properties of iodosilanes has been published, although they may be used as starting materials for electrosynthesis. As one exception, Hengge and Firgo[4b] have reported that the electroreduction of iodotrimethylsilane, unlike chlorosilanes, produces no hexamethyldisilane at all. In this paper, we report the electrolytic behavior of iodosilanes, and the formation of the silicon–*sp*-carbon bonds by the electrolysis of various halosilanes in the presence of phenylacetylene.

As we reported previously, the reduction of chloromethyldiphenylsilane (**1a**) in 1,2-dimethoxyethane (DME) with the use of Cu as the sacrificed anode affords 1,2-dimethyltetraphenyldisilane (**2**) in high yields (see Table 1, runs 1–2).[4g,h] However, DME is not a suitable solvent for the electrolysis of iodosilanes, since iodosilanes readily react with ethers to give siloxanes and iodoalkanes. Therefore, we chose alkylnitriles as the solvent and Al as the anode, because highly coordinating nature of nitriles towards Cu ions prevented the electrolysis.[4h]

In a typical run, 4–10 mmol of iodosilane was electrolyzed in 25 cm^3 of the solvent in an undivided cell using Pt (6 cm^2) as the cathode, Al (12 cm^2) as the anode, and Bu_4NBPh_4 (0.5 g) as the supporting electrolyte until iodosilane disappeared. The solvent was evaporated, and products were extracted with hexane and separated by chromatography on silica gel.[5] Results are summarized in Table 1, together with some of the previous works.[4g,h]

As expected, when iodomethyldiphenylsilane (**1b**) was electrolyzed in pivalonitrile (PN), disilane **2** was produced in 52% isolated yield (run 4), which is parallel with the value obtained from the corresponding chlorosilane (run 3). Similar reaction of iododimethylphenylsilane (**3b**) afforded tetramethyl-1,2-diphenyldisilane (**4**) in 66% isolated yield (run 5). These results clearly indicate that iodosilanes can be utilized as the starting material for synthesis of polysilanes. Analogous to chlorosilanes, silyl anions may be involved in the reaction pathway as the reactive species.

$$R^1R^2R^3SiX \longrightarrow R^1R^2R^3Si{-}SiR^1R^2R^3$$

1a, R^1=Me, R^2=R^3=Ph, X=Cl
1b, R^1=Me, R^2=R^3=Ph, X=I
3a, R^1=R^2=Me, R^3=Ph, X=Cl
3b, R^1=R^2=Me, R^3=Ph, X=I
7a, R^1=R^2=R^3=Et, X=Cl

2, R^1=Me, R^2=R^3=Ph
4, R^1=R^2=Me, R^3=Ph
13, R^1=R^2=R^3=Et

$$R^1R^2R^3SiI + CH_3CN \longrightarrow R^1R^2R^3SiCH_2CN$$

1b, R^1=Me, R^2=R^3=Ph
3b, R^1=R^2=Me, R^3=Ph
7b, R^1=R^2=R^3=Et

5, R^1=Me, R^2=R^3=Ph
6, R^1=R^2=Me, R^3=Ph
8, R^1=R^2=R^3=Et

Table 1. Electrolysis of halosilanes under various conditions[a]

Run	Silane	Anode	Electrolyte	F·mol^{-1}	Product/%[b]
1	$MePh_2SiCl$	Cu	ClO_4^-/DME	1.2	$(MePh_2Si)_2$ (83)[c]
2	$MePh_2SiCl$	Cu	BPh_4^-/DME	1.9	$(MePh_2Si)_2$ (84)[c]
3	$MePh_2SiCl$	Al	ClO_4^-/DME	1.2	$(MePh_2Si)_2$ (47)[c]
4	$MePh_2SiI$	Al	BPh_4^-/PN	1.6	$(MePh_2Si)_2$ (52)
5	Me_2PhSiI	Al	BPh_4^-/PN	1.4	$(Me_2PhSi)_2$ (66)
6	$MePh_2SiI$	Al	BPh_4^-/AN	2.0	$MePh_2SiCH_2CN$ (49)[d]
7	Me_2PhSiI	Al	BPh_4^-/AN	1.6	$Me_2PhSiCH_2CN$ (60)[d]
8	Et_3SiI	Al	BPh_4^-/AN	3.4	Et_3SiCH_2CN (54)[d]

[a] Bu_4N^+ salts were used. [b] Isolated yield. [c] Results of previous work (Ref. 4g,h). [d] Yield determined by GLC.

Interestingly, when the electrolysis of **1b** was carried out in acetonitrile (AN), (cyanomethyl)methyldiphenylsilane (**5**) was produced in 49% GLC yield, but not disilane **2** (run 6). Similar reaction of **3b** in AN afforded (cyanomethyl)dimethylphenylsilane (**6**) in 60% yield, while the reaction of iodotriethylsilane (**7b**) gave (cyanomethyl)triethylsilane (**8**) in 54% yield (runs 7–8). These products may arise from electrolysis of a C-H bond of AN rather than iodosilanes, followed by nucleophilic attack of the resulting cyanomethyl carbanion onto the Si–I bond.

In order to obtain more information, we carried out the electrolysis of iodosilanes in PN in the presence of phenylacetylene that has an active hydrogen (Table 2). When **3b** was electrolyzed in the presence of 2 equiv of phenylacetylene, dimethylphenyl(phenylethynyl)silane (**9**) was obtained in 88% isolated yield (run 1). Similar electrolysis of **7b** and diethyldiiodosilane (**11**) gave triethyl(phenylethynyl)silane (**10**) and diethylbis(phenylethynyl)silane (**12**) in 52% and 55% isolated yields, respectively (runs 2–3), suggesting that the acetylenic C-H bond is reduced in preference to the Si–I bond.

In contrast to these, when the corresponding chlorosilanes, chlorodimethylphenylsilane (**3a**) and chlorotriethylsilane (**7a**) were electrolyzed under the same conditions as above, **9** and

$$R^1R^2R^3SiX + PhC{\equiv}CH \longrightarrow R^1R^2R^3SiC{\equiv}CPh$$

3a, $R^1=R^2=Me$, $R^3=Ph$, X=Cl	**9**, $R^1=R^2=Me$, $R^3=Ph$
3b, $R^1=R^2=Me$, $R^3=Ph$, X=I	
7a, $R^1=R^2=R^3=Et$, X=Cl	**10**, $R^1=R^2=R^3=Et$
7b, $R^1=R^2=R^3=Et$, X=I	
14, $R^1=R^2=R^3=Me$	**15**, $R^1=R^2=R^3=Me$

$$R^1R^2SiX_2 + PhC{\equiv}CH \longrightarrow R^1R^2Si(C{\equiv}CPh)_2$$

11, $R^1=R^2=Et$, X=I	**12**, $R^1=R^2=Et$
16, $R^1=Me$, $R^2=Ph$, X=Cl	**17**, $R^1=Me$, $R^2=Ph$

Table 2. Electrolysis of halosilanes in the presence of PhC≡CH

Run	Silane	Anode	Electrolyte	$F\cdot mol^{-1}$	Product/%^{a}
1	Me_2PhSiI	Al	BPh_4^-/PN	1.6	$Me_2PhSiC{\equiv}CPh$ (88)
2	Et_3SiI	Al	BPh_4^-/PN	1.8	$Et_3SiC{\equiv}CPh$ (52)
3	Et_2SiI_2	Al	BPh_4^-/PN	2.0	$Et_2Si(C{\equiv}CPh)_2$ (55)
4	$Me_2PhSiCl$	Al	BPh_4^-/PN	1.9	$(Me_2PhSi)_2$ (51) $Me_2PhSiC{\equiv}CPh$ (13) $(Me_2PhSi)_2O$ (15)
5	Et_3SiCl	Al	BPh_4^-/PN	2.4	$(Et_3Si)_2$ (47) $Et_3SiC{\equiv}CPh$ (16) $(Et_3Si)_2O$ (15)
6	Me_3SiCl	Al	BPh_4^-/PN	2.2	$Me_3SiC{\equiv}CPh$ (23)
7	$MePhSiCl_2$	Al	BPh_4^-/PN	2.2	$MePhSi(C{\equiv}CPh)_2$ (29)
8	Me_2PhSiI	Pt	BPh_4^-/PN	1.9	$Me_2PhSiC{\equiv}CPh$ (82)
9	Et_3SiI	Pt	BPh_4^-/PN	1.3	$Et_3SiC{\equiv}CPh$ (80)
10	$Me_2PhSiCl$	Pt	BPh_4^-/PN	1.8	$Me_2PhSiC{\equiv}CPh$ (84)
11	Et_3SiCl	Pt	BPh_4^-/PN	2.0	$Et_3SiC{\equiv}CPh$ (89)
12	Me_3SiCl	Pt	BPh_4^-/PN	2.6	$Me_3SiC{\equiv}CPh$ (91)
13	$MePhSiCl_2$	Pt	BPh_4^-/PN	5.4	$MePhSi(C{\equiv}CPh)_2$ (56)
14	$MePh_2SiF$	Pt	BF_4^-/DME	3.4	$MePh_2SiC{\equiv}CPh$ (42)^b
15	Me_2PhSiF	Pt	BPh_4^-/DME	1.5	$Me_2PhSiC{\equiv}CPh$ (50)^b

^{a} Isolated yield. ^{b} Yield determined by GLC.

10 were obtained only in low yields, but disilane **4** (51%) and hexaethyldisilane (**13**) (47%) were produced as the main product (runs 4–5), indicating that reduction of the Si–Cl bond took place preferentially. This curious phenomenon is presumably ascribed to the formation of the Al–Cl bond with larger energy than the Al–I bond, which causes a shift in reduction potential of the chlorosilanes into a more positive region than that for phenylacetylene.

We have also found that the electrochemical ethynylation proceeds quite smoothly without using the Al anode. Thus, when iodosilanes **3b** and **7b** were electrolyzed using Pt plates as both anode and cathode, **9** and **10** were obtained in 82% and 80% yields, respectively (runs 8 and 9).

Interestingly, the reaction of chlorosilanes on the Pt–Pt electrodes showed that the ethynylation products are produced in much higher yields than those of the reaction on the Al–Pt electrodes, where the products are obtained only in 10–30% yields (see runs 4–7). For example, the reaction of **3a**, **7a**, and chlorotrimethylsilane (**14**) afforded **9**, **10**, and trimethyl(phenylethynyl)silane (**15**) in 82%, 80%, and 91% yield, respectively (runs 10–12). The present reaction is not restricted to monochlorosilanes but applied to dichlorosilanes (run 13). The reaction of dichloromethylphenylsilane (**16**) afforded methylphenylbis(phenylethynyl)silane (**17**) in 56% yield.

In the present reaction, phenylacetylene may be reduced[6] on the platinum cathode to give phenylethynyl carbanion as the reactive intermediate. In order to confirm this, we carried out the reaction of fluorosilanes, which are known to be highly resistive towards electrolytic reduction. In fact, the electrolysis of fluoromethyldiphenylsilane (**1c**) and fluorodimethylphenylsilane (**3c**) in DME in the presence of phenylacetylene afforded the ethynylation products, methyldiphenyl(phenylethynyl)silane (**18**) and **9** in 50% and 42% GLC yields, respectively (runs 14–15).

$$PhC{\equiv}CH + e^- \longrightarrow PhC{\equiv}C^- + 1/2\,H_2$$

$$MePhRSiF \xrightarrow{PhC{\equiv}C^-} MePhRSiC{\equiv}CPh + F^-$$

1c, R=Ph **3c**, R=Me **18**, R=Ph **9**, R=Me

References and Notes

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5 Structures of all products were verified by spectroscopic and elemental analyses, and by comparing with authentic samples. Spectral data for representative products are as follows. **5**: MS *m/z* 237 (M^+); ^1H NMR (δ in $CDCl_3$) 0.78 (s, 3H, Me), 2.01 (s, 2H, CH_2), 7.40–7.57 (m, 10H, Ph); ^{13}C NMR (δ in $CDCl_3$) -4.4 (Me), 3.8 (CH_2), 118.6 (CN), 128.3, 130.5, 134.3, 133.0 (Ph). **9**: MS *m/z* 236 (M^+); ^1H NMR (δ in $CDCl_3$) 0.49 (s, 6H, Me), 7.30–7.69 (m, 10H, Ph); ^{13}C NMR (δ in $CDCl_3$) -0.8 (Me), 92.0, 106.8 (C≡C), 127.9, 129.4, 133.7, 137.0, 122.9, 128.2, 128.7, 132.0 (Ph). **17**: MS *m/z* 322 (M^+); ^1H NMR (δ in $CDCl_3$) 0.71 (s, 3H, Me), 7.33–7.86 (m,15H, Ph); ^{13}C NMR (δ in $CDCl_3$) 0.1 (Me), 89.0, 107.4 (C≡C), 122.5, 128.2, 130.1, 132.2, 128.8, 129.02, 132.2, 134.2 (Ph).

6 A reduction peak due to PhC≡CH was observed at -2.56 V vs SCE (one electron process) by cyclic voltammetry.