Electroreductive Formation of Polysilanes

Tatsuya Shono,*[a] Shigenori Kashimura,[a] Manabu Ishifune,[a] and Ryoichi Nishida[b]

[a] *Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606, Japan*
[b] *Advanced Technology Center, Osaka Gas Co., Ltd., 5-11-61, Torishima, Konohana, Osaka 554, Japan*

Electroreduction of dichlorosilanes, such as 1,1-dichlorodialkylsilanes, 1,2-dichlorotetra-alkyldisilanes, and 1,4-bis(chlorodialkylsilyl)benzenes, with Mg electrodes in a single-compartment cell was found to yield the corresponding polysilanes.

We report our new findings that the electroreduction of chlorosilanes with an Mg anode and cathode is effective for the formation of Si–Si bonds. The electroreduction of trialkylchlorosilanes with Mg electrodes gave disilanes in excellent isolated yields (Scheme 1), and dichlorosilanes such as 1,1-dichlorosilanes,[1] 1,2-dichlorodisilanes,[2] and bis(chlorosilyl)benzenes,[3,4] yielded the corresponding polysilanes.[1] Other metal electrodes were less effective (Pt, Zn, Ni, and Cu). The products contained $< 2\%$ of the corresponding siloxane.

Table 1. Formation of polysilanes.

Run	Monomer	Electricity/ F/mol^{-1}	M_n[a]	M_w/M_n[a]	Yield (%)[b]
1	$PhMeSiCl_2$ (**1**)	6.4	3200	2.8	22
2	(**1**)	8.0	2790	1.4	33[c]
3	1,4-$(MePhClSi)_2C_6H_4$ (**2**)	7.9	2450	1.6	26
4	(**2**)	8.0	2510	2.6	45[c]
5	1,4-$(MeEtClSi)_2C_6H_4$ (**3**)	8.0	4130	1.4	22
6	(**3**)	8.0	3970	1.9	41[c]
7	$Me_2ClSiSiClMePh$ (**4**)	8.6	7170	1.8	5

[a] Obtained by GPC analysis using THF as eluent. [b] Isolated yields, obtained by reprecipitation from EtOH. [c] Reaction carried out under sonication.

$$R^1R^2R^3SiCl \xrightarrow{+\,e,\ 2\ F\ mol^{-1}} R^1R^2R^3SiSiR^1R^2R^3$$

	Yield (%)
$R^1 = R^2 = R^3 = Me$	82
$R^1 = R^2 = Me, R^3 = Ph$	92
$R^1 = R^2 = Ph, R^3 = Me$	77
$R^1 = R^2 = R^3 = Ph$	85
$R^1 = R^2 = Me, R^3 = PhCH_2$	78

Scheme 1. *Conditions*: $R^1R^2R^3SiCl$ (6 mmol), undivided cell, dry tetrahydrofuran (THF; 15 ml), $LiClO_4$ (6 mmol), Mg rod anode and cathode (1 × 1 cm, length 5 cm).

These results contrast with the report that the electroreduction of 1,1- and 1,2-dichlorosilanes with an Hg electrode in a divided cell did not give polysilanes,[†] since we have found that cathodic reduction with Mg electrodes in a single compartment cell was effective in leading to the formation of polysilanes.

As exemplified in Table 1, a variety of polysilanes were obtained by the electroreduction of compounds (**1**) (run 1), (**2**) (run 3), and (**3**) (run 5). In addition, it is noteworthy that sonication (47 kHz) (runs 2, 4, and 6) resulted in a marked increase in the yields of polysilanes. The electroreduction of the disilane (**4**) (run 7) gave a polysilane in low yield, although its molecular weight (M_n 7170; M_w/M_n 1.8) was much higher than that of the polymer prepared by the reduction of (**4**) with Na.[2]

Received, 3rd April 1990; Com. 0/01487G

References

1 R. West, *J. Organomet. Chem.*, 1986, **300**, 327, and references cited therein.

2 H. Watanabe, A. Ohta, M. Onozuka, and Y. Nagai, *Chem. Lett.*, 1988, 1883.

3 M. Ishikawa, N. Hongzhi, K. Matsusaki, K. Nate, T. Inoue, and H. Yokono, *J. Poly. Sci. Poly. Lett.*, 1984, **22**, 669.

4 M. Ishikawa, N. Hongzhi, H. Watanabe, and Y. Saheki, *Organometallics*, 1987, **6**, 1673.

5 M. Fujino, *Chem. Phys. Lett.*, 1987, **136**, 451.

[†] It has been reported that the electroreduction of 1,1- and 1,2-dichlorosilanes did not give a polysilane but rather polymeric material containing Si–O bonds and cyclotetrasilanes: E. Hengge and H. Firgo, *J. Organomet. Chem.*, 1981, **212**, 155; E. Hengge and G. Litscher, *Monatsh. Chem.*, 1978, **109**, 1217.