

Electrochemical Halogenation of Trisubstituted Germanes and Silanes

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Synopsis. Electrochemical halogenation of trisubstituted germanes and silanes in acetonitrile occurred in the cathode compartment in contrast to the well-known electrochemical halogenations which always occur in the anode compartment.

Organogermanium compounds and organosilicon compounds are interesting as the objects of electrochemical studies, because (1) they easily undergo electrochemical reactions as a result of their higher HOMO levels and lower LUMO levels compared with the carbon analogues,¹⁾ and (2) electrochemically generated germanium and silicon species, such as anions, radicals, and cations, may have chemical properties, which are different from those of the corresponding carbon species.²⁾

It is well-known that electrochemical halogenations occur in the anode compartment and dehalogenations in the cathode compartment.³⁾ Such electrochemical dehalogenations have also been reported for halogermanes and halosilanes.⁴⁾ The authors wish to report here an unusual cathodic halogenations, in which trisubstituted germanes and silanes afford halogenated germanes and silanes.

Experimental

All trisubstituted germanes and silanes were synthesized by the reduction of chloro-germanes and -silanes with LiAlH₄. They were identified by comparing their physical properties with those of reported values.⁵⁾

Constant current electrolyses were carried out in a two-compartment cell using platinum plates (electrode surface = 6 cm²) as the anode and the cathode. About 2.5 × 10⁻⁴ mol of trisubstituted germanes or silanes was dissolved in 20 cm³ of acetonitrile solution containing 0.1 mol dm⁻³ of tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium tetrafluoroborate (TBATFB). Current density passed was about 0.17 mA cm⁻².

After the electrolyses, aliquots were sampled from each compartment and analysed directly with GC-MS for qualitative analyses and with HPLC for qualitative and quantitative analyses.

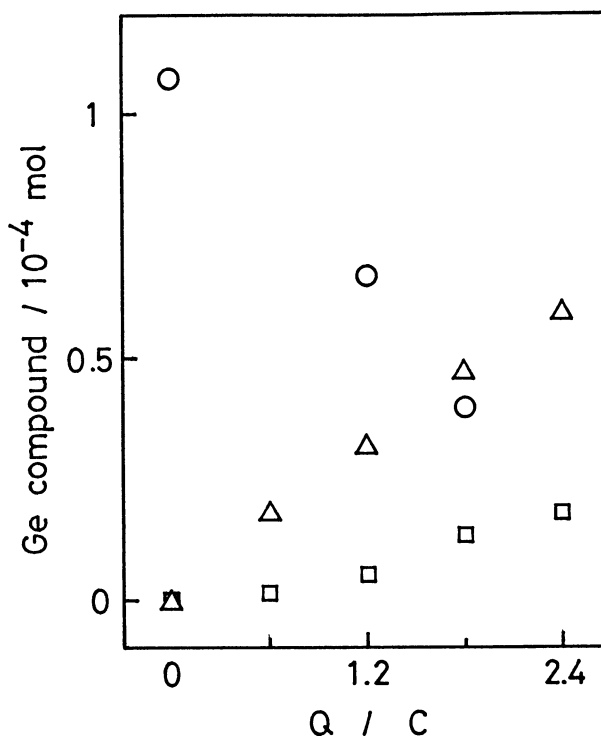


Fig. 1. Generation of Ph₃GeCl (Δ) and (Ph₃Ge)₂O (□) in the cathode compartment during the electroreduction of Ph₃GeH (○).

Results and Discussion

The results in Fig. 1 were obtained by the constant current (1 mA) electrolysis of Ph₃GeH in the presence of TBAP. In the cathode compartment, Ph₃GeCl and (Ph₃Ge)₂O were generated at constant rates while Ph₃GeH decreased at a constant rate. No such products were found in the anode compartment. After the passage of 0.21 F mol⁻¹ of electricity, 63% yield of Ph₃GeCl and 37% yield of (Ph₃Ge)₂O were obtained. A novel reaction pathway must be given for the formation of (Ph₃Ge)₂O in the catholyte because the hydro-

Table 1. Products in the Catholyte Solution Detected by GC-MS.
Typical Yields Determined by HPLC are Shown in Parentheses

Compound	Products (yield/%)			
	with TBAP		with TBATFB	
Ph ₃ GeH	Ph ₃ GeCl, (60)	(Ph ₃ Ge) ₂ O (40)	Ph ₃ GeF, (a)	(Ph ₃ Ge) ₂ O (70)
Ph ₃ SiH	—,	(Ph ₃ Si) ₂ O (80)	Ph ₃ SiF, (a)	(Ph ₃ Si) ₂ O (90)
Ph ₂ MeGeH ^{b)} Ph ₂ MeSiH ^{b)}	Ph ₂ MeGeCl, —,	(Ph ₂ MeGe) ₂ O (Ph ₂ MeSi) ₂ O	Ph ₂ MeGeF, —,	(Ph ₂ MeGe) ₂ O (Ph ₂ MeSi) ₂ O

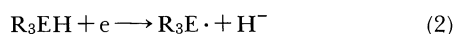
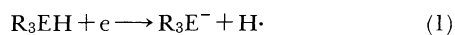
a) The yield could not be determined by HPLC. b) Yields are not shown because halogenated compounds were readily hydrolyzed.

lysis of Ph_3GeCl did not occur under the experimental conditions. Supposing a one electron reaction for the conversion of Ph_3GeH , the current efficiency is as high as 300–400%. Assuming again a one electron reaction for the following electrochemical generation of Ph_3GeCl , the current efficiency is calculated as 240% (see below Eqs. 1 and 2). The chlorine source for the Ph_3GeCl must be the electrolyte TBAP because there is no other chlorine source. Oxygen may come from TBAP, O_2 , and/or residual H_2O in the electrolyte solution.

Table 1 summarises the experimental data. Typical product yields are shown though they varied experiment to experiment. When TBATFB was used as the supporting electrolyte, Ph_3GeF was obtained. The fluorine source must be TBATFB. The generation of $(\text{Ph}_3\text{Ge})_2\text{O}$ here reveals that the oxygen source was O_2 and/or residual H_2O in the system. In the electrolysis of Ph_3SiH in the presence of TBAP, Ph_3SiCl was not obtained although the experiments were repeated carefully. Using TBATFB as the electrolyte, a trace amount of Ph_3SiF was detected by GC-MS, but it was not detectable by HPLC. These product distributions may be understood by means of the lower dissociation energy of Si-Cl bond compared with that of Si-O.⁶⁾

Electrolyses were also carried out with other compounds, such as Ph_2MeEH , PhMe_2EH , and Et_3EH (E = Ge and Si). However, the expected products, such as Ph_2MeEX , PhMe_2EX , and Et_3EX (X = Cl and F) were readily hydrolyzed under the experimental conditions. Among the expected products, only Ph_2MeGeCl and Ph_2MeGeF were detected by GC-MS analyses besides gemoxanes and siloxanes.

Germyl (silyl) anions and germyl (silyl) radicals are candidates for the reaction intermediates (see Eqs. 1 and 2).



Accordingly, the reactivity of anions was examined as follows. Firstly, Ph_3Ge^- was prepared in tetrahydrofuran (THF) from Ph_3GeBr and Li. An aliquot was added to a THF solution containing 0.1 mol dm^{-3} of TBAP. Another aliquot was added to an acetonitrile solution containing 0.1 mol dm^{-3} of TBAP. However, no halogenated products were obtained in either case. Therefore, it was concluded that anions do not react with TBAP directly. In addition, it was found that the anions are not stable in acetonitrile, because only trace amount of Ph_3GeH was observed after

hydrolysis.

Nextly, the reactivity of radicals was examined. Ph_3GeH was heated up to 80° in acetonitrile to generate $\text{Ph}_3\text{Ge} \cdot$. Trace amount of Ph_3GeCl was observed in the presence of TBAP after 6 h. Another experiment without Ar blanket gave $(\text{Ph}_3\text{Ge})_2\text{O}$ as an additional product.

These results suggest that radical species are more probable as the reaction intermediates. However, it should be noted that by the electrochemical method Ph_3GeCl was obtained with a good yield. It seems that the reaction mechanism is more complicated than the simple reaction scheme: the generation of radicals by electrochemical reduction followed by their attack toward TBAP (or TBATFB).⁷⁾

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- 7) Lately, it has been suggested by the authors that germyl and silyl radicals have a strong tendency to lose one electron to give the corresponding cations; M. Okano and K. Mochida, 37th Symposium on Organometallic Chemistry, Japan, 1990, Osaka. These cations are also candidates for the reaction intermediate. However, existence of such cations is not yet generally accepted in chemistry of organogermanium and organosilicon compounds and reactivity of them is still unknown.