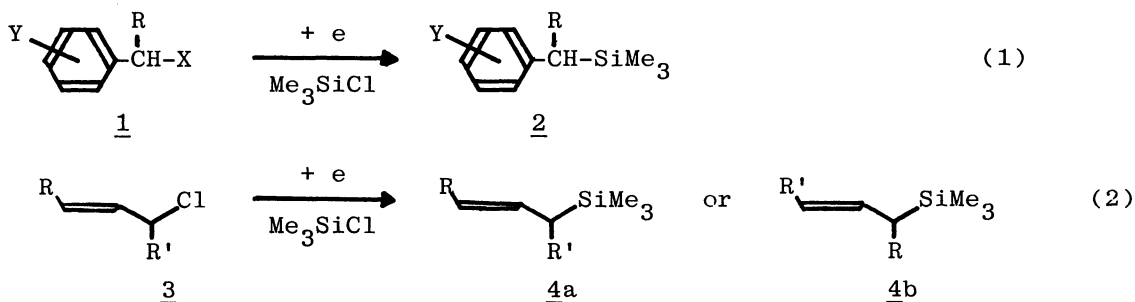


AN ELECTROREDUCTIVE SYNTHESIS OF ALLYLSILANES AND BENZYL SILANES¹⁾

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The electrochemical reduction of benzyl and allyl halides carried out in the presence of chlorotrimethylsilane afforded the corresponding benzylsilanes and allylsilanes in satisfactory yields.

Exploiting new convenient methods for the preparation of alkylsilanes is worthwhile since these compounds are often used as versatile materials in organic synthesis.²⁾ We report herein a new electroreductive method for the synthesis of benzylsilanes 2 and allylsilanes 4 from the corresponding halides 1 and 3, respectively (Eqs. 1 and 2), a part of which have been preliminarily presented in 1980.³⁾ Since this new method can be carried out under mild conditions without using any metal reducing agent,⁴⁾ it is not necessary to protect functional groups such as cyano and methoxycarbonyl groups.



A typical procedure for the synthesis of 2 is described below. A solution of tetraethylammonium *p*-toluenesulfonate (23 mmol) in anhydrous DMF (27 ml) was put into cathodic (20 ml) and anodic (7 ml) compartments of a cell equipped with a ceramic diaphragm and two platinum plate electrodes (2 cm x 2 cm). Into the cathodic solution were added benzyl chloride (6 mmol) and chlorotrimethylsilane (30 mmol) successively. The electroreduction was achieved under conditions of constant current (25 - 75 mA/cm²) with magnetic stirring. Although the initial terminal voltage was about 20 V, it increased to 40 - 50 V at the end of the reaction. After about 6 Fmol⁻¹ of electricity was passed, the catholyte was poured into water. The organic portion was extracted with ether (3 x 50 ml), and the combined ethereal solution was dried on MgSO₄. The residue obtained by evaporation of solvent was column-chromatographed to give 2⁵⁾ in satisfactory yields shown in Table 1.

Table 1. Electroreductive Synthesis of Benzylsilanes 2 from Benzyl Halides 1

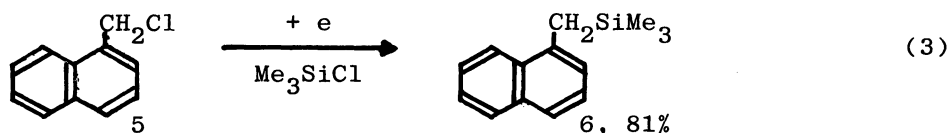
Run	<u>1</u>			Electricity passed ^{a)} Fmol ⁻¹	Isolated yield of <u>2</u> ^{a)} /%
	Y	R	X		
1	H	H	Cl	5	89
2	4-CH ₃	H	Cl	6	76
3	4-CH ₃ O	H	Cl	6	87
4	H	CH ₃	Br	6	76
5	4-CN	H	Br	5.3 (10) ^{b)}	54 (50) ^{b)}
6	4-CO ₂ CH ₃	H	Br	5.3 (10) ^{b)}	49 (50) ^{b)}
7	2-Cl	H	Cl	8.5	75
8	3-Cl	H	Cl	10	53
9	4-Cl	H	Cl	6	84

a) A diaphragm was used.

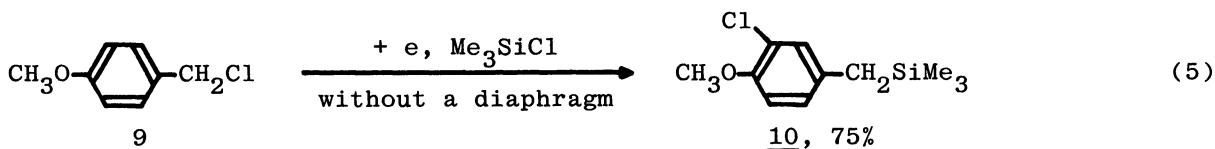
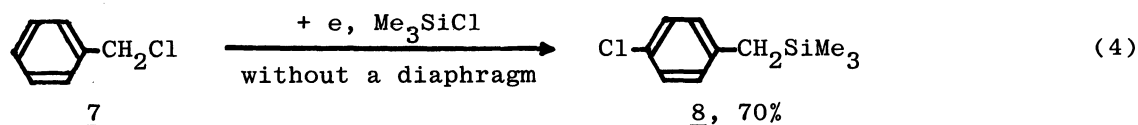
b) A diaphragm was not used.

The cyano and methoxycarbonyl groups on the aromatic nucleus remained intact (runs 5 and 6).

A naphthalene derivative 5 was similarly silylated (Eq. 3).⁵⁾



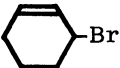
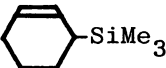
When the electrochemical reduction was carried out without using a diaphragm, both silylation and chlorination took place as shown in the formation of 8 and 10 from 7 and 9 respectively (Eqs. 4 and 5), whereas benzyl chlorides possessing an electron-withdrawing substituent were not chlorinated (runs 5 and 6).



The anodic chlorination on aromatic nucleus in the presence of Cl⁻ has been explained by the reaction of an active species of chlorine formed on the anode.⁶⁾

Allyl chlorides 3 were also satisfactorily silylated under the conditions similar to the reaction of 1.⁷⁾ Results are shown in Table 2.

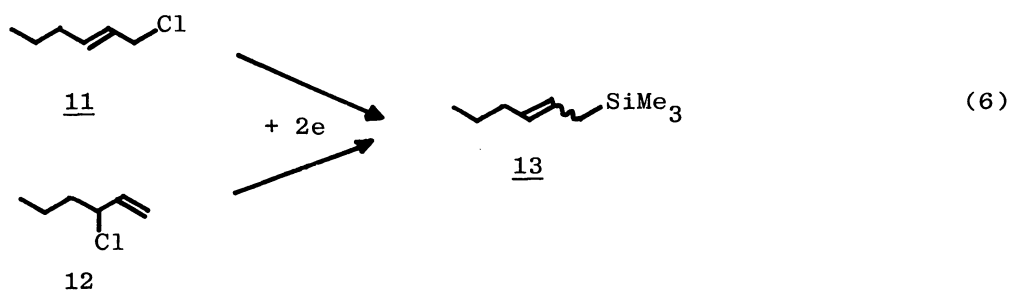
Table 2. Electroreductive Synthesis of Allylsilanes^{a), b)}

Run	Allyl halide	Electricity passed $Fmol^{-1}$	Allylsilane	Yield/% ^{c)}
1	<u>11</u>	6	<u>13</u>	60
2	<u>12</u>	6	<u>13</u>	60
3	$ClCH_2CH=CHCH_2Cl$	16	$Me_3SiCH_2CH=CHCH_2SiMe_3$	66 ^{d)}
4		6		67

- a) Carbon anode; Ni cathode. b) A diaphragm was used. c) GLC yield.
 d) Both *trans*-1,4-dichloro-2-butene and a mixture of *cis*- and *trans*-1,4-dichloro-2-butene (9:5) gave the same mixture of *cis*- and *trans*-2-butene-1,4-diylbis[trimethylsilane] (2:1); see Ref. 11).

Since chlorotrimethylsilane does not show any reduction wave at more positive potential than -3.0 V *vs.* SCE⁸⁾ and benzyl and allyl halides are electrochemically easily reducible,⁹⁾ the initiation of the silylation may be the reductive C-X bond cleavage of 1 and 3 to benzyl and allyl anions followed by the trapping of the anions with chlorotrimethylsilane. Thus, the electrochemically inert functional groups can remain intact in this silylation.

It seems interesting that both isomeric allyl chlorides 11 and 12 gave exclusively the same product 13 silylated at the terminal position (Eq. 6), since this result contrasts with the fact that the reaction of a Grignard reagent prepared from crotyl chloride with chlorotrimethylsilane yields a mixture of products silylated at the external and internal positions, the ratio of which depends on the reaction conditions.¹⁰⁾



The mechanistic details and the silylation of other electrogenerated carbanions are now under investigation.

References

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- 11) The ^1H NMR spectrum shows a sharp singlet of $\text{CH}_3\text{-Si}$ for *trans* isomer ($\delta=0$), and *cis* isomer ($\delta=0.02$).^{5g)} Since each isomer of *cis*- and *trans*-2-butene-1,4-diylbis[trimethylsilane] was hardly separable, the *cis/trans* ratio was determined by NMR method.

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