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Electrochemical Trimethylsilylation of *o*-Dichlorobenzene: A Selective Route to Silylated Cyclo-C_6 Synthons

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The electrochemical trimethylsilylation of *o*-dichlorobenzene in an undivided cell, using a sacrificial anode, and a constant current density, constitutes a simple, versatile, and competitive method for successive creation of SiC bonds. Thus one-pot syntheses of *o*-(trimethylsilyl)chlorobenzene, *o*-bis(trimethylsilyl)benzene, 2,3,5,6-tetrakis(trimethylsilyl)cyclohexa-1,3-diene, 1,2,3,4,5,6-hexakis(trimethylsilyl)cyclohexene, and *o*-(trimethylsilyl)benzoic acid were effected. The cardinal role of metallic cations and of HMPA was displayed in these reactions. The selectivity of the C–Cl bond silylation could be interpreted on the basis of the difference between the reduction potential values of the starting *o*-dichlorobenzene and of the intermediate *o*-chloro(trimethylsilyl)benzene, measured in THF.

Introduction

o-Dichlorobenzene (**1**) constitutes a very convenient substrate for preparing 1,2-difunctional benzene derivatives: it is much less expensive than the other commercially available 1,2-difunctional substrates, especially the 1,2-dibromo- and 1-bromo-2-chlorobenzenes, it exhibits a relatively low tendency to give benzyne by Cl^- elimination during the functionalization, in contrast with the dibrominated starting materials.[1] In order to extend the synthetic applications, given the very large potential of arylsilanes in organic synthesis,[2–7] silylation of *o*-dichlorobenzene was extensively investigated, especially in our laboratory.[8–10] Thus *o*-(trimethylsilyl)chlorobenzene,[8,11–13] *o*-bis(trimethylsilyl)benzene,[9] 2,3,5,6-tetrakis(trimethylsilyl)cyclohexa-1,3-diene,[9] and 1,2,3,4,5,6-hexakis(trimethylsilyl)cyclohexene[10] were prepared from *o*-dichlorobenzene (Scheme 1). The motivation of this research was the efficiency and the versatility of the organosilicon route for 1,2-, 1,3-, 1,4-, 1,2,4-, 1,2,4,5-polyfonctionalization of the benzene ring starting from *o*-dichlorobenzene.[9]

An established chemical route allows the preparation of compounds **2**-**5** (Scheme 1). This strategy, however, suffers from several drawbacks: (i) the synthesis of **2** requires a special experimental procedure and the observed yields are erratic;[8] (ii) the use of HMPA, a potentially toxic compound,[13] as the solvent, especially at 80–100 °C and *a fortiori* at 140–150 °C, is definitely unadvisable; (iii) there is no simple experimental procedure allowing the successive synthesis of **2**–**5** by progressive silylation of *o*-dichlorobenzene.

Another general route to arylsilanes from haloarenes and disilanes was extensively investigated,[14,15] but polysilylation was not taken into account in this approach. Moreover, although the potential formation of **2** by this method was included in some patents, no explicit preparation of **2** (or *o*-(trimethylsilyl)bromobenzene) was given and, from more recent results,[15,16] it is thought that the disilane route is not convenient for preparing **2**.

Considering the experience of our laboratory in this field, as well as the results obtained by Yoshida *et al.*[17] in the electrochemical trimethylsilylation of iodoarenes and, more recently, by us in the electrochemical silylation of arenes and chloroarenes,[18–20] it appeared to us that the inexpensive, industrially feasable electrochemical route

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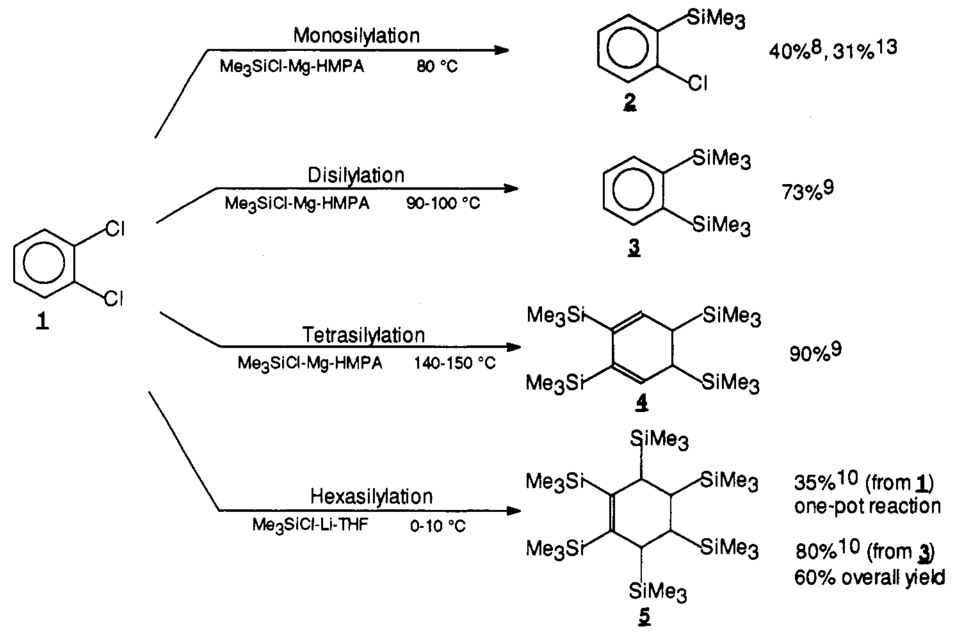
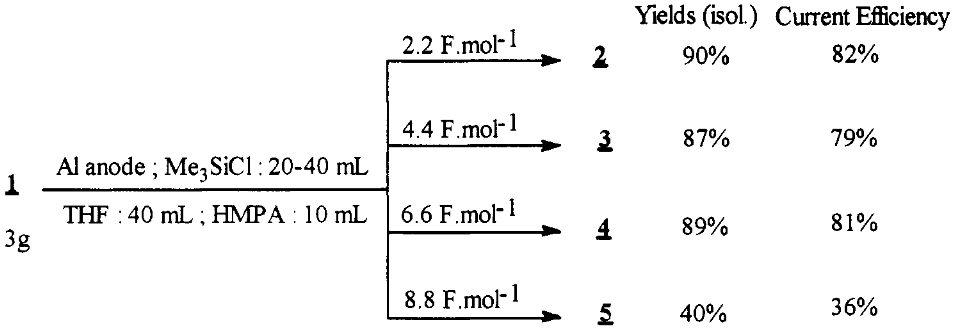
Scheme 1. Silylation of *o*-Dichlorobenzene



Scheme 2. Electrochemical Trimethylsilylation of *o*-Dichlorobenzene



involving an undivided cell, a sacrificial anode, and a constant current density[21] could offer a competitive alternative way for obtaining progressive silylation of 1. The latter could successively afford **2–5** in high yields, via a unique experimental procedure, the products formed depending only on the quantity of electricity used. Here we report our results.

Results and Discussion

1. Controlled Stepwise Electrochemical Trimethylsilylation of *o*-Dichlorobenzene. Silylations were carried out at room temperature using an aluminum bar as the anode, a cylindrical stainless steel grid as the cathode, and THF as the solvent. In all cases, a small amount of HMPA was necessary to perform electrosilylation in optimal conditions, and Bu_4NBr was used as the supporting electrolyte at a very low concentration (0.02 M), compared with that of the substrate (0.2 M or more).

Results obtained are summarized in Scheme 2.

2–4 were formed almost quantitatively in a one-pot reaction, but **5**, which is easily obtained in high yield from **3** and **4**, was formed in a lower yield under these conditions. Dynamic GL chromatography shows the control of the formation of each product from its less silylated precursor according to the quantity of electricity involved. Results are depicted in Scheme 3.

When the quantity of electricity passed was increased above 8.8 F·mol^{-1}, the chemical yield of **5** increased, but not very significantly (50% maximum), whereas the faradaic yield strongly decreased due to competitive reduction of other species present in the medium (supporting electrolyte, solvent, $AlCl_3$): consequently, the reaction was not investigated beyond 9 F·mol^{-1}.

2. Influence of the Amount of Chlorosilane. Depending on the proportion of trimethylchlorosilane to **1**, a competition can be observed between the expected silylation and protonation (or H atom transfer) reactions, as shown in Table 1 for the monosilylation obtained after 2 F/mol of **1** was passed. H^+ or H° are thought to be abstracted from the solvent or the supporting electrolyte, but protonation by traces of water can also occur in total absence of Me_3SiCl. These side reactions were minimized, however, and became negligible for a molar ratio of $Me_3SiCl/1 \approx 10$.

3. Monosilylation without THF: Substrate and Trimethylchlorosilane as the Solvent. A high concentration of Me_3SiCl being favorable to the silylation reaction, the first step of the reaction (formation of **2**) was also investigated in the absence of THF, using the *o*-dichlorobenzene itself as the solvent. Indeed, this substrate seemed convenient for that purpose since its

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Scheme 3. Progress in the Trimethylsilylation of *o*-Dichlorobenzene According to the Quantity of Electricity Passed

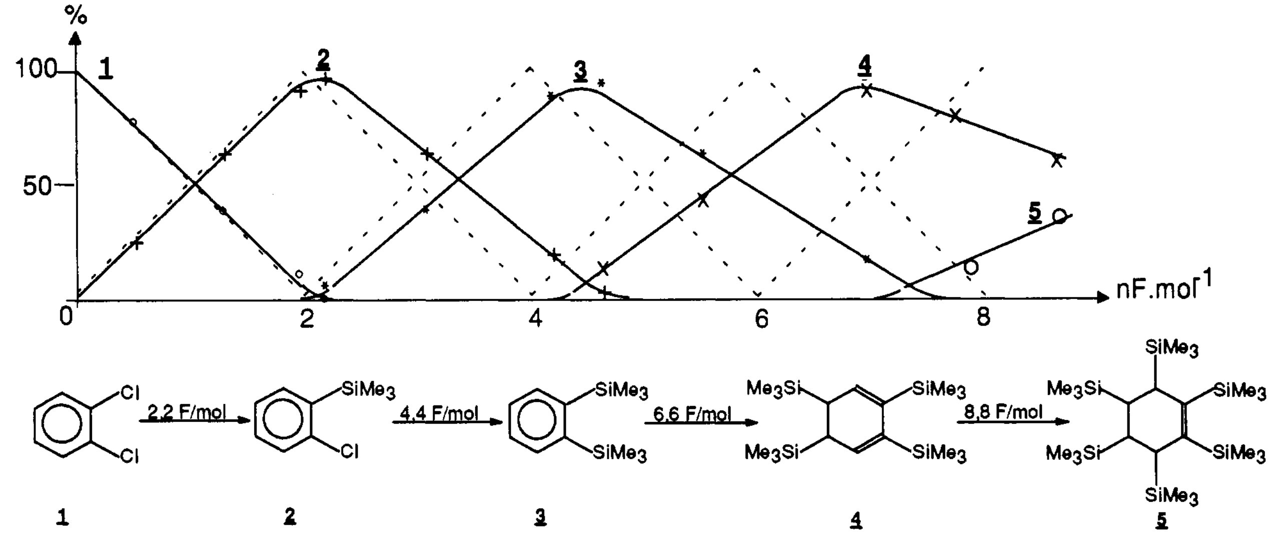
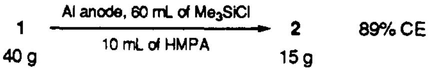


Table 1. Influence of the Amount of Chlorosilane on the Electrochemical Monosilylation of *o*-Dichlorobenzene (2 F·mol^{-1})

initial molar ratio $Me_3SiCl/1^a$	amt of recovered substrate (1) (mol %)	amt of monosilylated product (2) (mol %)	amt of protonation or H transfer product (PhCl) (mol %)
0	15	0	72^b
1	9	60	24^b
2	9	72	17^b
5	7	79	9
10	5	92	2

[a] Concentration of 1: 0.2 M. [b] When Me_3SiCl was absent or in low excess, a small amount of dichlorinated biphenyl was also formed (analyzed by GC–MS); the latter, however, was not detected when $Me_3SiCl/1 \approx 10$.

Scheme 4. Monosilylation of 1 Using 1 as the Solvent



$$\underset{40\ g}{1} \xrightarrow[\text{10 mL of HMPA}]{\text{Al anode, 60 mL of }Me_3SiCl} \underset{15\ g}{2} \quad 89\%\ CE$$

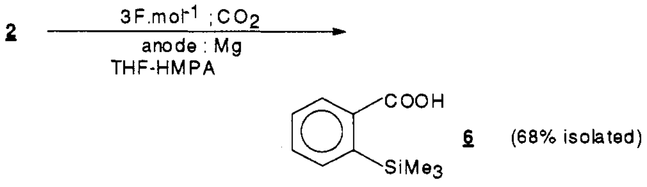
relatively high dielectric constant ($\epsilon = 9.93$ at 25 °C) suggested that dissolution of salts (Bu_4NBr and $AlCl_3$) would be important enough to assure a convenient conductivity. As expected, even without optimization, the formation of 2 occurred with 89% current efficiency (CE) after consumption of 33% of 1, and only traces of 3 (<5%) were detected (Scheme 4).

Under these conditions, 15 g (80 mmol) of 2 can be obtained in a 100-mL cell in one run. For the preparation of the same quantity, in the presence of solvent, a 500-mL cell with 200 mL of THF (0.2 M in 1) would be required.

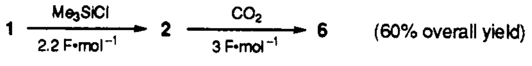
By comparison with the chemical routes to 2–5, the electrochemical silylation is quite competitive: in the case of 2, the chemical routes consist (i) of using 1 and $Me_3SiCl/Mg/HMPA$ (40% yield, use of HMPA as the solvent at 80 °C),[8] (ii) of starting from o-$ClC_6H_4SiCl_3$ and $MeBr/Mg/Et_2O$ (22% yield, but it is necessary to initially prepare the trichlorosilyl derivative),[11] and (iii) of starting from *o*-chloroiodobenzene instead of 1 and $Me_3SiCl/Mg/Et_2O$ (74% yield).[12] In the case of 3–5 the competitivity of the electrochemical way is mainly due to the mild reaction conditions and to the higher yields obtained.

4. Dissymmetrical Difunctionalization of *o*-Dichlorobenzene. Other cases of the possible difunctionalization of 1 were investigated. First we attempted to synthesize *o*-(trimethylsilyl)benzoic acid (6) from 2 upon carboxylation of the anion resulting from the reduction of the C–Cl bond, since 6 possesses a trimethylsilyl group susceptible to being regiospecifically replaced by electrophilic substitution[2,23,24] (Scheme 5).

Scheme 5. Carboxylation of *o*-(Trimethylsilyl)chlorobenzene (2)



Scheme 6. One-Pot Preparation of *o*-(Trimethylsilyl)benzoic Acid (6) from *o*-Dichlorobenzene (1)



$$1 \xrightarrow[\text{2.2 F·mol}^{-1}]{Me_3SiCl} 2 \xrightarrow[\text{3 F·mol}^{-1}]{CO_2} 6 \quad \text{(60\% overall yield)}$$

The two-step but one-pot synthesis of 6 from 1 was successfully carried out (Scheme 6).

Thus, the electrochemical silylation is an attractive means of successive one-pot functionalizations.

5. Nature of the Anode and Role of the Metal Cations Generated. The use of a sacrificial anode in an undivided cell allows a good complementarity between anodic and cathodic reactions, because of the formation of metallic cations by anodic oxidation of the anode metal. In our previous work concerning the electrochemical silylation of haloaromatic substrates,[18–20] we have shown that the formation of metallic halide(s) allowed us to avoid X^- oxidation into X_2 and, consequently, to prevent the undesirable halogenation of the substrates which occurs with a Pt anode.[34] Furthermore, Périchon *et al.*[25] have shown that the presence of magnesium cations, formed by oxidation of a magnesium anode in the electrochemical

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Table 2. Silylation of *o*-Dichlorobenzene (1) in a Two-Compartment Cell

Q (F·mol^{-1})	unreacted substrate (1) (mol %)	amt of formed products (mol %)				
		2	3	PhCl (7)	PhSiMe$_3$ (8)	PhH (9)
0	100	0	0	0	0	0
2.5	73	10.5	0	14	2.5	0
5	45	17	2	27	7	2
7	22	19	4	27	14	14

Chart 1. Silylation of *o*-Dichlorobenzene 1 in a Two-Compartment Cell—Substrate Evolution and Formation of the Expected Products 2 and 3

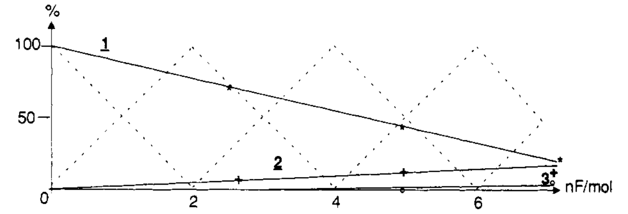
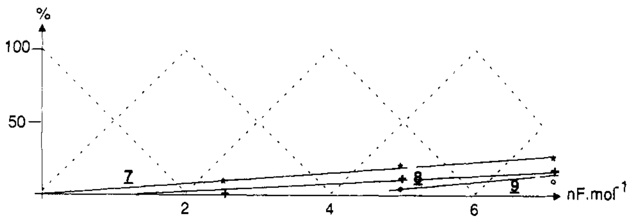


Chart 2. Silylation of *o*-Dichlorobenzene in a Two-Compartment Cell—Formation of Protonated Products



carboxylation of benzyl chlorides, lowers the nucleophilicity of the carboxylate formed, avoiding the formation of the ester (which occurs in the absence of metallic cations by the condensation of the carboxylate anions with the starting halide). Magnesium ions presumably also shift the reduction potential of CO_2 toward more cathodic values, increasing the current efficiency of the reaction.

In order to point out the role of the metallic cations, we first studied the silylation of 1 in their absence, in the cathodic chamber of a two-compartment cell fitted with a stainless steel cathode and containing a 0.03 M solution of Bu_4NBr in a mixture of THF/HMPA (*ca.* 60/10 v/v). The anodic compartment was equipped with an aluminum anode and contained the same electrolyte solution. Results are given in Table 2 and depicted in Charts 1 and 2.

From these results it must be pointed out that the current efficiency is very low in the absence of metallic

Table 3. Silylation of *o*-Dichlorobenzene in an Undivided Cell without HMPA in THF When up to 2.2 F·mol^{-1} Was Passed

unreacted substrate (1) (mol %)	products formed (mol %)				
	2	3	7	8	9
41	7	7	26	14	5

cations, which favor the conductivity (only 22% of 1 was consumed when up to 2 F·mol^{-1} was passed). Under these conditions, it is important to note that mainly products resulting from protonation or H transfer were formed. This could explain why Yoshida[17] chose iodobenzene (and not chlorobenzene) to perform the silylation in a two-compartment cell: the presence of metallic cations, which certainly make the anion generated a softer base, is necessary to conveniently perform the silylation of C_{Ar}–Cl bonds.

In order to make clear the role of the nature of the anodic metal on the monosilylation reaction, we also tested the reaction under the standard conditions corresponding to Scheme 2, with a current quantity of 2.2 F·mol^{-1}. Thus, when we used *copper* as the anode, 1 was not reduced at all and a deposition of copper was observed at the cathode, the copper cations at the anode being more readily reduced than the organic halide. With *zinc*, the yield for 2 was lower (40%) than that with *aluminum* (95%), the zinc cations being reduced concurrently with the substrate (E_p($ZnCl_2$) = −1.55 V/SCE in DMF[26]). With these two metals, however, the chemoselectivity for the monosilylation, compared with protonation and disilylation, was excellent (96% for both). With magnesium, the chemoselectivity (82%) and the chemical yield (80%) of the monosilylation are lower than those with Al, due to the formation of 18% of 3. This result coupled with an abnormally high anodic faradaic yield of 240% (amount of metal consumed compared to the charge passed) shows that a chemical reduction occurred at the anodically scoured metal.

In conclusion, the best anodic metal for the selective silylation of aromatic halides is aluminum.

6. Influence of HMPA. The solvent plays a cardinal role in these reactions, and in particular, the presence of HMPA is necessary for reasons beyond ensuring a satisfactory conductivity. For instance, when the silylation of 1 was carried out in solution, under our standard conditions but without HMPA, after passing 2.2 F·mol^{-1} of charge, (i) the cathodic CE was very low (only 59% of 1 was consumed in spite of the presence of an aluminum salt) and a deposition of aluminum occurred on the cathode, and (ii) mainly protonation (or H transfer) products (7–9) were formed (45%) despite a large excess of chlorosilane (molar ratio chlorosilane/substrate = 10) (Table 3).

Thus, the complexation of HMPA with aluminum (or magnesium) chloride renders the reduction potential of the salts more cathodic, avoiding the transferring of the metal from the anode to the cathode. Moreover, in the absence of HMPA, complexation of aluminum chloride with THF increases the acidity of this solvent, and protonation becomes important. Finally, HMPA increases the electrophilicity of the chlorosilane, as shown by Corriu *et al.*[27]

7. Large-Scale Laboratory Synthesis. The preparative interest of the sacrificial anode method for the electrocarboxylation of organic halides has been demonstrated by the design of several larger laboratory- and pilot-

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Scheme 7

$$\text{Ar–X} + e^- \rightleftharpoons \text{Ar–X}^{\circ -} \qquad (1)$$

$$\text{Ar–X}^{\circ -} \longrightarrow \text{Ar}^{\circ} + \text{X}^- \qquad (2)$$

$$\text{Ar}^{\circ} + e^- \longrightarrow \text{Ar}^- \qquad (3)$$

$$\text{Ar}^{\circ} + \text{Ar–X}^{\circ -} \longrightarrow \text{Ar}^- + \text{Ar–X} \qquad (4)$$

$$\text{Ar}^- + \left[\begin{array}{l}\text{SH}\\ \text{H}_2\text{O (residual)}\\ \text{R}_3\text{N}^+\text{–CH}_2\text{R}'\end{array}\right. \longrightarrow \text{Ar–H} + \left[\begin{array}{l}\text{S}^-\\ \text{OH}^-\\ \text{R}_3\text{N}^+\text{–CH}_2\text{R}'^-\end{array}\right. \qquad (5)$$

$$\text{Ar}^{\circ} + \text{SH} \longrightarrow \text{Ar–H} + \text{S}^{\circ} \qquad (6)$$

$$\text{S}^{\circ} + e^- \rightleftharpoons \text{S}^- \qquad (7)$$

$$\text{S}^{\circ} + \text{Ar–X}^{\circ -} \longrightarrow \text{S}^- + \text{Ar–X} \qquad (8)$$

scale cells.[25] Concerning the electrochemical silylation, for large-scale syntheses, we have adapted a classical 1-L reactor containing six metallic rods as anodes and six stainless steel grids as cathodes connnected in parallel and separated with polypropylene mesh (Figure 2b). A circular plate of aluminum ensured the electrical contact of the anodes and the rigidity of the assembly. With such a simple cell we could prepare about 0.17 mol of **3** (30 g) from a 0.2 M solution of **1** in THF/HMPA using a current of 1 A for 23 h at room temperature, simply maintained by a water bath. This is particularly interesting in comparison with classical chemical methods, which need 24–50 h of heating depending on the temperature (90 or 100 °C).

8. Voltammetric Measurements and Mechanism. Two mechanisms can be proposed to explain our results, the first one supposing the initial reduction of trimethylchlorosilane to the corresponding silyl anion, the second one involving the initial reduction of the carbon–halogen bonds, or even the initial reduction of the aromatic ring.

It is known that Me_3SiCl does not show a reduction wave at more positive potential than −3 V *vs* SCE[27a,34] (the −3.2-V literature value was proposed without specifying the conditions[35]), but it actually can be reduced and dimerized into hexamethyldisilane.[35-39]

The reduction of an aromatic ring is very cathodic, too: several values for the half-wave reduction potential of benzene have been reported.[40] These are −3.38 V (by direct measurement at −90 °C in THF-Bu_4NPF_6),[40a] −3.42 V (obtained at −60 °C in DME–Bu_4NPF_6),[40b] −3.31 V (obtained at −90 °C in DME–Bu_4NClO_4 solution),[40c] −3.31 V (by extrapolation from the reduction potentials of 20 hydrocarbons),[40d] and −3.5 V (by calculation from the reduction potential of naphthalene).[40e] Under our experimental conditions, we have not yet been able to detect any reduction waves for Me_3SiCl, **3**, or **4**; experiments are under progress for their determination. In spite of this lack of information, the first hypothesis can be excluded, given that a chlorosilane is a much better electrophile than the other species (C–Cl bonds, aromatic rings): if the silyl anion was preferentially formed in a medium containing a large excess of chlorosilane, the exclusive product obtained would be hexamethyldisilane and, consequently, **1**, **2**, **3**, or **4** (depending on which step the formation of the silylation could occur) would be recovered unchanged.

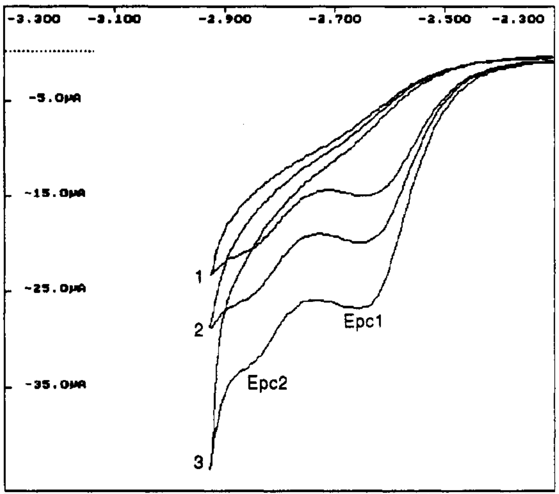

Figure 1. Cyclic voltammetry of **1** in THF–0.1 M Bu_4NBF_4 at a 1-mm-diameter Pt disk. Voltage scan (V vs SCE): 0/1/−2.93/0 (expansion −2.3 to −2.93 V). Sweep rates (V s^{-1}): (1) 0.05; (2) 0.1; (3) 0.2.

8-1. Reduction of the C–Cl Bonds of *o*-Dichlorobenzene. The objectives of this study were (i) the determination of the reduction potentials of phenyl chlorides under our conditions and (ii) the determination of the effect of the trimethylsilyl group relative to a hydrogen atom on the reduction potential of an ortho C–Cl bond in **2**.

The electrochemical reduction of aromatic halides (ArCl, ArBr, ArI)[31,32] in DMF or DMSO, which leads to ArH, generally involves the cleavage of the carbon–halogen bond of the initially generated radical anion, (1) and (2) (Scheme 7).

The neutral radical thus formed, which is easier to reduce than the starting ArX molecule, may be reduced at the electrode (3) or in solution (4). The anion obtained is then protonated by the solvent, residual water, or the supporting electrolyte (5). Ar° may also abstract a hydrogen atom from the solvent SH (6). The radical S° thus formed may then undergo an electrode (7) or a solution reduction (8). The overall process then appears as a two-electron irreversible mechanism leading entirely to ArH.

In order to obtain more information about the electroreduction mechanism of **1** under our conditions, and in the context of a wide study concerning the electrochemical silylation of haloaromatics (investigation under progress), the voltammetric reduction behaviors of **1** and intermediate products **2** and **3** have been examined in THF, as no data were available for this solvent in the literature.

We first tried a direct study of the electroreductive silylation, but strong difficulties were encountered in recording the cyclic voltammograms (CV) using Me_3SiCl (in a THF + HMPA–0.1 M Bu_4NBr medium). Thus, we preferred to carry out the study under classical protonation conditions. Better accuracy and resolution for the CV were obtained in THF–0.1 M Bu_4NBF_4; we also noticed that the addition of HMPA with Bu_4NBr as the supporting electrolyte afforded only a very weak cathodic shift of the peak potentials (about 10–20 mV).

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Table 4

	conditions			
	Pt THF–0.1 M Bu_4NBF_4[a]			Hg/Pt[31] DMSO–0.1 M Bu_4NBr
	0.05 V/s	0.1 V/s	0.2 V/s	0.142 V/s
1 E_{p1} (V/ECS)	−2.62	−2.63	−2.64	−2.218
E_{p2} (V/ECS)	−2.85	−2.86	−2.87	−2.440
$E_{p1} - E_{p2}$ (mV)	230	230	230	222
7 E_p (V/ECS)	−2.85	−2.86	−2.87	−2.440
2 E_p (V/ECS)	−2.84	−2.85	−2.86	
3	no peak			

[a] E_p ± 0.01V. [b] E_P ± 0.005 V.

Thus, as previously observed in DMSO,[31] the CV of **1** obtained in THF–0.1 M Bu_4NBF_4 at moderate sweep rates (Figure 1) presents two irreversible peaks of similar intensity, showing that this compound undergoes a stepwise reduction of the two carbon–chlorine bonds, each carbon–chlorine reduction corresponding to a two-electron process, as shown by our dynamic GC study (Scheme 3) and as generally accepted.[31,32]

However, three exceptions are known for this stepwise replacement of halogens by hydrogens: *o*-dibromobenzene, *o*-diiodobenzene and *o*-bromoiodobenzene are reduced in a single four-electron step to benzene, the suggested mechanism for which involves the formation of benzyne as an intermediate; for *o*-bromochlorobenzene, both mechanisms are competitive.[1,33]

We have verified that the peak currents in the CV of **1** are proportional to the square root of the sweep rate within experimental uncertainty ($i_p v^{-1/2} = 45 \pm 1\ \mu A\ V^{-1/2}\ s^{1/2}$).

In accordance with the previous studies in DMSO,[31] the absence, in THF, of anodic peaks during the reverse voltage sweep and the observation that the peak potentials (Table 4) shift cathodically by 10–20 mV for an increase in sweep rate from 0.05 to 0.2 V s^{-1} ($\partial E_p/\partial \log v = -33$ mV/unit) suggest that the mechanism proceeds with a reversible electron transfer followed by a rapid irreversible chemical reaction, for each C–Cl bond reduction.

The values of the peak potentials obtained for **1** (Table 4) are about 300–400 mV more cathodic than those previously measured by Farwell[31] under different conditions (hanging mercury electrode, DMSO–0.1 M Et_4NBr, interrupted-sweep voltammetry), but it is interesting to point out that (i) the second peak potential, E_{p2}, matches that of the protonation product of the first step, PhCl (−2.86 V), and (ii) the $E_{p1} - E_{p2}$ difference, 230 mV, is similar to that obtained by Farwell and is sufficiently high to explain the excellent selectivity of the electrochemical reduction of **1**. Moreover, we could show that these conclusions are available for the trimethylsilylation, since replacing an ortho hydrogen in the intermediate product PhCl by a trimethylsilyl group has a very weak effect on the peak potential (Table 4).

For the electrochemical silylation of both C–Cl bonds of **1**, Me_3SiCl obviously acts as the electrophile, and we can propose the following mechanism:

$$\mathrm{Ar{-}X} + e^- \rightleftharpoons \mathrm{Ar{-}X}^{\circ -}$$

$$\mathrm{Ar{-}X}^{\circ -} \rightarrow \mathrm{Ar}^{\circ} + \mathrm{X}^-$$

$$\mathrm{Ar}^{\circ} + \text{“}e^-\text{”} \rightarrow \mathrm{Ar}^-$$

$$\mathrm{Ar}^- + \mathrm{Me_3SiCl} \rightarrow \mathrm{Ar{-}SiMe_3} + \mathrm{Cl}^-$$

“e^-” indicates that the radical may be reduced at the electrode or in solution.

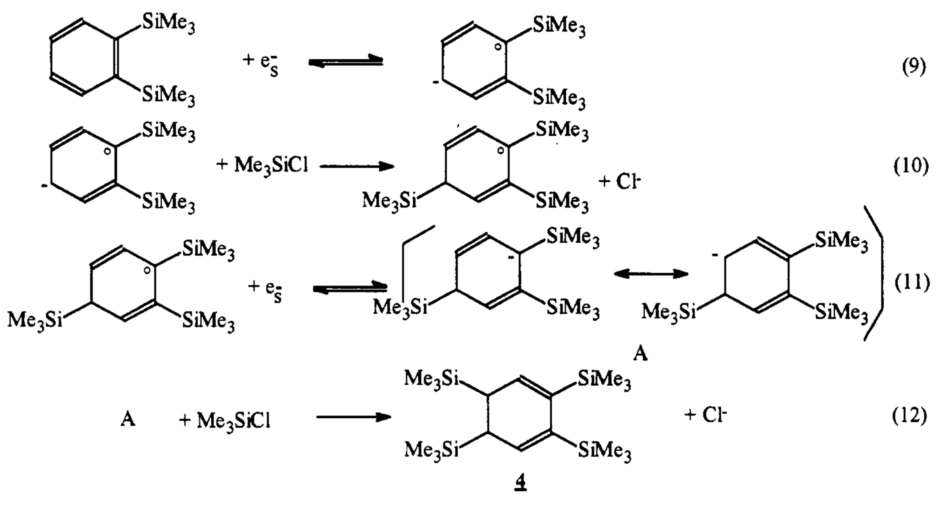
8-2. Reduction of the Aromatic Ring of 3. The first step is most likely the direct cathodic generation of solvated electrons ($e^-(M) \rightarrow e_s^-$) since, as we have previously shown,[20] such a primary process is favored in HMPA solutions[28,29] and possible in the absence of dissolved alkali metal ions.[30] The transfer of an electron to the *o*-disilylbenzene would generate a radical anion (9) which, in the absence of a proton donor but in the presence of Me_3SiCl, would be trimethylsilylated (10) (Scheme 8). From the resulting trimethylsilylated aryl radical a further electron transfer (11) with subsequent trimethylsilylation (12) would explain the formation of the tetrasilylated cyclohexadiene **4**, itself converted into **5** via a similar disilylation process.

Experimental Section

General Methods. The electrolysis of magnetically stirred solutions was performed on a small scale under dry argon, under constant current density ($J = 0.10 \pm 0.05$ A·dm^{-2}), in an undivided cylindrical cell fitted with a sacrificial aluminum bar (an alloy containing 2% copper) as the anode and a concentrically fitted cylindrical stainless steel grid as the cathode (1.0 ± 0.2 dm^2, surface area) (Figure 2a).

A constant current (0.1 A) was provided by a Sodilec EDL 36–07 regulated dc power supply. The working potential of the cathode was measured relative to a silver wire (as a simple, nonpolluting reference electrode) and recorded during the

Scheme 8. Reduction of the Aromatic Ring of 3



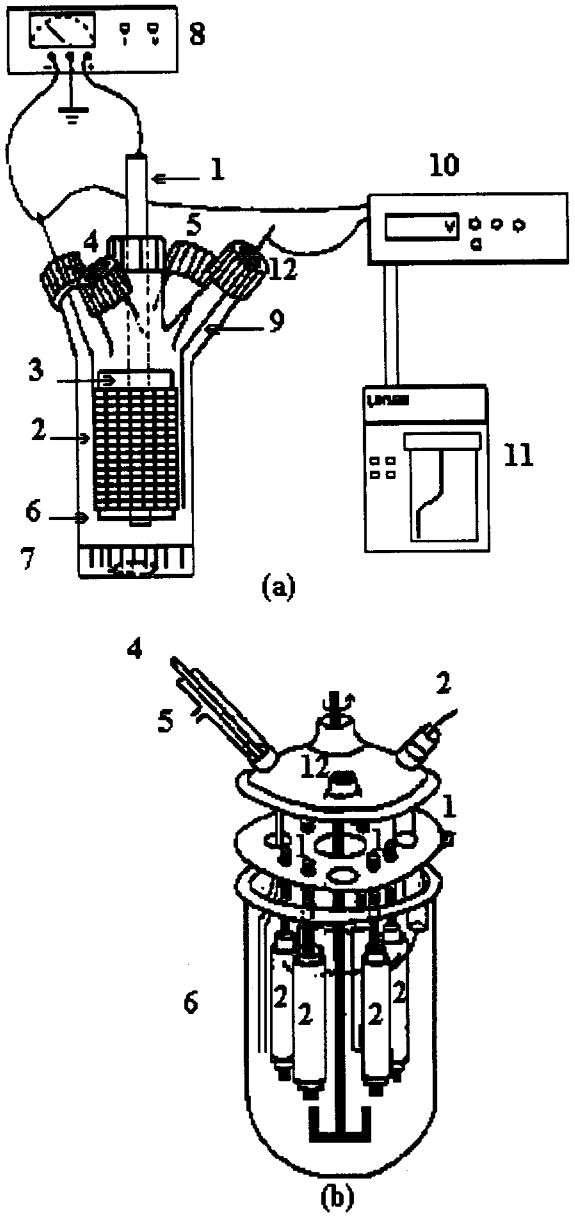


Figure 2. Electrochemical cells used. Key: (1) anode (1-cm diameter bar), (a) 10-cm length, (b) 20-cm length; (2) cathode(s), surface area (a) 1.0 ± 0.2 dm^2, (b) 6.0 ± 0.6 dm^2; (3) separator, polypropylene mesh; (4, 5) input and output of dry argon; (6) volume of the cell, (a) 100 mL, (b) 1 L; (7) magnetic bar; (8) regulated dc power supply; (9) silver wire (1-mm diameter) used as the reference electrode; (10) potentiometer; (11) chart recorder; (12) injection port equipped with a septum.

electrolysis. The silver wire was presumed to be covered with a thin layer of AgCl in the chlorosilane medium.

Bu_4NBr (0.5 g, 1.6 mmol) was added to the previously dried cell as the supporting electrolyte. The cell was then deaerated twice under vacuum and then with purified argon gas. THF (40 mL), HMPA (20 mL), and a large excess of Me_3SiCl (between 20 mL for a monosilylation and 40 mL for an hexasilylation) were introduced through a septum by syringe. The solution was degassed by bubbling with argon for 10 min. Any HCl that was produced by the reaction of Me_3SiCl with traces of water was removed by pre-electrolysis of the solution (I = 0.1 A). The other hydrolysis product, $(Me_3Si)_2O$, is electrochemically inert. The end of the pre-electrolysis was detected by measuring the working potential of the cathode (*vs* Ag wire), a more accurate end point than the end of H_2 evolution. Thus, after remaining constant (−0.7 to −0.8 V) for about 0.5 h, a sudden drop in the potential to about −2 V was observed. The substrate (20 mmol) was then introduced by means of a syringe. The electrolysis (I = 0.1 A) was then performed until the theoretically required charge had been passed (11 h for 2 F·mol^{-1}). The progress of the reaction was followed by GC. After elimination of most of the salts from the resulting solution by the addition of anhydrous pentane (50 mL), filtration, and evaporation of the Me_3SiCl and the solvents, the residue was extracted with Et_2O (3 × 50 mL) and washed with water (2 × 10 mL). After drying over Na_2SO_4, the Et_2O was evaporated. The crude product was crystallized or analyzed by GC and, most often, distilled. The current efficiency (CE) was calculated on the basis of yield (%) × theoretical number of electrons/quantity of electricity (F·mol^{-1}) supplied.

All the products obtained were identified by comparison of their physical data with those of authentic samples. Gas chromatography was performed with a temperature-programmable Hewlett Packard 5890 apparatus equipped with a 25-m × 0.25-μm CP-Sil capillary column.

^1H NMR spectra were recorded in $CDCl_3$ at 250 MHz with a Bruker AC 250 spectrometer, using residual $CHCl_3$ (δ = 7.27 ppm) as the internal standard. The signals are designated s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{13}C NMR spectra were obtained at 62.86 MHz with a Bruker AC 250 using $CDCl_3$ (δ = 77.70 ppm) as the internal standard. The signals are designated P (primary carbon), T (tertiary), or Q (quaternary). Electron-impact mass spectra were recorded at an ionization voltage of 70 eV with a VG Micromass 16 F spectrometer coupled with a gas chromatograph Intersmat IGC 121 M equipped with a capillary column.

The cyclic voltammetry experiments were carried out in a THF solution containing Bu_4NBF_4 (0.1 M). The used working electrode was a platinum disk of 1-mm diameter. The reference electrode was an aqueous saturated calomel electrode. Ferrocene (10^{-3} M) was also used as an internal standard (E_{pa} = 0.63 V, E_{pc} = 0.56 V). The solution resistance was compensated for with a positive feedback device. The potentiostat used (SIRIUS) consisted of two hard cards incorporated in a PC computer: one for high-speed data acquisition (12 bits, 2 DAC, 4 ADC, 1 PLA, 1 timer) and the other for electrochemistry (a potentiostat: ±2 mA, ±10 V, a linear analog integrator and a pulse circuit); the resolution was 10 nA and 2.5 mV.

Materials. THF and HMPA (Aldrich) were dried by distillation over sodium benzophenone ketyl and CaH_2, respectively. n-Bu_4NBr (Aldrich) was used without purification, whereas Me_3SiCl, a generous gift from Rhône-Poulenc Co., was distilled over Mg powder just before use.

Silylated Cyclo-C_6 Synthons from the Electroreductive Trimethylsilylation of *o*-Dichlorobenzene and Related Compounds. (a) *o*-Chloro(trimethylsilyl)benzene (2). (i) Electrolysis of 3 g (20 mmol) of 1 in THF/HMPA solution (see before) by application of 0.1 A until 2.2 F/mol of 1 had been passed (11.8 h) gave 3.3 g of 2 (90% yield, 82% CE, after distillation). (ii) Electrolysis, in the same 100-mL cell, of 40 g (270 mmol) of 1 without THF but with 60 mL of Me_3SiCl, 10 mL of HMPA, and 0.5 g of Bu_4NBr gave 15 g of 2 (89% CE) after the passage of 0.20 F at 0.1 A over 53.6 h and the consumption of 33% of 1. Bp (740 mm Hg) : 207–8 °C. ^1H NMR: δ 0.51 (s, 9H, $SiMe_3$); 7.40 (m, 4H, $4CH_{arom}$). ^{13}C NMR: δ −0.6 (3P, $SiMe_3$), 141.1 (1Q, C_1, C–Si), 138.8 (1Q, C_2, CCl), 129.3 (1T, C_3), 130.6 (1T, C_4), 126.1 (1T, C_5), 135.7 (1T, C_6). MS [m/e (%)]: 184 (12) (M^+), 171 (35), 169 (100), 73 (3.5), 45 (1.6), 43 (5.4).

(b) *o*-Bis(trimethylsilyl)benzene (3). Electrolysis of 3 g (20 mmol) of 1 in solution by application of 0.1 A until 4.4 F/mol of 1 had been passed (23.6 h) gave 3.9 g of 3 (87% yield, 79% CE, after distillation). Bp (20 mmHg): 135–7 °C. ^1H NMR: δ 0.59 (s, 18H, 2 $SiMe_3$), 7.48–7.90 (m, 4H, 4 CH_{arom}). ^{13}C NMR: δ 2.3 (6P, $SiMe_3$), 146.3 (2Q (C_1, C_2), 2C–Si), 135.5 (2T (C_3, C_6)), 128.1 (2T (C_4, C_5)). MS [m/e (%)]: 222 (11) (M^+), 208 (21.7), 207 (100), 191 (89.9), 73 (81.7), 45 (30.8), 43 (13.8).

(c) 2,3,5,6-Tetrakis(trimethylsilyl)cyclohexa-1,3-diene (4). Electrolysis of 3 g (20 mmol) of 1 by application of 0.1 A until 6.6 F/mol of 1 had been passed (35.4 h) gave 6.6 g of 4 (89% yield, 81% CE, after distillation). Bp (0.1 mmHg): 105–7 °C. ^1H

NMR: δ 0.00 (s, 18H, 2 C_{sp^3}, SiMe$_3$), 0.14 (s, 18H, 2C_{sp^2}, SiMe$_3$), 1.71–1.74 (d, 2H, 2CHSi, $^3J_{1-6} = {}^3J_{4-5} = 7.34$ Hz), 6.03–6.06 (d, 2H, 2 C_{sp^2}H, $^3J_{1-6} = {}^3J_{4-5} = 7.34$ Hz). ^{13}C NMR: δ −2.7 (6P, 2SiMe$_3$ bound to C_{sp^3}), 1.1 (6P, 2 SiMe$_3$ bound to C_{sp^2}), 139.1 (2T (C_1, C_4)), 135.2 (2Q (C_2, C_3)), 27.2 (2T (C_5, C_6)). MS: [*m/e* (%)]: 368 (3.4) (M^+), 208 (22.4), 207 (100), 191 (44.3), 73 (95.8), 45 (13.4), 43 (1.3).

(d) 1,2,3,4,5,6-Hexakis(trimethylsilyl)cyclohexene (5). Electrolysis of 3 g (20 mmol) of **1** by application of 0.1 A until 8.8 F/mol of **1** had been passed (47.2 h) gave 4.1 g of **5** (40% yield, 36% CE, after crystallization). Mp (EtOH): 243–5 °C. ^{1}H NMR: δ 0.03 (s, 18H, 2SiMe$_3$ bound to C_4 and C_5), 0.13 (s, 18H, 2SiMe$_3$ bound to C_3 and C_6), 0.20 (s, 18H, 2SiMe$_3$ bound to C_1 and C_2), 1.24 (s ($^3J \approx 0$ Hz), 2H (C_4H and C_5H)), 2.40 (s ($^3J \approx 0$ Hz), 2H, C_3H and C_6H). ^{13}C NMR: δ −2.8 (6P, 2SiMe$_3$ bound to C_4 and C_5), −2.6 (6P, 2SiMe$_3$ bound to C_3 and C_6), 1.2 (6P, 2SiMe$_3$ bound to C_1 and C_2), 148.7 (2Q (C_1, C_2)), 28.9 (2T (C_3, C_6)), 15.7 (2T, (C_4, C_5)). MS [*m/e* (%)]: 208 (22.1), 207 (100), 193 (13.4), 131 (13.4), 73 (79.9).

(e) *o*-(Trimethylsilyl)benzoic Acid (6). THF (60 mL), HMPA (10 mL), Bu$_4$NBr (0.3 g), and **2** (1 g, 5.4 mmol) were introduced into the electrolysis cell fitted with a magnesium anode and a stainless steel cathode. After CO$_2$ was bubbled through the magnetically stirred solution for a few minutes, the current was held at 0.1 A for 4.3 h, corresponding to a charge of 3 F/mol of **2**. The THF was evaporated, cold 3 N HCl (10 mL) added, and the solution extracted with Et$_2$O (3 × 10 mL). The organic layer was treated with cold 2 N KOH (20 mL) and extracted with Et$_2$O (2 × 10 mL) to remove the neutral byproducts. After acidification of the aqueous layer, the organic acid was extracted with Et$_2$O (3 × 30 mL) and evaporated to dryness (yield: 0.7 g, 68%). Mp (aqueous EtOH): 99–100 °C.[30] ^{1}H NMR: δ 0.27 (s, 9H, SiMe$_3$), 7.17–8.11 (m, 4H, 4 C_{Ar}H), 11 (s, 1H, COOH) (under our conditions). ^{13}C NMR: δ 0.4 (3P, SiMe$_3$), 135.7 (1 Q, C_1-COOH), 143.9 (1 Q, C_2-SiMe$_3$), 135.5 (1 T, C_3), 132.3 (1T, C_4), 128.7 (1 T, C_5), 130.8 (1 T, C_6), 173.9 (1Q, COOH).

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