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Electrochemical reactions of organosilicon compounds

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Abstract. Data on the processes of electrochemical reduction and oxidation of organosilicon compounds of various classes as well as on the interaction of these compounds with electrically generated reagents are generalised and surveyed systematically. The electrochemical reactivity of organic derivatives of silicon is considered taking into account their structures and reaction conditions. The bibliography includes 245 references.

I. Introduction

Electrochemical procedures are widely used for the synthesis of various organic and organoelement compounds including organic derivatives of silicon, the chemistry of which has developed especially intensely in recent years. Up to now, vast experimental material has been accumulated in this field. On the one hand, numerous highly selective preparative procedures for the synthesis of target products or intermediates of the functionalisation of organosilicon compounds have been developed. On the other hand, in the studies of redox reactions involving these compounds, a clear-cut relationship between various intramolecular interactions and electrochemical reactivity has been elucidated. Thus, the electrochemistry of organosilicon compounds, apart from its purely preparative aspect, is necessarily concerned with the problems of physical organic chemistry, *i.e.* the structures of the frontier orbitals, transfer of electronic effects in the molecules and their influence on reactivity.

The purpose of this review is to consider systematically the known processes, classifying them according to the type of reaction and to follow, where possible, the roles of various factors determining the reactivity of organosilicon compounds in electrochemical transformations.

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II. Electroreduction of chlorosilanes

Chlorosilanes are among the first organic derivatives of silicon synthesised. At present, they are the most frequently encountered and most readily accessible organosilicon compounds. Apparently, it is for this reason that chlorosilanes were first to attract the attention of electrochemists. Chlorosilanes themselves are difficult to reduce electrochemically, and the cathodic processes involving them are associated most frequently with the initial electrogeneration of a carbanion (or another nucleophile), which then replaces a Cl atom in the chlorosilane molecule. Most of the cathodic reactions involving chlorosilanes are versions of this process. Anodic processes involving organosilicon compounds are more diverse (regarding the types of compounds and reactions), although the number of publications dealing with reduction is much greater than that on oxidation.[1 – 13]

The first studies on the electrochemistry of chlorosilanes (R_nSiCl_{4-n}, where R = Me, Et, Vin, Ph) were published more than twenty years ago;[14 – 16] however, they were only indirectly associated with the problem under consideration, because they described electroreduction of the protons of the hydrogen chloride arising *via* hydrolysis of chlorosilanes.[14, 17 – 20] Nevertheless, these studies have resulted in the development of two efficient methods: a method for electrochemical dehydration of dimethylformamide (DMF)[21] and a procedure for determining the quantity of water in this solvent.[22] Both methods are based on fast hydrolysis of chlorosilanes.

Later, various researchers have obtained electrochemical characteristics for the reduction of chlorosilanes (Table 1); these characteristics were markedly dissimilar even for the same compounds. Since the reduction of chlorosilanes is irreversible and they are highly electrophilic and extremely susceptible to hydrolysis, the effective reduction potentials of these compounds are influenced by many factors (material of the electrode, solvent, supporting electrolyte and, obviously, nucleophilic impurities). Therefore, the fairly contradictory data presented in Table 1 can be rather regarded as an illustration of the confusion reigning in this field. It can be only noted that the nature of the halogen (all other factors being equal), apparently, exerts no significant influence on the reduction potentials.[23, 24] The nature of the organic substituent at the Si atom is more important. Chlorotrimethylsilane **1** accepts an electron at a more negative potential than chlorotriphenylsilane **2**,[25] although the discussion about the

Table 1. Characteristics of electroreduction of chlorosilanes (the first wave for polychlorosilanes).

Chlorosilane	E/ V (*vs* SCE)		Conditions	Ref.
	$-E_{1/2}$/ V	$-E_p$/ V		
Me_3SiCl (**1**)		0.1	$DME/Bu_4NClO_4/Pt$	36
	2.2 [a]		$DME/Bu_4NClO_4/Pt$	37
		3.3 [b]		29
		1.11 [c]	$PhOMe/Bu_4NClO_4$	18
		> 3	DMF/Et_4NOTs	28
Ph_3SiCl (**2**)	3.1 [a]		$DME/Bu_4NClO_4/Hg$	22, 39
	2.39		$THF/Bu_4NClO_4/Hg$	23, 40
		0.2	$DME/Bu_4NClO_4/Pt$	36
	1.2		DME/Bu_4NClO_4	37
		2.4 [b]		29
$MePh_2SiCl$ (**3**)		2.55	$AN/Bu_4NPPh_4/Pt$	27
		2.65	$AN/Bu_4NClO_4/GC$	38
		2.06	$DME/Bu_4NClO_4/Hg$	40
Ph_3SiBr	2.37		$DME/Bu_4NClO_4/Hg$	40
Ph_3SiF	2.59 [d]		$DME/Bu_4NClO_4/Hg$	40, 24
Me_2SiCl_2 (**4**)		2.28 [e]	$DME/Bu_4NBF_4/Hg$	41
		> 2.5		42
$PhMeSiCl_2$ (**5**)		> 1.8		42
Ph_2SiCl_2 (**6**)		2.5	$AN/Bu_4NClO_4/GC$	38
	1.9 [a]		$DME/Bu_4NClO_4/Hg$	39, 43
		> 1.5		42
Mes_2SiCl_2 (**7**)	2.8 [f]		DME/ME	44
$SiHCl_3$	1.7 – 1.75 [b]		AN/Et_4NCl/graphite	45
		1.9 [g]	THF/Pt	46
$SiCl_4$	1.66 – 1.70 [b]		AN/Et_4NCl/graphite	45
		2.2 [b]	THF/Pt	46

Note. SCE is saturated calomel electrode, DME is dimethoxyethane, DMF is *N,N*-dimethylformamide, THF is tetrahydrofuran, AN is acetonitrile, GC is glassy carbon, Mes is mesityl, ME is dropping-mercury electrode.

[a] *vs* 0.001 M $Ag/AgClO_4$; [b] *vs*. Ag/AgCl; [c] *vs*. $Ag/AgNO_3$; [d] *vs*. Ag/AgI (recalculated for SCE); [e] apparently, the E_p value is presented; [f] *vs*. $A-g/Ag^+$ ($E = E_{SCE} + 0.6$ V); [g] reduction of the Si – H bond.

potential for the cathodic reduction of the silane **1** has not yet been completed.[23, 26 – 37]

The reduction potentials of most of the studied chlorosilanes, determined by various authors, have relatively large negative values (Table 1). Evidently, this is due to an activation mechanism of the electron transfer, which is accompanied by the simultaneous rupture of the Si – Cl bond. Jammegg *et al.*[36] claim that the peaks they detected at -0.1 and -0.2 V (*vs* SCE) refer to the products of reduction of this bond, although no products with the Si – Si bond were detected after the electrolysis of the chlorosilane **1** at E ≈ -1 V. It follows from the experimental procedure described in this study that the researchers aimed at minimising the content of the residual water and HCl but ignored the presence of dissolved oxygen, which produces reduction peaks in this range of potential. Therefore, the signals at -0.1 and -0.2 V are most likely associated with the reduction of oxygen.[36]

An important role in the electrochemical reduction of chlorosilanes belongs to the solvent[23, 24, 32 – 34] and to the supporting electrolyte used,[35] because nucleophilic solvents can be coordinated by chlorosilanes, and, consequently, the silicon atoms acquire a planar configuration favourable for nucleophilic reactions.

The reduction of 6,6-dichloro(or fluoro)-6*H*-dibenzo-[*c*,*e*][1,2]oxasilanes in the DME/Bu_4NI system occurs as a single-electron reduction of the phenanthrene type ring ($E_{1/2} = -1.96$ and -0.96 V *vs* Hg pool for fluoro- and chloro-derivatives, respectively) and the subsequent two-electron transfer accompanied by the abstraction of a halogen ($E_{1/2} = -2.31$ and -1.41 V *vs* Hg pool).[47]

The products obtained by electroreduction of chloro(phenyl)-silanes in DME have been identified as phenylsilanes based on a comparison of their UV spectra with the spectra of individual compounds.[39]

$$\underset{\mathbf{2}}{Ph_3SiCl} \xrightarrow[-3.1\ V]{+e} \underset{\mathbf{8}}{Ph_3SiH},$$

$$\underset{\mathbf{6}}{Ph_2SiCl_2} \xrightarrow[-1.9\ V]{+2e} Ph_2SiH_2.$$

(The E values are given with respect to 0.001 M $Ag/AgClO_4$.)

It has been believed that DME or the Bu_4N^+ cation serves as the source of the hydrogen atoms needed for the formation of silanes. According to more recent studies,[37, 48 – 52] reduction of chloro(phenyl)silanes under similar conditions yields mostly di- and tetra-silanes. Nevertheless, the results of the electrolysis of chlorotriphenylsilane **2** in the presence of phenol serving as a donor of protons[23] attest to the formation of the Ph_3Si^- anion, because this reduction affords hydride **8** rather than the dimer. The fact that 1 F of electricity is consumed for the reduction of 1 mole of the chlorosilane **2** indicates that the electrode process includes the reaction between the nucleophile PhO^- and the initial chlorosilane molecule.

$$Ph_3Si^- + PhOH \longrightarrow Ph_3SiH + PhO^-,$$

$$PhO^- + Ph_3SiCl \longrightarrow Ph_3SiOPh + Cl^-.$$

When chlorotrimethylsilane **1** was reduced in MeCN using Bu_4NClO_4 as the supporting electrolyte, hexamethyldisiloxane was obtained, whereas in the presence of Bu_4NCl, the process gave hexamethyldisilane **9**.[25] Electroreduction of chlorosilane **1** in DME with a platinum or lead cathode and mercury anode[48,53] under non-controlled conditions (output voltage 80 V, current density 1 – 6 mA cm^{-2}) for 4 – 10 days gives rise to disilane **9** in a current yield of 100%.[37] The researchers[37] mentioned that the disilane **9** was also produced at the anode; however, since the electrolysis was carried out in an undivided cell, they were, most likely, mistaken.

It is assumed that the electrosynthesis of disilanes from chlorosilanes R_3SiCl in aprotic solvents follows two competing pathways.[23, 24, 40] The first pathway includes nucleophilic interaction of the R_3Si^- anion (resulting from the two-electron reduction of chlorosilane) with the initial chlorosilane, while the second pathway consists in the radical dimerisation of the products of its single-electron reduction ($R_3Si^{\bullet}$ radicals).

$$R_3SiCl \xrightarrow[-Cl^-]{+e} R_3Si^{\bullet} \xrightarrow{R_3Si^{\bullet}} (R_3Si)_2$$

$$R_3Si^{\bullet} \xrightarrow{+e} R_3Si^- \xrightarrow{R_3SiCl} (R_3Si)_2 + Cl^-$$

Electroreduction of a great number of monochlorosilanes occurs with the consumption of 1 F mol^{-1} of electricity and yields symmetrical disilanes (Table 2).

Table 3 presents the results of preparative electroreduction of mixtures of chlorosilanes giving asymmetrical disilanes with various substituents at the silicon atoms. Electrolysis of a 1 : 1 mixture of triarylchlorosilane and chlorotrimethylsilane **1** yields an asymmetrical disilane as the only product; hence, this is a convenient method for the synthesis of these compounds.

$$R_3SiCl + Me_3SiCl \xrightarrow{+2e} R_3SiSiMe_3$$

R = Ph, *p*-FC_6H_4, *p*-MeC_6H_4.

The above proves that triarylchlorosilane rather than chlorotrimethylsilane is the first to be reduced.[37] The reduction of

Table 2. Cathodic synthesis of symmetrical disilanes by electroreduction of chlorosilanes $R^1R^2R^3SiHal$.

Chlorosilane	Product	Conditions of electrolysis [a]	Yield (%)	Ref.
Me_3SiCl (**1**)	$(Me_3Si)_2$	Mg anode and cathode, THF/$LiClO_4$	100 [b]	25
		THF : HMPT (8 : 2)/LiCl, $AlCl_3$, Bu_4NBr, Al(Mg) anode, SS cathode	93	29
		Mg anode and cathode, THF/$LiClO_4$	74 – 78	41
		Silicon carbide anode, THF/HMPT	82	51
		Hydrogen anode, THF/HMPT	65 [b]	36
			73 [b]	36
Me_3SiBr	$(Me_3Si)_2$		20	25
$Me_2PhSiCl$ (**10**)	$(Me_2PhSi)_2$	THF : HMPT (8 : 2)/LiCl, $AlCl_3$, Bu_4NBr, Al(Mg) anode, SS cathode	80 – 83	41
		Hg anode, Pt cathode in DME	84 (37 [b])	54
		Mg anode and cathode, polarisation by alternating current in THF/$LiClO_4$	92 (69.5 [c])	51
		The same in THF/$LiBF_4$	2.3 (10 [c])	51
		The same in THF/Bu_4NClO_4	75.1 (49.6 [c])	51
		The same in THF/Bu_4NBF_4	11.7 (2.0 [c])	51
$MePh_2SiCl$ (**3**)	$(MePh_2Si)_2$	THF : HMPT (8 : 2)/LiCl, $AlCl_3$, Bu_4NBr, Al(Mg) anode, SS cathode	60 – 68	49
		Hg anode, Pt cathode in DME	89 (57 [b])	54
		Al anode, Pt cathode in DME	47 (40 [b])	54
		Ag anode, Pt cathode in DME	85 (62 [b])	54
		Mg anode and cathode, THF/$LiClO_4$	77	51
		Cu anode and cathode, DME/Bu_4NClO_4	83	55
		Cu anode and cathode, DME/Bu_4NBPh_4	84	35
Ph_3SiCl (**2**)	$(Ph_3Si)_2$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/Bu_4NClO_4	100 [b]	37
		THF : HMPT (8 : 2)/LiCl, $AlCl_3$, Bu_4NBr, Al(Mg) anode, SS cathode	70 – 71	49
		Mg anode and cathode, THF/$LiClO_4$	85	51
$PhCH_2Me_2SiCl$	$(PhCH_2Me_2Si)_2$	The same	78	56
$(p\text{-}FC_6H_4)_3SiCl$	$[(p\text{-}FC_6H_4)_3Si]_2$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/Bu_4NClO_4	82 [b]	37
$(p\text{-}FC_6H_4)_2MeSiCl$	$[(p\text{-}FC_6H_4)_2MeSi]_2$	The same	50 [b]	37
$Ph_3SiSiPh_2Cl$	$(Ph_3SiPh_2Si)_2$	The same	0.3	37
$Me_3SiSiPhMeCl$	$(Me_3SiPhMeSi)_2$	Cu anode and cathode, DME/Bu_4NClO_4	90	55

[a] HMPT is hexamethylphosphoric triamide; SS is stainless steel; [b] current yield; [c] the values obtained under the same conditions but using DME instead of THF are given in parentheses.

Table 3. Cathodic synthesis of asymmetrical disilanes by joint electroreduction of arylchlorosilanes and chlorotrimethylsilane **1**.

Chlorosilane	Product	Conditions of electrolysis	Yield (%)	Ref.
$Me_2PhSiCl$ (**10**)	$Me_2PhSiSiMe_3$	Hg anode, Pt cathode in DME/Bu_4NClO_4	72 (22 [a])	54
		Al(Mg) anode, SS cathode, THF/TDA [b] (HMPT)	80 – 83	49
$MePh_2SiCl$ (**3**)	$MePh_2SiSiMe_3$	Hg anode, Pt cathode in DME/Bu_4NClO_4	77	55
		Ag anode, Pt cathode in DME/Bu_4NClO_4	78 (65 [a])	54
		Hg anode, Pt cathode in DME/Bu_4NClO_4	94 (30 [a])	54
		Al(Mg) anode, SS cathode, THF/TDA [b] (HMPT)	90 [b]	41
	$MePh_2SiSiMe_2Bu^t$ (see [c])	Hg anode, Pt cathode in DME/Bu_4NClO_4	78 (30 [a])	54
Ph_3SiCl (**2**)	$Ph_3SiSiMe_3$	Hg,Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/Bu_4NClO_4	6.5 (100 [a])	37
		Al(Mg) anode, SS cathode, THF/TDA [b] (HMPT)	74 – 77	49
$(p\text{-}FC_6H_4)_3SiCl$	$(p\text{-}FC_6H_4)_3SiSiMe_3$	Hg,Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/Bu_4NClO_4	46 [a]	37
$(p\text{-}MeC_6H_4)_3SiCl$	$(p\text{-}MeC_6H_4)_3SiSiMe_3$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/Bu_4NClO_4	61 [a]	37
$(p\text{-}F_3CC_6H_4)_3SiCl$	$(p\text{-}F_3CC_6H_4)_3SiSiMe_3$	Hg, Cd anode, Pt(Hg, Pb, Ti, Fe) cathode, DME/Bu_4NClO_4	46	37
$Me_3SiSiPhMeCl$	$Me_3Si(PhMe)SiSiMe_3$	Cu anode, Pt(Cu) cathode in DME/Bu_4NClO_4	74 [d]	55

[a] Current yield; [b] TDA is tris(3,6-dioxaheptyl)amine; [c] using Me_2Bu^tSiCl instead of Me_3SiCl; [d] 4% of a symmetrical tetrasilane was also obtained.

chloro(methyl)diphenylsilane **3** (to give disilane in 90% yield) and dichloro(methyl)phenylsilane **5** occurs according to a similar scheme.[57] † In the latter case, trisilane **11** is formed in 25% yield, together with the monosilylation product formed in 75% yield.

† From this point on, the amounts of electricity (Q) consumed in the electrolysis per mole of the substance were taken from the original publication; in those cases where the originial source contains no coulometry data, the numbers of electrons per molecule (n) calculated according to the stoichiometry of the process are presented in the schemes.

$$\underset{\mathbf{3}}{Ph_2MeSiCl} + Me_3SiCl \xrightarrow[2.2\ F\ mol^{-1}]{-2.5\ V} Ph_2MeSiSiMe_3,$$

$$\underset{\mathbf{5}}{PhMeSiCl_2} + Me_3SiCl \xrightarrow[2.2\ F\ mol^{-1}]{-1.8\ V}$$

$$\longrightarrow PhMeClSiSiMe_3 + \underset{\mathbf{11}}{Me_3SiSi(PhMe)SiMe_3}.$$

Since the chlorosilane **1** is more difficult to reduce than most other chlorosilanes,[27–29] while the rate of nucleophilic substitution in **1** is markedly higher than the rate of the S_N2 reaction

involving the second chlorosilane, asymmetrical chlorosilanes are formed predominantly. It is noteworthy that Bordeau *et al.*[49] obtained only an asymmetrical product in the reduction of a mixture of two chlorosilanes, whereas other researchers[37,58] have detected some quantity of a symmetrical disilane (derived from the chlorosilane, the reduction potential of which was less negative) in the reaction products; finally, Shono[56] has reported that equal amounts of symmetrical and cross-disilanes are formed.

The reduction of chlorosilanes R_3SiCl and $R_2R'SiCl$ yields symmetrical dimeric derivatives $(R_3Si)_2$ and $(R_2R'Si)_2$ as the major products (see Table 3). In the case of the chlorosilanes **1** and **2**, these dimers are obtained in nearly quantitative yields,[37] while in the case of bromotrimethylsilane, the yield of the dimer is 20%, and iodotrimethylsilane gives no dimer at all.[25,43] It should be noted that symmetrical and asymmetrical disilanes are produced in good yields in the electrochemical reactions of appropriate chloro-derivatives even in those cases where the corresponding chemical reactions with metals give no results.

The main products resulting from the reduction of dichlorosilanes are the corresponding polysilanes.[37,43,48] Thus the electroreduction of dichlorodiphenylsilanes under conditions similar to those described in Ref. 37 yields insoluble octaphenylcyclotetrasilane **12** and some quantity of polymeric products.[48]

$$\underset{\mathbf{6}}{4\,Ph_2SiCl_2} \xrightarrow{+8e} \underset{\mathbf{12}}{(Ph_2Si)_4} + 8Cl^-,$$

$$2Cl(SiPh_2)_2Cl \xrightarrow{+4e} \mathbf{12} + 4Cl^-,$$

$$Cl(SiPh_2)_4Cl \xrightarrow{+2e} \mathbf{12} + 2Cl^-.$$

Reduction of chloropentaphenyldilsilane has led to a mixture of products.[48]

$$Ph_3SiSiPh_2Cl \xrightarrow{+2e} (Ph_3Si)_2 + Ph_3SiSiPh_2SiPh_3 + \text{oligomers}.$$

The reactions of chloro(methyl)phenylsilanes follow a more complex pathway. For example, in the case of dichloro(methyl)-phenylsilane **5**, apart from the dimer, a product resulting from reaction with DME used as the solvent was obtained.

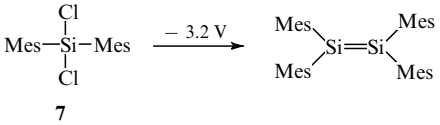
$$\mathbf{5} \xrightarrow[-Cl^-]{+e} MePh\dot{S}iCl \begin{cases} \rightarrow ClMePhSiSiPhMeCl \\ \xrightarrow{DME} MePhClSiOCH_2CH_2OMe \end{cases}$$

Data on the cathodic reduction of trichlorosilanes are contradictory. It has been reported[48] that electrolysis of $PhSiCl_3$ **13** also affords a product formed in reaction with the solvent.

$$\underset{\mathbf{13}}{PhSiCl_3} \xrightarrow[-Cl^-]{+e} Ph\dot{S}iCl_2 \xrightarrow{DME} PhCl_2SiOCH_2CH_2OMe.$$

The fact that no polymeric compounds with Si–Si bonds were detected among the reaction products was explained[48] by steric reasons. Conversely, the electrolysis of $MeSiCl_3$ results in the formation of the polymer $(MeSiCl_{0.22})_n$ unstable in air, while the electrolysis of $SiCl_4$ gives rise to the polymer $(SiCl_{0.77})_n$.[28,59]

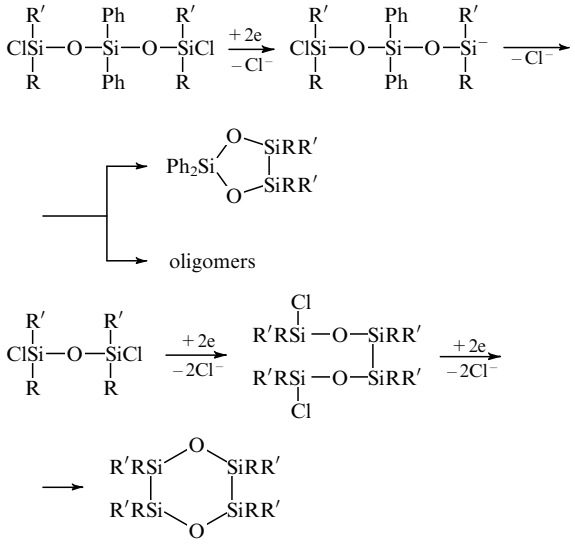
A rare case where tetramesityldisilene is formed in the reduction of dichlorodimesitylsilane has been described.[44] This is the only example of electrosynthesis of a compound incorporating a Si = Si double bond.



7

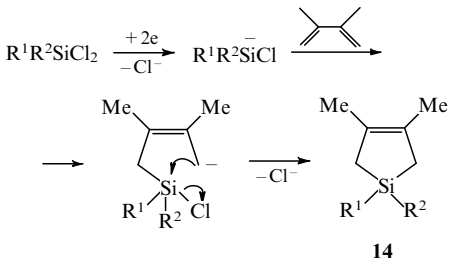
The reduction of dichlorodimesitylsilane **7** was carried out in the potentiostatic regime at −3.2 V *vs* Ag/Ag^+ in DME/Bu_4NClO_4 using an Hg cathode and an Ag anode with separated cathode and anode chambers. The yield of tetramesityldisilene of the 'pure for analysis' grade amounted to 20%.

Electroreduction of terminal dichlorosiloxanes affords cyclic compounds containing Si–O and Si–Si bonds.[30,60,61] The five-membered cyclic product is formed in one step, while the six-membered product is formed *via* a linear dimeric dichlorodisiloxane, which can be isolated from the reaction mixture.



R, R′ = Me, Vin, Et.

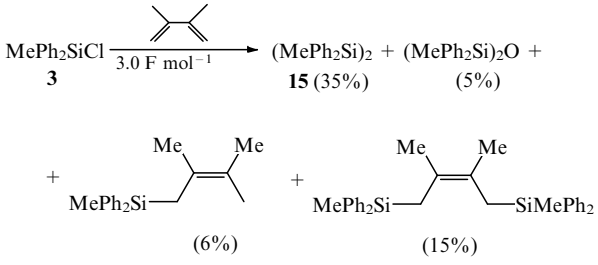
When silyl intermediates generated at the cathode react with 2,3-dimethylbutadiene, 1,1-disubstituted 3,4-dimethyl-1-silacyclopent-3-enes **14** are produced together with linear polysilanes.[38]



14

The results of cathodic electrosynthesis of substituted silacyclopentenes **14** under various conditions are presented in Table 4.

Electrosynthesis involving the monochlorosilane **3** and carried out in DME with tetrabutylammonium perchlorate as the supporting electrolyte yields symmetrical disilane **15**, some quantity of disiloxane and products resulting from the addition to the diene, namely, 1-(methyldiphenylsilyl)-2,3-dimethylbut-2-ene and 1,4-bis(methyldiphenylsilyl)-2,3-dimethylbut-2-ene.



Trimethyl(phenylethynyl)silane **16** is formed in the electroreduction of halotrimethylsilanes Me_3SiHal (Hal = I, Cl, F)[31,62–64] in the presence of phenylacetylene **17**. Using the method of latent limiting currents, the stoichiometry of the interaction of the latter with electrically generated silyl anions was found to be 1 : 1. This corresponds to the protonation of the silyl anion by phenylacetylene to give the $PhC{\equiv}C^-$ carbanion, which substitutes

Table 4. Electroreduction of dichlorosilanes in the presence of 2,3-dimethylbutadiene.

Chlorosilane	Chlorosilane/ /diene (mmol)	Solvent/electrolyte	Q/ F mol^{-1}	Yields of the silacyclopentenes **14** (%) [a]	Yield of the polymer (%) [a]
$MePhSiCl_2$	5.8/16.1	DME/Bu_4NClO_4	1.7	10	9
Ph_2SiCl_2	4.9/14.7	DME/Bu_4NClO_4	2.4	27	41
	5.0/14.9	DME/Bu_4NBPh_4	3.5	23	38
	5.0/15.8	THF/Bu_4NClO_4	3.0	23	42
	3.1/9.9	THF/Bu_4NBPh_4	2.8	28	44
$(o\text{-Tol})_2SiCl_2$	5.2/15.9	DME/Bu_4NBPh_4	7.0	10	4
$(p\text{-Tol})_2SiCl_2$	4.8/16.0	DME/Bu_4NClO_4	1.6	4	5[b]

Note. Conditions of the electrolysis: Pt cathode, Cu anode, undivided cell, galvanostatic regime, current density 3.3 mA cm^{-2}.
[a] Chromatographic yields are presented; [b] the yield of octa-*p*-tolylcyclotetrasiloxane is presented.

nucleophilically the chlorine in a molecule of the initial chlorosilane **1**.

$$Me_3SiCl \xrightarrow[-Cl^-]{+2e} Me_3Si^- \xrightarrow[-Me_3SiH]{PhC\equiv CH} PhCC^- \xrightarrow[-Cl^-]{\mathbf{1}} PhCCSiMe_3.$$
1 **16**

The compound **16** can be once again silylated. In this case, the process is accompanied by a decrease in the multiplicity of the bond and affords a nucleophilic addition product, 1,2-bis(trimethylsilyl)-1-phenylethene **18**.

$$Me_3Si^- + \mathbf{16} \longrightarrow PhC(SiMe_3)\bar{C}SiMe_3 \xrightarrow[-D^-]{HD}$$

$$\longrightarrow PhC(SiMe_3)=CHSiMe_3.$$
18

It is of interest that when this process is conducted at a **1**:**17** ratio of 4:1 by passing 5 F mol^{-1} of electricity in a flow-type electrolyser consisting of two coupled cells[31] (an ECE cell), in which the $R^1R^2R^3Si^-$ anions electrically generated at the cathode of the first cell are partially oxidised in the second cell to give $R^1R^2R^3Si^{\bullet}$ radicals, disilylated product **18** is obtained in a yield of up to 75%.

Under similar conditions, styrene yields only products of addition at the double bond.[63]

$$PhCH=CH_2 \xrightarrow{R^1R^2R^2Si^-} PhC\bar{H}-CH_2SiR^1R^2R^3 \xrightarrow[-D^-]{HD}$$

$$\longrightarrow PhCH_2CH_2SiR^1R^2R^3.$$

Silyl anions resulting from the reductive cleavage of the Si–Cl bonds in chlorosilanes can be 'stabilised' as organometallic intermediates *via* the formation of a Si–M bond (M is the metal that forms the soluble anode). The nature of these intermediates is not completely clear, but they can be kept in solution for several days and used in reactions with electrophilic reagents.[27,65,66]

$$R_3SiCl \xrightarrow{+2e} [\,R_3Si-M] \begin{cases} \xrightarrow{H_2O} R_3SiH \\ \xrightarrow{D_2O} R_3SiD \\ \xrightarrow{\mathbf{1}} R_3Si-SiMe_3 \\ \xrightarrow{R'C(=O)Cl} R'C(=O)SiR_3 \end{cases}$$

R' = Ar, Alk.

Cyclohexylsilyl derivatives have been prepared by electroreduction of a number of chlorosilanes in the presence of cyclohexene.[63,67–70] Since cyclohexene is not prone to enter into nucleophilic substitution, this reaction was suggested to occur by a radical mechanism.

It has been reported[45] that the intermediates formed in the electroreduction of tetrachlorosilane do not react with acrylonitrile, although the same researchers have described[46] a reaction of silyl anions electrically generated by the reduction of the Si–H bond in trichlorosilane (at $E = -1.6$ V *vs* Ag/AgCl) with acrylonitrile to give trichloro(β-cyanoethyl)silane **19**.[46]

$$Cl_3SiH \xrightarrow{+e} Cl_3Si^- + H^{\cdot}\ (\tfrac{1}{2}H_2),$$

$$Cl_3Si^- + H_2C{=}CHCN \xrightarrow{H^+} Cl_3SiCH_2CH_2CN.$$
19

The compound **19** can also be obtained from trichlorosilane and acrylonitrile by a purely chemical procedure, namely, radical hydrosilylation. Therefore, it is quite probable that either the signal of reduction of $SiCl_4$ (Table 1) does not refer to the reduction of a Si–Cl bond or the rate of interaction of the electrically generated Cl_3Si^- anions with the highly electrophilic $SiCl_4$ molecule is much higher than the rate of the addition at the double bond.

III. Cathodic syntheses of tri- and poly-silanes

Polysilanes $(-Si-)_n$ containing more than two silicon atoms in the chain can be obtained by coupling of two chlorosilanes during their joint reduction, which leads to the formation of one or two Si–Si bonds. Chloro-derivatives of di-, tri- and poly-silanes are used as the initial monomers, depending on the required length of the chain of silicon atoms.

Electrosynthesis of trisilanes is carried out by the following schemes.

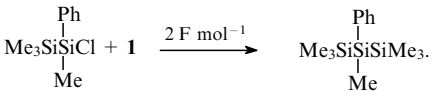
$$\underset{\displaystyle R^2}{\overset{\displaystyle R^1}{\overset{|}{Cl-Si-Cl}}} + 2\,Me_3SiCl \xrightarrow{4.2\text{ F mol}^{-1}} \underset{\displaystyle R^2}{\overset{\displaystyle R^1}{\overset{|}{Me_3Si-Si-SiMe_3}}}$$
1

(60%, $R^1 = R^2 = Me$);[41]
(45%, $R^1 = Me$, $R^2 = Ph$);[54]
(61%, $R^1 = Me$, $R^2 = Ph$).[55]

$$2Ph_2MeSiCl + Me_2SiCl_2 \xrightarrow{4\text{ F mol}^{-1}} \underset{\displaystyle Me}{\overset{\displaystyle Me}{\overset{|}{Ph_2MeSi-Si-SiMePh_2}}}$$
3 **4**

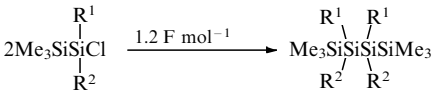
(48%)[54]

Trisilanes are also formed in the reductive coupling of chlorodisilanes and the chlorosilane **1**, for example:



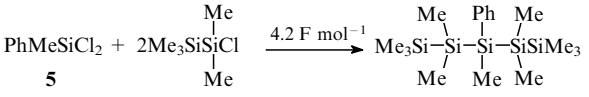
(74%)[55]

Electrosynthesis of tetrasilanes is accomplished by coupling of disilanes.



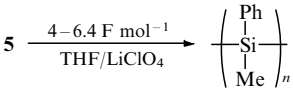
(85%, R^1 = Me, R^2 = Ph);[49]
(90%, R^1 = Me, R^2 = Ph);[55]
(83%, R^1 = R^2 = Me);[49]
(89%, R^1 = R^2 = Me).[55]

Electrosynthesis of pentasilanes is accomplished by coupling of dichlorosilanes and chlorodisilanes.



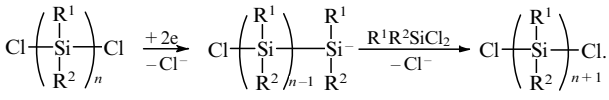
(75%),[49] (79%).[55]

Electroreduction of a number of chlorosilanes [for example, dichloro(methyl)phenylsilane **5** and 1,4-bis(dialkylchlorosilyl)-benzenes[51,56]] at Mg electrodes in an undivided cell affords polysilanes in 5%–26% yields. It has been noted that treatment of the reaction mixture with ultrasound with a frequency of 47 kHz leads to a substantial increase in the yield of polysilanes (to 33%–45%).[51]

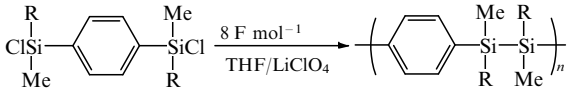


M_n = 930;[57]
M_n = 3200.[51]

It has been assumed that the formation of polysilanes in the electroreduction of dichlorosilanes involves an ionic mechanism for the chain lengthening consisting of a number of electroreduction–S_N2 successive steps.[56] The initial molecule characterised by a more negative reduction potential undergoes the nucleophilic attack.



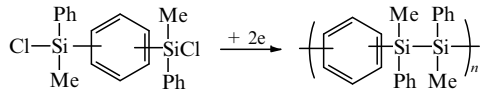
The reduction of 1,4-bis[chloro(methyl)phenylsilyl]benzene in THF/$LiClO_4$ with polarisation by alternating current and with ultrasonic treatment of the reaction mixture leads to a polymer consisting of the (–C_6H_4–SiSi–) units.



M_n = 8570 (R = Et).

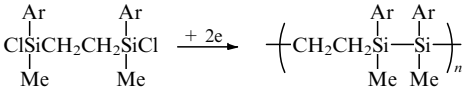
When the amount of the electricity passed is increased from 8 to 12 F mol^{-1}, the molecular mass of the polymer M_n (at R = Et) increases to 9960.[56]

The reduction of *ortho*- and *meta*-substituted bis-[chloro(methyl)phenyl]benzene at a Pt cathode (Cu anode, DME/Bu_4NClO_4 or Bu_4NBPh_4) in the galvanostatic regime also yields disilanylene polymers.[71]



(24%, *ortho*-isomer);
(8%, *meta*-isomer).

Polymeric products with high molecular masses consisting of the (–CH_2CH_2–SiSi–) fragments have been prepared by electroreduction of 1,2-bis[chloro(methyl)phenylsilyl]ethane and 1,2-bis[chloro(methyl)(*p*-tolyl)silyl]ethane at Cu electrodes.[35,71]

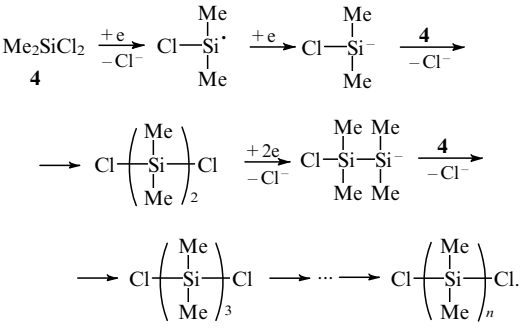


(39%, Ar = Ph);
(54%, Ar = *p*-Tol).

Optimisation of this process using various solvents (DME, MeCN, DME/DMF, DME/propylene carbonate) and various supporting electrolytes [Bu_4NBF_4, Bu_4NClO_4, $Bu_4NOC(O)CF_3$, Bu_4NBPh_4, LiCl) showed that the best conditions for polymerisation are created by conducting the process in DME/Bu_4NBPh_4.[71] When a supporting salt incorporating a trifluoroacetate anion was used, chlorine in the initial chlorosilane molecules was found to exchange with fluorine.[71]

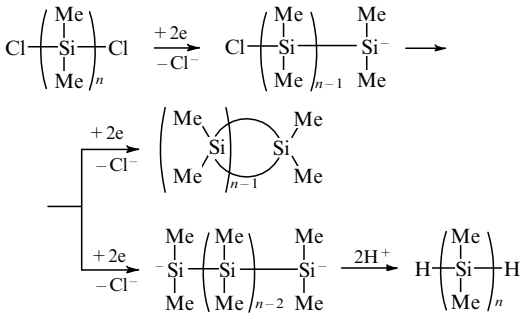
A series of studies have been devoted to electropolymerisation of dichlorodimethylsilane **4**.[42,58,72] Umezawa *et al.*[72] studied the influence of the conditions of electrolysis (ion-exchange membrane in a divided cell, metals and alloys of various purity grades as electrode materials) on the efficiency of electroreductive polymerisation. High yields of the products are achieved when the process is carried out in the DME/Bu_4NCl system in a diaphragmless cell with polarisation of Al electrodes by alternating current.

Since the reduction of chlorotriphenylsilane **2** in the presence of Me_3SiCl yields cross-disilane (*cf.* Refs 37, 49), while that in the presence of Me_2SiCl_2 yields a polymer containing both phenyl and methyl groups,[58] a nucleophilic rather than a radical mechanism for the formation of polysilane units has been assumed. It has been noted[16,73] that dichloropolysilanes with longer chains are reduced at more positive potentials than short-chain polysilanes.‡ Therefore, it has been assumed that polymerisation occurs *via* a nucleophilic attack by the monochloropolysilyl anion on the silicon atom in the initial molecule[42,58,72] (*cf.* Ref. 56), according to the following scheme



Termination of the polymerisation chain was assumed to occur either *via* intramolecular nucleophilic attack yielding cyclic polysilane or *via* protonation.

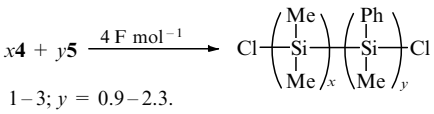
‡ This regularity is apparently valid, taking into account the effects of σ-Si conjugation in polysilane chains;[74] however, judging from the potentials reported in one of these studies,[73] the researchers did not deal with the reduction of Si–Cl bonds.



Therefore, in order to ensure initiation of the polymerisation and chain termination, it has been proposed to add to the electrolyte small amounts of a monochlorosilane (for example, Ph_3SiCl), which is reduced at less negative potentials than the dichlorosilane **4** forming the chain.[75]

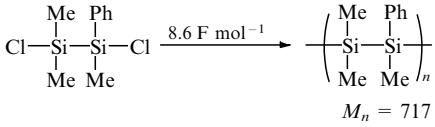
Dimethylpolysilane was prepared in a current yield of 72%–90% by electroreduction of dichlorodimethylsilane **4** without a solvent or with the addition of hexamethylphosphoric triamide (HMPT) or tris(3,6-dioxoheptyl)amine as a complex-forming agent in an undivided cell with a stainless-steel cathode and Al anode.[76] The highest yield is achieved when the mixture is treated with ultrasound with a frequency of 35 kHz.

Electrosynthesis of heterosubstituted polysilanes by joint reduction of the dichlorosilanes **4** and **5** has been reported.[49] The composition of the polymer varies as a function of the ratio of the initial silanes.



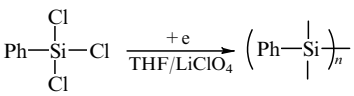
$x = 1-3$; $y = 0.9-2.3$.

A similar polymer has been obtained by electroreduction of 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane.[51]



$M_n = 717$

Electroreduction of trichloro(phenyl)silane **13** in a THF/$LiClO_4$ solution at a Mg electrode results in the formation of polysilanes with a two-dimensional structure of the silicon skeleton.[77] The electrolysis was carried out with ultrasonic treatment of the mixture and potential sweep from 0 to -3 V (*vs* Ag/Ag^+) during the process. The yield of the polymer ranged from 13% to 71%. The molecular weight of the resulting polyphenylsilane was estimated as $M = 5000-7100$.[56]



13

A series of studies have been devoted to reductive polymerisation of polyfunctional silanes R^1SiX_3, $Cl(SiR^1_2)_nCl$, R^1SiCl_3, $SiCl_4$ and $ClR^1R^3SiSiR^2R^4X$ (R^{1-4} = H, Alk, Ar, AlkO, NR_2, SiR_3) (see, for example, Refs 37, 78–81). This process giving rise to polysilane products is of interest as an alternative route for the synthesis of compounds used in the production of ceramic materials.

Poly(pentafluorophenylsilyne) has been synthesised by cathodic polymerisation of trichloro(pentafluorophenyl)silane.[82]

In conclusion, it should be noted that studies on electroreduction of chlorosilanes are mostly synthetic. At present, there is scarcely any information on the kinetics and thermodynamics of the electron transfer and rupture of the Si–Cl bond, and the conclusions about the nature of species resulting from the transfer of electrons have been based on the structures of final products of electrolysis or on retro-synthetic analysis.

IV. Reactions of electrically generated nucleophiles with an electrophilic silicon atom

1. C-Nucleophiles

Electroreduction of organic compounds that are converted into carbanions by two-electron cleavage of the C–X bond (X = H, Hal, OCR, OAc) is widely used in the preparative organic electrochemistry of silicon to synthesise various compounds with Si–C bonds. In this case, the role of the electrode reduces to the generation of C^--nucleophiles, which replace chlorine in chlorosilane molecules. It has been assumed that only relatively stable carbanions (All, Vin, Ar) are suitable for these reactions. Later, it has been found that when a soluble anode is used (Mg, Al, Zn, Cu) and the process is conduced in the presence of a complex-forming agent [DMF, HMPT, tetramethylurea, tris(3,6-dioxoheptyl)-amine], electrically generated aliphatic carbanions can also be involved in the reaction.

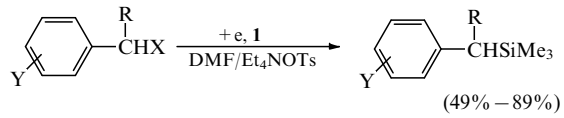
Evidently, the first example of this type of synthesis is provided by the cathodic synthesis of benzyltrichlorosilane [83] by electrolysis of benzyl chloride in $MeCN/Et_4NCl$ at a Pb cathode in the presence of silicon tetrachloride (Eqns 1 and 2).

$$PhCH_2Cl \xrightarrow{+2e} PhCH_2^- + Cl^-, \qquad (1)$$

$$PhCH_2^- + SiCl_4 \longrightarrow PhCH_2SiCl_3 + Cl^-. \qquad (2)$$

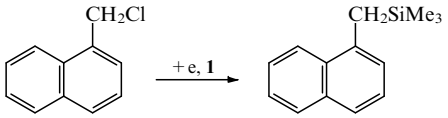
Benzyltrichlorosilane is formed in a substance yield of 19.1% and a current yield of 5%. When chlorosilane **1** is used instead of $SiCl_4$,[59 84] this process gives benzyltrimethylsilane **20**.

β-Silylated compounds with functionally substituted phenyl, naphthalene and alkenyl fragments were also obtained in good yields by a similar scheme.

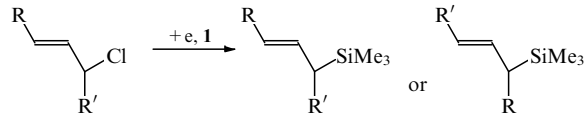


(49%–89%)

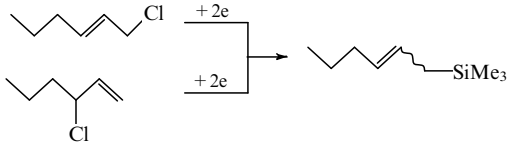
R = H, Me;
X = Br, Cl;
Y = H, Me, MeO, CN, CO_2Me.



(81%)



Isomeric allyl chlorides that differ in the position of the chlorine atoms in their molecules undergo cathodic silylation to give the same compound with a terminal Me_3Si group as the only product.[59]



Chemical silylation with a Grignard reagent usually affords a mixture of products with inner and terminal Me_3Si groups.

Electroreduction of $PhCH_2Cl$, PhCl and PhBr in various solvents susceptible to complex formation [DMF, HMPT, $(Me_2N)_2CO$] in an undivided cell with a soluble Mg anode[84] leads to similar results. Carbanions resulting from electroreduction of allyl, vinyl, aryl and hetaryl halides (DMF/Et_4NOTs, divided cell, Pt electrodes) react with chlorosilanes **1**, **3** and **10** according to Eqns. (1)–(2) to give the corresponding organosilicon compounds[85] in preparative yields (47%–98%). Only chlorosilanes are suitable as silylating agents under these conditions; *O*,*N*-bis(trimethylsilyl)acetamide **21** and methoxytrimethylsilane **22** are inactive in this reaction.

Aryl halides containing two different halogen atoms in their molecules (in particular, 4-bromoiodobenzene) are selectively silylated with the chlorosilane **1** at the C–I bond thus yielding (4-bromophenyl)trimethylsilane.[86]

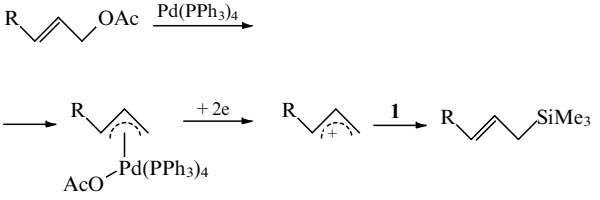
Cinnamyltrimethylsilane can be obtained by electrosynthesis not only from cinnamyl chloride but also from other cinnamyl derivatives. In fact, the intermediates of reductive decarboxylation of cinnamyl acetate are converted into a silylated product in a yield of 25%–50%. Cinnamyl carbonate and cinnamyl sulfone can be converted into the same product in lower yields.[86] Evidently, this process occurs according to the following general scheme that includes formation of allylic anionic intermediate **23**:

$$PhCH=CH-CH_2-X \xrightarrow[-X^-]{+2e} \left[PhCH=\overset{H}{\overset{|}{C}}=CH_2\right]^- \xrightarrow[-Cl^-]{R_3SiCl} PhCH=CHCH_2SiR_3$$

23

X = Cl, OAc, OCO_2Me.

Allyltrimethylsilanes have also been obtained by homogeneous reduction of allyl acetates with $Pd(PPh_3)_4$ in the presence of an excess of chlorotrimethylsilane.[87] This reaction yields an inner alkene as the major product. This has been suggested to be due to the fact that the chlorosilane attacks the electrically generated carbanion from its sterically less shielded side.

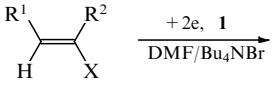


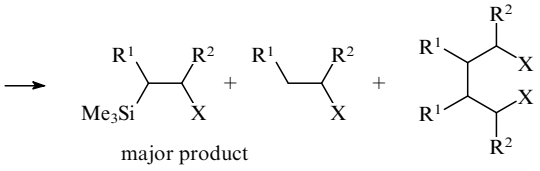
Electrocatalytic reduction of PhBr and hex-1-ene with the $[NiL_3]^0$ complex (L is 2,2-dipyridyl, PPh_3) in the presence of the silane **1** also affords cross-coupling products.[10]

$$PhBr + \mathbf{1} \xrightarrow[[NiL_3]^{2+}/[NiL_3]^0]{+2e} PhSiMe_3,$$

$$BuCH=CH_2 + \mathbf{1} \xrightarrow[[NiL_3]^{2+}/[NiL_3]^0]{+2e} BuCH=CHSiMe_3.$$

Electroreductive silylation of α,β-unsaturated esters, nitriles or ketones in an undivided cell with a Mg, Al or Zn anode results in the formation of the corresponding β-silyl derivatives (β-silyl propionates, nitriles or ketones).[88] When this process is conducted with a graphite or Pt anode, it gives no silylation products.

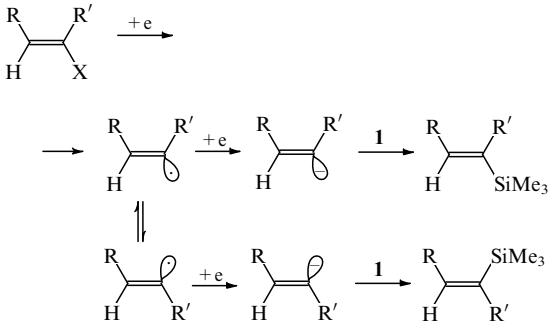




major product

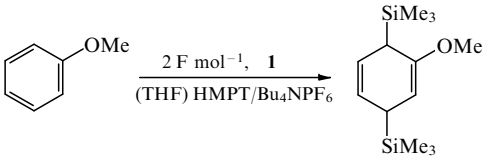
X = CO_2Et, CN, COMe.

When individual (*E*)-vinyl halides are introduced in this reaction, mixtures of (*E*)- and (*Z*)-isomers of vinyl silanes are always formed. Disubstituted (*E*)-vinyl halides yield mostly silylated (*Z*)-derivatives. This isomeric distribution is due to the fact that the following equilibrium involving the intermediate vinylic radical is established.



Since the (*E*)-radical is more stable than the (*Z*)-radical, it is the former that is reduced predominantly to give an (*E*)-vinylic anion; this anion reacts with **1** yielding (*Z*)-vinylsilane. A similar *cis-trans* isomerisation of the radical controls the stereochemistry of silylation of halostyrenes (Hal = I, Br, Cl).[86] Since the potential for the transfer of the second electron ($E_{R\cdot/R^-}$) does not depend on the nature of the halogen, whereas the reduction potential of the halide is, conversely, determined by the nature of the halogen ($E_{C-I} > E_{C-Br} > E_{C-Cl}$), the styryl radicals generated from the iodo-derivatives, for kinetic reasons, have more time to isomerise than those generated from the corresponding chlorides. Thus, the proportion of the *cis*-isomer varies in the opposite direction with respect to the ease of reduction of the halostyrene.

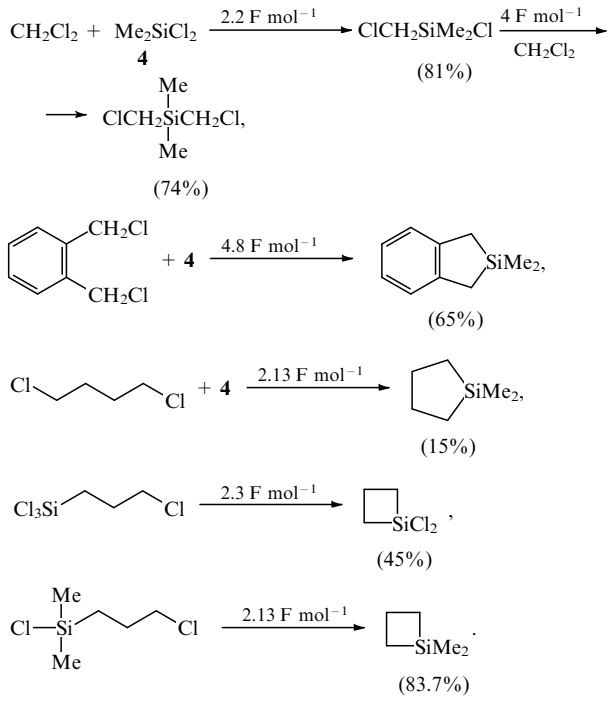
1-Methoxy-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene, a precursor of ketoprofen, was prepared in a current yield of 70% by electroreduction of anisole (undivided cell, a stainless-steel cathode and an aluminium anode) in the presence of Me_3SiCl in a solution in THF/HMPT (4 : 1) or without THF but with addition of a complex-forming agent (HMPT).[89]



Based on an approach proposed in a series of studies,[84, 85, 90–93] an electrochemical technique for the synthesis of carbosilanes, including cyclic ones, has been developed and described in a patent.[94]

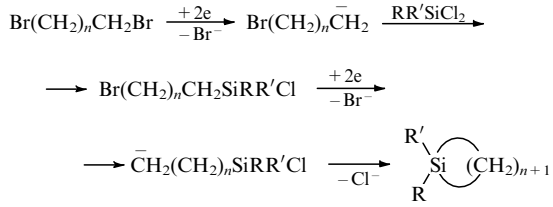
$$CH_2Cl_2 + SiCl_4 \xrightarrow{2.2\ F\ mol^{-1}} Cl_3SiCH_2Cl + Cl_2Si(CH_2Cl)_2 + Cl(SiCH_2Cl)_3,$$

(58%) (15%) (3%)



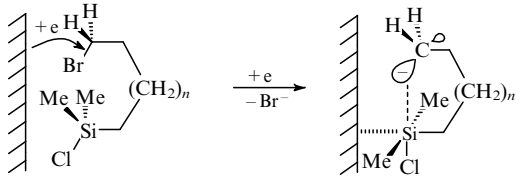
When this process is carried out with iodo-derivatives, the yields of the products are higher than in the case where bromides and chlorides are used.

Reduction of organic dihalides in the presence of Si-containing dichlorides under similar conditions [95,96] affords cyclic carbosilanes. Their yields (7%–91%) depend on the structure of the initial dihalide (the nature of the halogen and the length of the chain) and on the strain in the resulting ring. As the size of the ring increases, the yield of the reaction product first increases, reaches its maximum, as should have been expected, for 5- and 6-membered rings and then diminishes. The yields of cyclic disilanes depend also on the concentration of the halogenated substrates and on the electrode potential; an increase in either of these parameters leads to a decrease in the yields of silacycloalkanes.



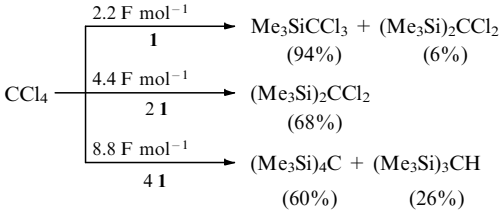
$n = 2-5$.

It is assumed that at the step of the linear silylated intermediate,[95] an orienting influence of the cathode is manifested; owing to this influence, silicon assumes a penta- or hexa-coor-dinated configuration favourable for the intramolecular nucleophilic attack.

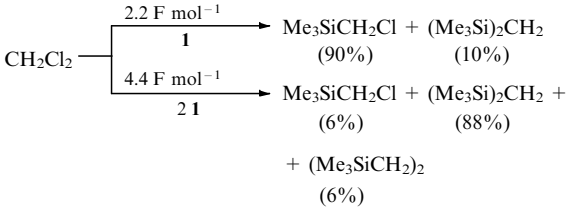


Electroreduction of 1,4-dibromobutane in the presence of tetrachlorosilane at a 1,4-dibromobutane : tetrachlorosilane ratio of 2 : 1 permits preparation of a bicyclic product, 5-silaspiro[4.4]nonane, in a yield of 24%.

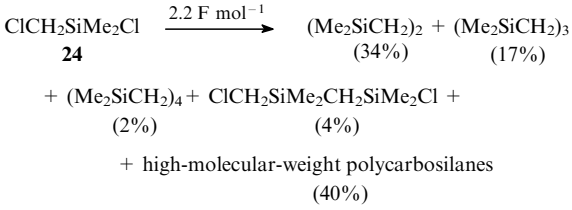
Electroreductive silylation of CCl_4, $CHCl_3$ and CH_2Cl_2 [90] is much more selective than the classical silylation. The use of soluble anodes made of various metals (Zn, Al, Mg), the cations of which are reduced at different potentials, permits selective preparation of chlorine-containing products of partial silylation, the reduction potentials of which are more negative than those of the M^+. For example, monosilylation of CCl_4 and $CHCl_3$ is carried out using a Zn anode, while disilylation occurs with a Mg anode and for trisilylation, an Al anode is used.



Mono- and disilylation of CH_2Cl_2 (Al anode) have been carried out in a similar way.[57,90]

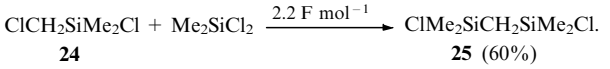


Under similar conditions, chloro(chloromethyl)dimethylsilane **24** is converted into a mixture consisting of cyclic 4-, 6- and 8-membered carbosilanes, a linear dimerisation product and polycarbosilanes [26,69,91] (the yields were taken from Ref. 26).



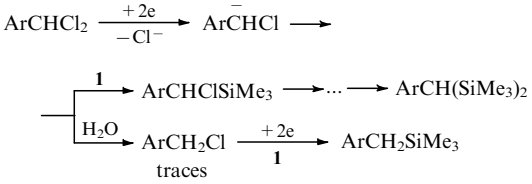
When a Mg anode is used (DMF/$MgCl_2$), the four-membered product is not formed.[26] It is of interest that the yield of the intermediate linear terminal dichlorocarbosilane increases from 4% to 43% when the solution is diluted 8-fold,[26,97] although this compound is formed by an intermolecular S_N2 mechanism and, hence, its proportion should have decreased following a decrease in the concentration.

The reduction of the chlorosilane **24** in the presence of dichlorodimethylsilane [26] (used as an electrophilic trap for the chlorodimethylsilyl carbanion) has given rise to bis(chlorodimethylsilyl)methane **25** in a preparative yield (60%). The high chemical selectivity of the process was achieved by maintaining the 1:1 ratio of the reactants during the electrolysis. For this purpose, Me_2SiCl_2 was gradually added to the reaction mixture, and its excess in the solution was thus avoided.



The electroreduction of benzal chloride in DMF/$LiClO_4$ in the presence of the chlorosilane **1** results in the formation of (α-chlorobenzyl)trimethylsilane or geminal benzaldisilane, depending on the amount of electricity passed.[98] Since the reduction potential of the dihalide is 560 mV more positive than that of the (α-chlorobenzyl)silane, the reduction of the latter yielding benzaldisilane starts only when the initial dichloride has reacted almost completely. Chromatographic monitoring of the process makes it possible to stop the reaction at the stage of monosilylation and thus to obtain the product in 57%–98% yield. The subsequent electrolysis affords the disilylated product (yield 72%–91%). When a stainless-steel cathode is used, the yields of mono- and

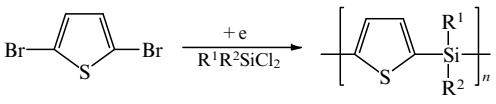
disilylated products are higher than those obtained at a graphite cathode.



Ar = Ph, *o*-, *m*-, *p*-MeC_6H_4, *p*-FC_6H_4, 2-Cl-6-F-C_6H_3.

Under the same conditions, benzal bromide gives only (α-bromobenzyl)trimethylsilane. Apparently, the second methyl group is not introduced because of the passivation of the electrode by bromide anion.[98]

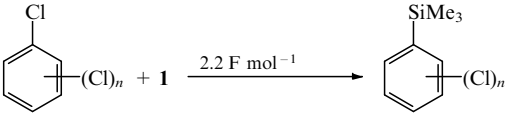
Compounds containing alternating thiophene and diorganyl silyl fragments have been obtained by electroreduction of 2,5-dibromothiophene in the presence of various dichlorosilanes.[99, 100]



$R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = Me$;
$R^1 = Vin$, $R^2 = Me$; $R^1 = R^2 = Ph$; $n = 1-3$.

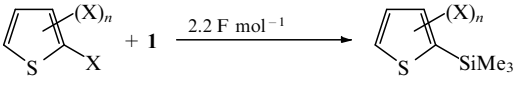
Compounds with high molecular weights ($n = 3$) are mostly formed at the beginning of the electrolysis (< 1 F mol^{-1}). As the amount of electricity passed increases, the mixture becomes enriched in compounds with lower molecular weights ($n = 1, 2$) resulting apparently from the reductive cleavage of higher-molecular-weight products.

Polychlorobenzenes and polychloro(or bromo)thiophenes are selectively monosilylated by the reduction in the presence of the chlorosilane **1** (THF/HMPT, Bu_4NBr, Al anode) when not more than 2.2 F mol^{-1} of electricity is passed.[101]



(69%–92%)

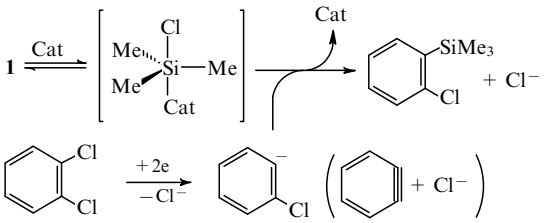
$n = 1-5$;



(73%–88%)

$n = 1, 3$; X = Cl, Br.

Hexamethylphosphoric triamide plays an important role in this process, acting both as a solvent and as a complex-forming agent. In the absence of this compound, the overall yield and selectivity of silylation are markedly lower. It has been assumed that HMPT can participate in the process as a catalyst, the role of which consists in an increase in the electrophilicity of silicon (*cf.* Refs 18, 23, 32–34). For this reason, the THF/HMPT ratio has an influence on the chemical selectivity of silylation and has no influence on its regioselectivity, the latter being determined by the charge distribution in the aromatic ring.[92, 101]

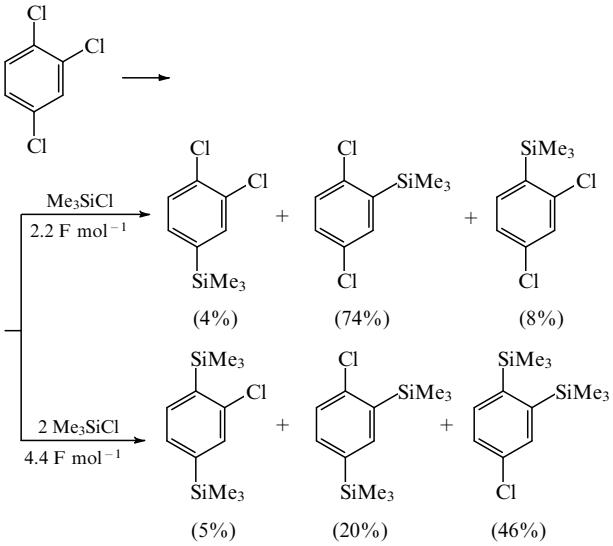


Cat is the catalyst.

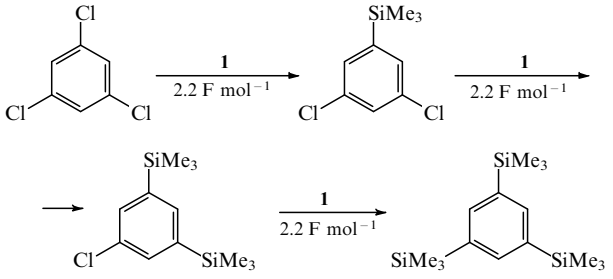
Evidently, in the case of *o*-dichlorobenzene, the process can involve the intermediate formation of dehydrobenzene, which then reacts with the chlorosilane **1** to give the same product.

The current density in the electrolysis is inversely related to the chemical selectivity of the process and, like the temperature, has no influence on its regioselectivity. Silylation at a Cu anode does not occur, while a Mg anode reacts only as a chemical reducing agent.

During more extensive reduction of polychlorobenzenes (4.4 F mol^{-1}), in particular, of 1,2,4-trichlorobenzene, disilylation occurs.[101] Owing to the orienting influence of the first silyl substituent introduced in the molecule, the process yields mostly 4-chloro-1,2-bis(trimethylsilyl)benzene.

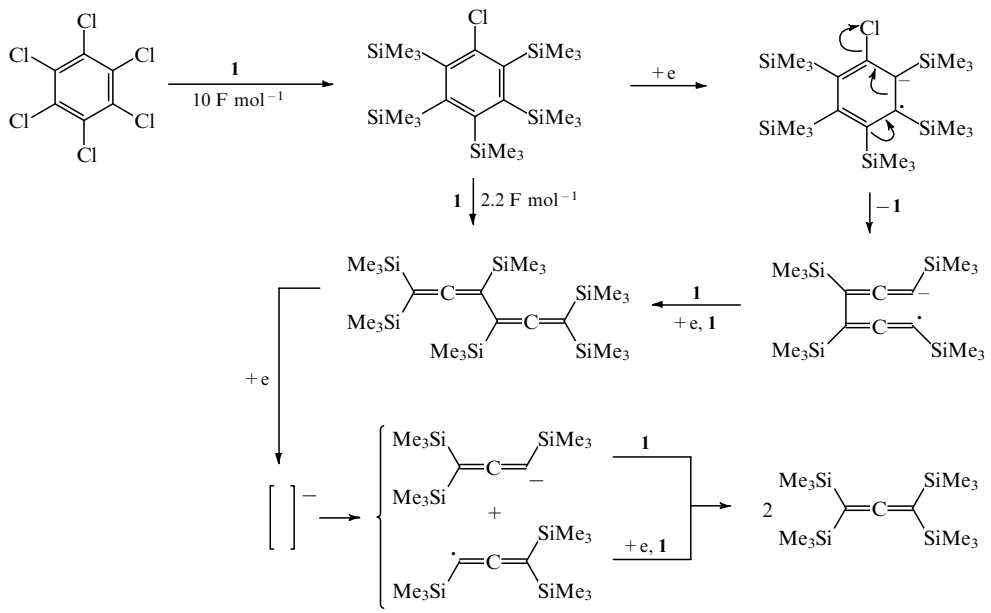


Generally, all the three chlorine atoms can be replaced successively by the electroreductive silylation of trichlorobenzenes. In each of these stages, 2.2 F mol^{-1} of electricity is consumed.

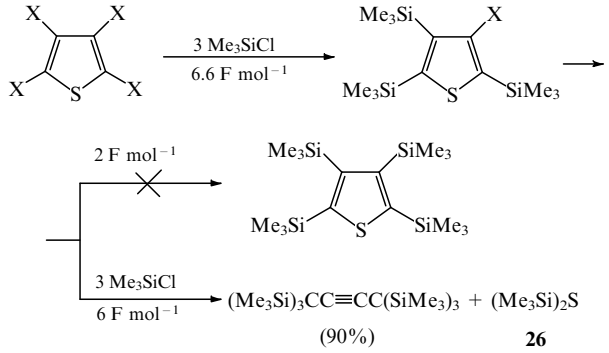


An attempt to carry out complete silylation of hexachlorobenzene and tetrahalothiophene was unsuccessful. The reaction yielded products of ring opening. A scheme for the process, which accounts for the formation of various products depending on the amount of electricity passed, has been proposed (Scheme 1).

Scheme 1

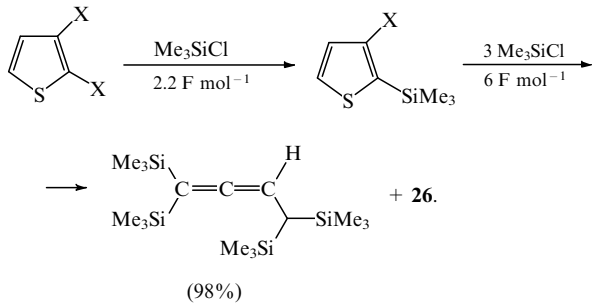


Cleavage of the ring in tetrahalothiophene is accompanied by the formation of hexamethyldisilathiane **26**.



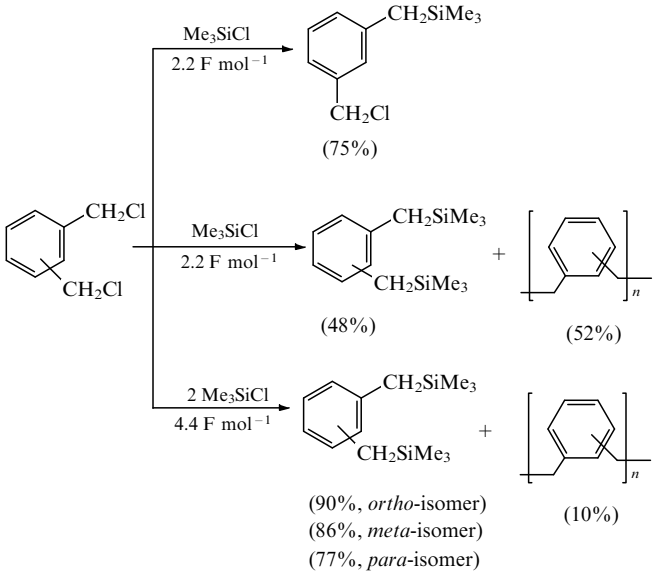
X = Br, Cl.

Silylation of 3-halo-2-trimethylsilylthiophene also yields products of ring opening in almost quantitative yield.

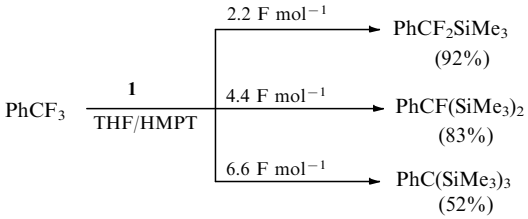


Using the correlation between the reduction potentials (E_p) of 1-R-3,4-dichloro- or 4-R-1,2-dichlorobenzenes and the sum of the σ_m and σ_p constants of substituents, it has been shown that substituents for which the $\sigma_m - \sigma_p > 0$, direct silylation to the *meta*-position, while those with $\sigma_m - \sigma_p < 0$ lead to *para*-silylation.

An interesting regularity has been observed in the silylation of disubstituted chloromethylbenzenes. Only *meta*-derivatives undergo monosilylation, whereas *ortho*- and *para*-isomers afford no monosilylation products.[101] When 2.2 F mol^{-1} of electricity is passed, the latter are immediately converted (by approximately 50%) into disilylated derivatives. It has been assumed that this is due to the intermediate formation of *o*- or *p*-xylylene, which is converted into the corresponding polymer in 52% yield.



Silylation of the C–F bond in trifluoromethylbenzene carried out under the same conditions[102] permits preparation of any of the three possible products by passing the appropriate amount of electricity (chromatographic yields are presented).



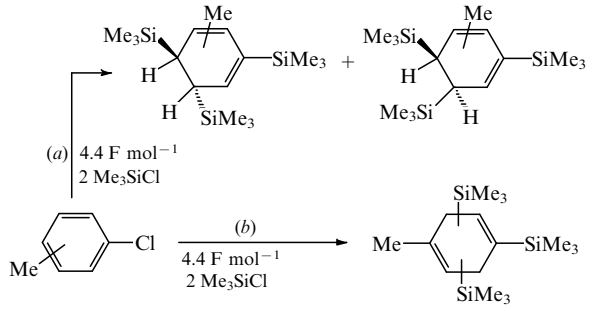
Synthesis of trimethylsilylcyclopentadiene (in a current yield of 96% based on the single-electron process) by the reaction between the electrically generated cyclopentadienyl anion and the chlorosilane **1** has been reported.[103] Cyclopentadiene was reduced at a Fe cathode in a divided cell in MeCN in the presence of Et_4NBr. Then a solution of the chlorosilane **1** in MeCN was added to the resulting catholyte (the solution contained some NaBr

added in order to shift the equilibrium in the reaction between $C_5H_5^-$ and **1** through binding the liberated chloride anion into insoluble NaCl).

$$C_5H_6 \xrightarrow{+e} C_5H_5^- + H^{\bullet},$$

$$C_5H_5^- + \mathbf{1} \longrightarrow C_5H_5SiMe_3 + Cl^-.$$

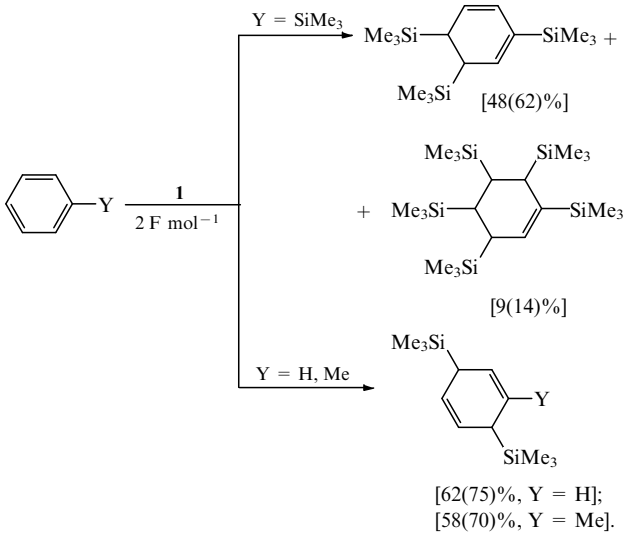
A reduction of monochlorotoluenes in the presence of the chlorosilane **1**, more extensive than the two-electron reduction, involves the aromatic ring and leads to the loss of aromaticity.[76, 92]



(*a*) *ortho*- and *meta*-isomers, (*b*) *para*-isomer.

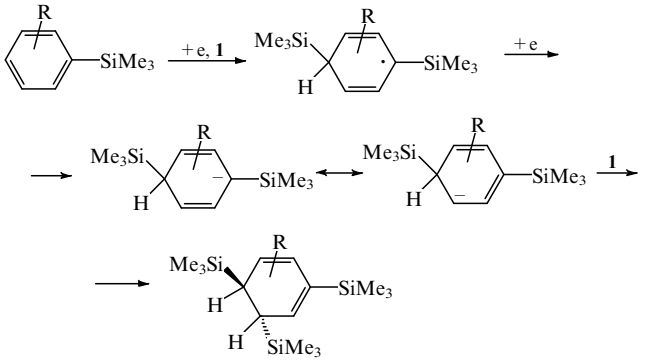
trans-Isomers predominate in the product mixture. When the DMF/$MgCl_2$/Mg system is used, only bromobenzene is silylated.

The nature of the unsaturated products resulting from silylation of aromatic compounds depends on the structure of the initial compound (chromatographic yields are given in parentheses).[92]



Benzene and toluene are converted into bis(trimethyl-silyl)cyclohexa-1,4-dienes. In the case of benzene, a 7 : 3 mixture of *trans*- and *cis*-products was obtained, while toluene gave only the *trans*-isomer.

Chemical silylation of systems of this type yields at once pentakis(trimethylsilyl)cyclohexanes, whereas electrochemical silylation can be selectively terminated when tris(trimethylsilyl)-containing conjugated dienes have been formed. The stereochemical control of the electrosilylation of aromatic systems is due to the steric effect of the first trimethylsilyl group entering the molecule. In fact, the second silylation occurs from the less shielded side of the molecule. This attack affords the kinetically controlled product; in the case of *trans*-isomer, this is also the thermodynamically controlled product.[92]



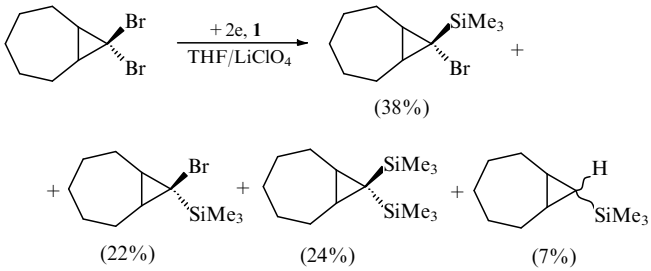
The electrochemical method for the synthesis of Ruppert's reagent was proposed in two publications at almost the same time.[104, 105] In these studies, CF_3Br served as the source of the CF_3 group; the solution was saturated with this compound at −30 to −15 °C.

$$CF_3Br \xrightarrow{+2e,\ \mathbf{1}} F_3CSiMe_3.$$

The authors of both studies advise the same electrodes (an Al anode and a Ni cathode) but different solvents and supporting electrolytes [DMF/Bu_4NBr [104] and PhOMe : HMPT (10 : 1)/Bu_4NPF_6 [105]].

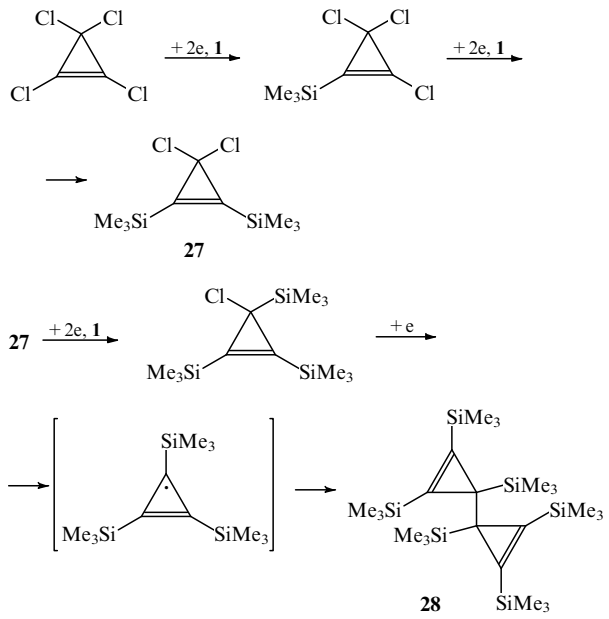
It is of interest that together with F_3CSiMe_3, 10% – 15% of hexamethyldisilane is formed,[105] although the chlorosilane **1** is not yet reduced at the potential of electrolysis. It was assumed that the disilane is formed from the Si – Br derivative, which appears in the mixture *via* the Br/Cl exchange accelerated by Al^{3+} ions.

Successive substitution of the Br atoms in 1,1-dibromocyclopropanes by Me_3Si groups has been accomplished by electroreduction of this compound in the presence of the chlorosilane **1**.[106] The same process involving 8,8-dibromobicyclo[5.1.0]octane affords various silylated derivatives with moderate selectivity.[107] In addition to the silylated products, 10% of the unreacted initial dibromide was detected in the product mixture. Ultrasonic treatment of the reaction mixture doubles the apparent current yield. Since the process was carried out with a Mg anode, it was assumed that in this case, the silylated product has also been formed in a competing purely chemical (sonochemical) reaction with the participation of Mg.



Since sonochemical processes usually stop at the monosilylation stage, the electrochemical version yielding disilylated products is a convenient method for the synthesis of these cyclopropane derivatives.[107]

Successive reduction of tetrachlorocyclopropene in the presence of the chlorosilane **1** made it possible to prepare its mono-,[108] di- and trisilylated derivatives.[109] When this process was carried out in the THF/HMPT (10 : 1) system using a Ni cathode, an Al anode and 8 F mol^{-1} of electricity, hexakis(trimethylsilyl)-3,3′-bi(cyclopropenyl) **28** was obtained in 40% yield; silylated dichloropropene **27** was formed simultaneously.



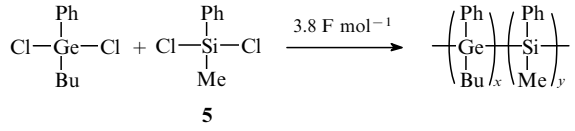
When a Mg anode is used, compound **28** is scarcely formed.[109]

Thus, the reduction of a C–Hal bond is, obviously, the most convenient method for the electrical generation of C-nucleophiles, because most organic halides are reduced at less negative potentials than chlorosilanes. Generation of a carbanion by reduction of a C–H bond requires more negative potentials and it often can be accomplished only at cathodes made of transition metals.[103] The reduction of aromatic systems is accompanied by their degradation; however, this process can be used for electrosynthesis of silylated dienes and alkenes, which are of interest for Diels–Alder reactions.

2. Organoelement nucleophiles

This Section deals with processes consisting of electrical generation of nucleophiles based on Ge^-, Sn^-, O^-, N^-, S^-, Se^- and so on, *i.e.* elements other than carbon, and their subsequent reactions with reagents containing electrophilic silicon, most frequently, with the chlorosilane **1**.

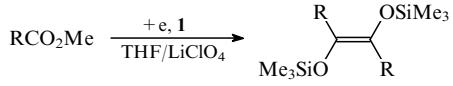
Electroreduction of chlorotrimethylgermane[110] in the presence of the chlorosilane **1** (Mg anode and Mg cathode, THF/$LiClO_4$) affords a heteroelement dimer containing a Ge–Si bond, whereas its reduction in the presence of the dichlorosilane **5** gives rise to a heterocopolymer.



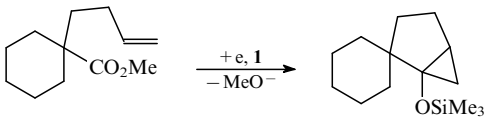
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Reduction of tributylchlorostannane in the presence of the chlorosilane **1** under similar conditions and at ratios of the initial chlorides of 1:1, 1:5 and 1:10 leads to tributyl(trimethylsilyl)stannane (10%, 35% and 50%) and hexabutyldistannane (59%, 55% and 41%, respectively).[29]

Esters of carboxylic acids[50, 111, 112] are reduced with Mg electrodes (anode and cathode) in an undivided cell in the presence of Me_3SiCl to give products of the acyloin condensation.

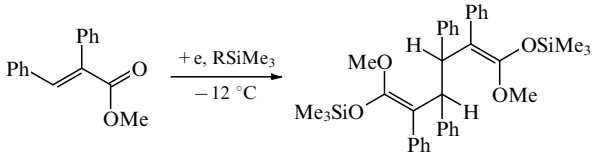


The same process involving an unsaturated ester that has a more positive reduction potential than the chlorosilane **1** results in the formation of a bicyclic spiro-compound.[113]



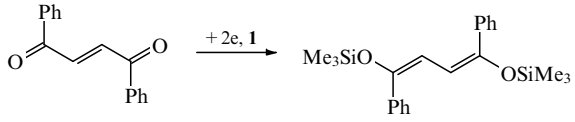
(67%)

Electroreduction of unsaturated carbonyl compounds under aprotic conditions in the presence of *O*,*N*-bis(trimethyl-silyl)acetamide **21** or the chlorosilane **1** affords products identified as silyl ethers.[114] It is of interest that acetamide **21** is inactive in the reaction with C-nucleophiles[85, 86] but reacts with the O-nucleophile to give dimeric trimethylsilyl unsaturated diether **29**.



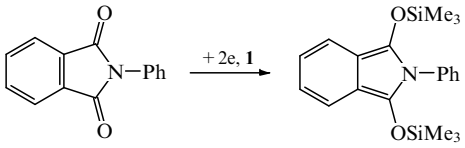
29 (16%)

The product of two-electron reduction of 1,2-dibenzoylethene attacks nucleophilically the chlorosilane **1** to give 1,4-diphenyl-1,4-bis(trimethylsilyloxy)buta-1,3-diene.



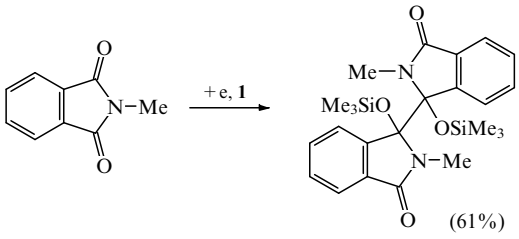
(63%)

2-Phenyl-1,3-bis(trimethylsilyloxy)isoindole has been prepared by two-electron reduction of *N*-phenylphthalimide in $MeCN/Et_4NCl$ in the presence of the chlorosilane **1**.[115]



The resulting isoindole was not isolated in a pure state owing to its high sensitivity to moisture and air; however, this compound is quite stable in a catholyte under a layer of dry argon and can be trapped by an appropriate dienophile after the electrolysis.[115]

Single-electron reduction[115] of *N*-methylphthalimide under the same conditions yields a dimeric silylated bis-lactam.

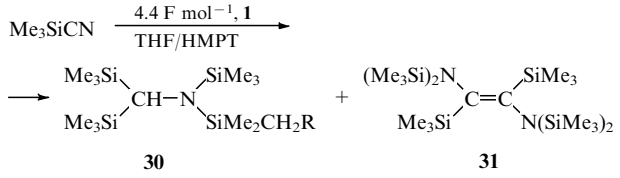


(61%)

This process is assumed to include the formation of a radical anion, which is able either to react directly with an electrophile in two E + C_{S_N2} steps (two-electron process) or to undergo dimerisation followed by silylation to give the bislactam (single-electron process).

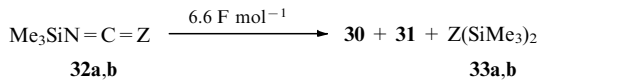
Electroreduction of acylimidazoles in the presence of the chlorosilane **1** gives rise to acylsilanes[116] including those containing Cl and C(O)OAlk groups.

The products of electroreduction of Me_3SiCN react with the chlorosilane **1** affording silylated products **30** and **31**, the protolysis of which makes it possible to synthesise bis(trimethylsilyl)-methylamine.[117]

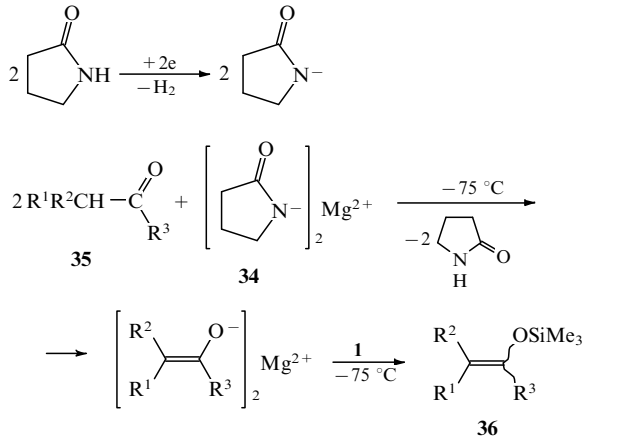


R = H, Cl.

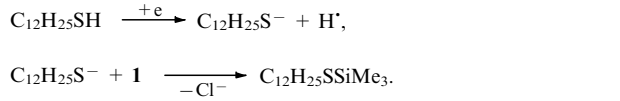
The same products, together with tris(trimethylsilyl)amine **33a** and hexamethyldisiloxane **33b** were obtained by electrochemical silylation of trimethylsilylcarbodiimide (Z = $NSiMe_3$) **32a** and trimethylsilyl isocyanate (Z = O) **32b**.[117]



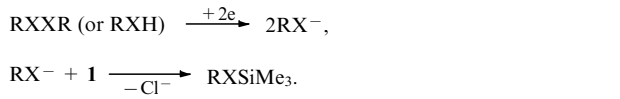
Magnesium salt **34** prepared by electroreduction of 2-pyrrolidone in an undivided cell with a soluble Mg anode[118] has been used as an electrically generated base for functionalisation of carbonyl compounds. Thus the magnesium enolate formed upon addition of ketone **35** to two equivalents of the electrically generated base at a low temperature reacts with the chlorosilane **1** to give enoxysilane **36**; *N*-trimethylsilyl-2-pyrrolidone is formed as a side product.



Magnesium thiolate electrically generated upon reductive rupture of the S–H bond in dodecanethiol[119] reacts with the chlorosilane **1** to give thiosilane **37** in a current yield of 78%.



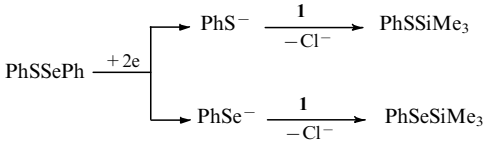
Reduction of diorganodisulfides and -diselenides as well as thio- and seleno-phenols (in the two latter cases, a Fe cathode is used) carried out in the presence of mono- and dichlorosilanes[63,120,121] gives rise to the corresponding thio- and selenosilanes in good preparative yields (60%–87%). Chromatographic analysis of reaction mixtures shows that the reaction proceeds almost quantitatively.



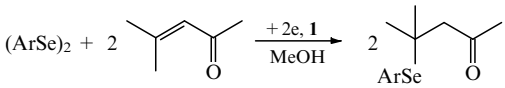
R = Ar, Alk; X = S, Se.

By means of an electrochemical variant of the method of competing reactions in the classical and reversed schemes (Scheme 2), it has been shown that the rates of S_N2 reactions of electrically generated PhS^- and $PhSe^-$ anions with chlorosilanes (Me_3SiCl, $MeVinSiCl_2$, Me_2SiCl_2 and $SiCl_4$) are related as 1 : 1.97 : 2.34 : 4.61 and 1 : 1.45 : 2.5 : 4.1, respectively. The rate of nucleophilic selenation is 9.3 times higher than the rate of thiylation due to the higher nucleophilicity of the Se-containing anion.[122]

Scheme 2

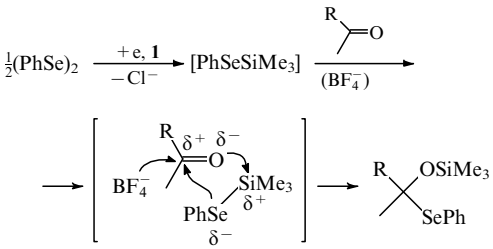


Cathodic arylselenation of α,β-unsaturated carbonyl compounds has been described. It was assumed that trimethylsilyl selenide resulting from interaction of the electrically generated $ArSe^-$ anion with the chlorosilane **1** participates in the process.[123] Methanolysis of the silyl selenide yields arylselenol, and the latter acts as the reactive intermediate in this *in situ* silylation of enones.

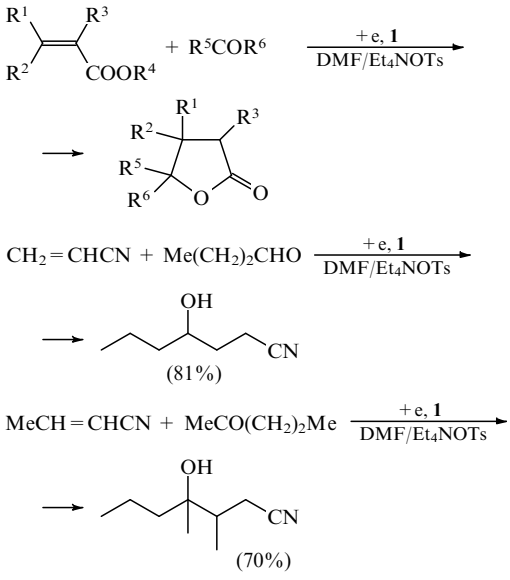


Electrically generated silyl chalcogenides have been used for functionalisation of carbonyl compounds (Scheme 3).[121,124–128]

It is assumed that the addition of selenosilane to the C=O bond under the conditions of electrolysis involves anionic catalysis by the anion of the supporting electrolyte.[121,129]

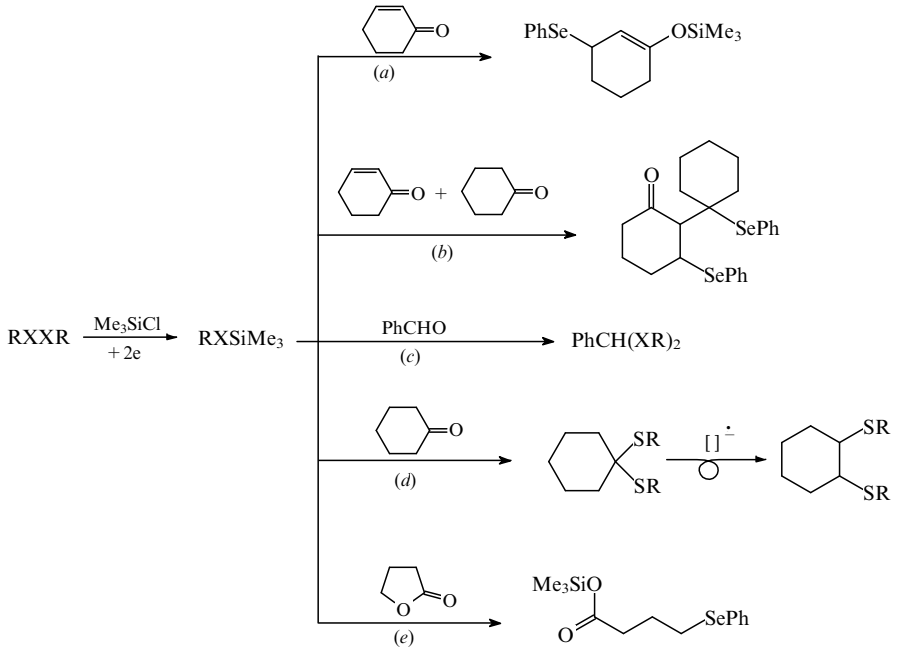


Electroreductive cross-hydrocoupling of α,β-unsaturated esters with aldehydes or ketones[28] in the presence of the chlorosilane **1** results in the formation of γ-lactones in good yields (51%–86%). Similarly, α,β-unsaturated nitriles are converted into γ-hydroxynitriles.



Although the molecules of the reaction products do not contain Me_3Si groups, the presence of the chlorosilane **1** is necessary, because coupling does not occur without it. The mechanism of the process has not been studied in detail; however, it is assumed that **1** is coordinated to the carbonyl compound thus activating the carbonyl group. Then this complex reacts with the radical anion resulting from single-electron reduction of the acrylate.

Scheme 3



(*a*, *b*) X = Se; R = Ph; divided cell;
(*c*) X = S, Se; R = Et, Ph; divided cell;
(*d*) X = S; R = Et, Ph; one-compartment cell, Al(Mg) anode;
(*e*) X = Se; R = Ph; one-compartment cell, Al(Mg) anode.

Electrocatalytic reduction of Ph_2PCl by the complex NiL_3 (L is 2,2-dipyridyl or PPh_3) in the presence of the chlorosilane **1** yields diphenyl(trimethylsilyl)phosphine.[10]

$$Ph_2PCl + \mathbf{1} \xrightarrow[[NiL_3]^{2+}/[NiL_3]^0]{+2e,\ -2Cl^-} Ph_2PSiMe_3.$$

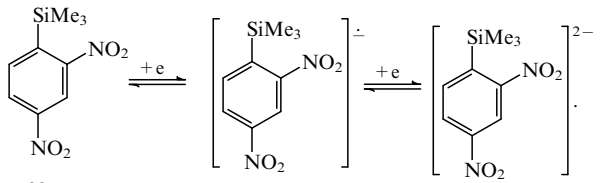
V. Reduction of other classes of organosilicon compounds

The interpretation of the stabilising influence of the silicon atom on radical-anion intermediates has changed following the evolution of the views on the electronic effects of silicon-containing substituents (from the idea that electron-withdrawing properties of α-silyl substituents are associated with participation of the vacant 3*d* orbitals of silicon atoms to the concept rejecting this participation [130] and based on the acceptor hyperconjugation interactions of σ* orbitals). At present, none of the theoretical concepts can fully explain the experimental data on the electronic effects of silyl substituents. The concept according to which the overall influence of a silyl substituent on the energies of frontier molecular orbitals (FMO) is determined by a combination of various electronic interactions [131] — inductive effect (+*I*), σ,π and σ,π*-conjugation, mixing of the $\sigma_{(Si-C)}$ and 3*d* orbitals of Si, mixing of *d*,σ* orbitals with σ,π* and σ,π orbitals and the formation of LUMO (*d*,π*) — should be regarded as the most comprehensive (but also the most complex).

Since the 3*d*-orbital hypothesis (see Refs 130 and 131) agrees qualitatively with general quantum-mechanical views on intramolecular electronic interactions and with statements of the general concept [131] (this hypothesis has been used in a number of original studies), we decided not to introduce the more recent interpretation but to remain within the framework of the $d_\pi - p_\pi$-conjugation concept used by the researchers cited (see, for example, Refs 132–134).

The results of reversible polarographic reduction of 4-trimethylsilyl- and 4,4′-bis(trimethylsilyl)biphenyls ($E_{1/2}$ = −2.03 and −1.94 V *vs* Hg pool, respectively),[132] and of a number of trimethylsilyl-substituted polyphenyls [15] have been used to estimate the ε_{LUMO} values, which proved to be close to the ε_{LUMO} values obtained using EPR data. Interpretation of the spectra of the radical anions in terms of a model involving *d* orbitals of silicon made it possible to calculate the multiplicity of the C–Si π-bond, which was found to be approximately 0.18 in all the aromatic compounds studied.

The potentials of the reduction peaks (DMF/Bu_4NClO_4, Pt) of *o*-, *m*- and *p*-nitrophenyltrimethylsilanes (E_p = −1.62, −1.50 and −1.26 V *vs* SCE, respectively) [133] are several tens of millivolts more positive than the reduction potentials of the corresponding toluene derivatives. The radical anions formed upon the transfer of a single electron are quite stable ($i_a/i_k \cong 1$); however, although the process is reversible, $\Delta E_p/\Delta \lg(\upsilon)$ = 400 mV for potential sweep rate υ ranging from 40 to 400 mV s^{-1}. The reduction of 2,4-dinitrophenyltrimethylsilane **38** is characterised by two reversible peaks and occurs according to the equation



38

The stabilising influence of the trimethylsilyl group on the radical anion was explained [133] by the $d_\pi - p_\pi$-conjugation of the Si atom with the aromatic ring.

The possible structures of the radical anions derived from *p*- and *m*-trimethylsilylnitrobenzenes have been discussed;[134] the distribution of the electron density in these species during the reduction was elucidated by EPR.

It has been reported [135] that α-silyl aryl ketones have lower reduction potentials ($\Delta E_{1/2}$ = 270 mV) than their carbon analogues and that the energies of charge transfer in the π-complexes of α-silyl aryl ketones with tetracyanoethylene are higher than those in the complexes of carbon derivatives.

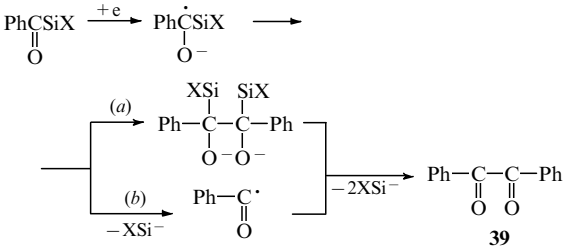
The polarogram of reduction of 5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]silinone [136] exhibits two waves typical of ketones. The first wave ($E_{1/2}$ = −1.64 V *vs* Hg pool, $\Delta E_{3/4-1/4}$ = 60 mV) corresponds to the formation of a radical anion; the second wave is irreversible ($E_{1/2}$ = −2.27 V, $\Delta E_{3/4-1/4}$ = 90 mV). The decrease in the splitting constants in the EPR spectra attests to a decrease in the spin density in the benzene rings, which is due to the electron-withdrawing influence of the silicon atom.

The slight differences between the reduction potentials of 4-biphenylyltrimethylsilane ($E_{1/2}$ = −1.948 V *vs* Hg pool) and 4,4′-bis(trimethylsilyl)biphenyl ($E_{1/2}$ = −1.856 V) and between those of bis(4-biphenylyl)dimethylsilane ($E_{1/2}$ = −1.904 V) and 4,4′-bis(4-biphenyldimethylsilyl)biphenyl ($E_{1/2}$ = −1.801 V) have been attributed [137] only to the effect of the second silicon atom, participation of the *d* orbitals of silicon in the transfer of conjugation between the benzene rings being completely ruled out.

Contrary to this and also to the conclusion made by Makarov and Kazakova [138] that the unpaired electron in the radical ions derived from phenylsilanes is not delocalised through the $SiMe_2$ bridges, Il'yasov *et al.*[139] have found, based on the EPR spectra of the electrically generated radical anions $Ph_4Si^{-\bullet}$, that the unpaired electron does interact with all the phenyl groups.

Reduction of mono- and bis-trimethylsilyl-substituted naphthalenes [140] occurs by a mechanism typical of reduction of aromatic hydrocarbons with reversible electron transfer giving a radical ion; in this case, the $E_{1/2}$ potentials are more positive than those for reduction of compounds with *tert*-butyl substituents ($\Delta E_{SiMe_3-CMe_3}$ = 220–290 mV), which is a result of the simultaneous influence of two opposite effects: +*I* effect of the Me_3Si group and the electron-withdrawing effect of vacant 3*d* orbitals of Si on the π-system of the ring.

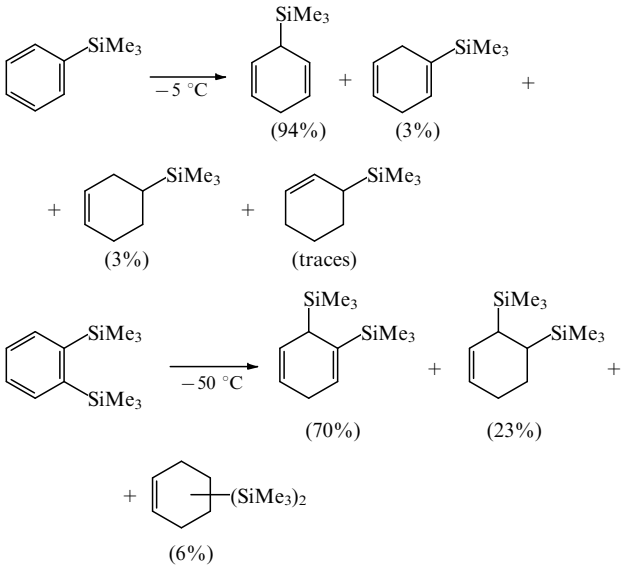
The reduction of a number of benzoylsilanes substituted in the ring in $MeCN/Bu_4NClO_4$ at a glassy carbon electrode involves the formation of a relatively unstable radical anion, which was detected at −80 °C by EPR.[141] At room temperature, the process is irreversible and, unlike the electroreduction of arylketones which affords pinacols, it occurs according to Scheme *a* or *b* and yields diketone **39**.



X = $PhMe_2$.

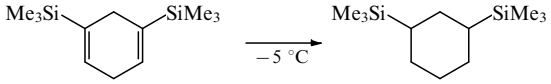
The potentials of the two reversible steps of electroreduction of 2,5-bis(trimethylsilyl)-1,4-benzoquinone ($E_{1/2}$ = 0.04 and −0.51 V *vs* Hg pool; $MeCN/Bu_4NI$) are 200 mV more positive than the potentials of electroreduction of the corresponding di-*tert*-butyl derivative,[142] which is due to the electron-withdrawing influence of the Si atom (the mechanism of $d_\pi-p_\pi$-conjugation).

Electroreduction of aryltrimethylsilanes in $MeNH_2/LiCl$ at a Pt electrode in an undivided cell is a promising method for the synthesis of trimethylsilyl-substituted cyclohexa-1,4-dienes.[143, 144] This reaction is assumed to proceed as an electrochemical variant of the Birch reaction with participation of the metallic lithium resulting from the cathodic reduction of Li^+. With substituents occupying various positions in the aromatic ring, the nature of the products is determined by steric and electronic interactions.



In addition to the products mentioned above, disilylated cyclohexenes with a different position of trimethylsilyl groups are formed in 6% yield.

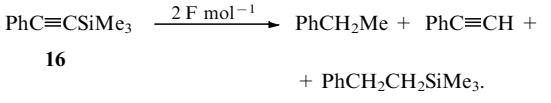
It is noteworthy that at potentials more negative than reduction potentials of arylsilanes, electroreduction of silylated alkenes can also be achieved.[144]



cis : *trans* = 1 : 9

Rupture of the double bond during the reduction of 6-trimethylsilylhept-6-en-2-one and intramolecular cyclisation lead to *cis*-1-methyl-3-trimethylsilylcyclohexanol.[145]

Reduction of trimethyl(phenylethynyl)silane **16** ($E_{1/2}$ = −2.02 V *vs* Hg pool; DMF/Bu_4NI [146]) in an undivided cell in $MeNH_2/LiCl$ at a Pt electrode requires 2F mol^{-1} of electricity and affords a mixture of products that contains ethylbenzene (38%), phenylacetylene (47%) and trimethyl(2-phenylethyl)silane **40** (13%).[143] The reduction occurs presumably *via* the formation of trimethyl(phenylethynyl)silyl radical anion $[\mathbf{16}]^{-\bullet}$, which undergoes either fragmentation at the C–Si bond (in $MeNH_2$) or protonation with retention of the C–Si bond (in the presence of Pr^iOH). In the latter case, compound **40** is formed in a markedly higher yield (31%).



16 **40**

The $E_{1/2}$ values for the reversible reduction of silylbutadienes have been reported.[147] Since the interactions of silyl-substituted unsaturated compounds in excited states cannot be measured directly, some correlations were made on the assumption that the $E_{1/2}$ potentials of reversible electron transfer reflect the relative LUMO energies in neutral π-electron systems in the ground state. Thus the +*I* effect of the Me_3Si group dominating in the ground state is replaced by $d-\pi^*$ interaction at the singly occupied molecular orbital (SOMO) of the radical anion, and the sequence of potentials of di(trimethylsilyl)-substituted butadienes [$E_{1/2}$ for 1,4-, 1,3-, 1,2- and 2,3-bis(trimethylsilyl)butadienes are −1.80, −1.85, −1.90 and −2.13 V, respectively, with respect to the Hg

pool] is consistent with the sequence expected according to the theory of FMO with first-order perturbations (1,4- < 1,3- ~ 1,2- < 2,3-isomers). Moreover, the electrically generated radical anion from 1,4-bis(trimethylsilyl)butadiene is so stable that its EPR spectrum can be observed at room temperature. Splitting constants indicate that the spin density of the radical anion is partly delocalised to the Me_3Si group.[147]

Polarograms of silaacenaphthenes, 2-silaphenalanes and 1,3-disilaphenalanes and the EPR spectra of the corresponding electrically generated radical anions have been studied.[148] Since the molecules of these compounds are fairly strained, stability of their radical anions is lower than that of the radical anions derived from other silicon-containing aromatic compounds of this series.

The results of the polarographic single-electron reversible reduction of phenyl- and naphthyl silyl ketones,[149] vertical ionisation potentials (IP) and the data of electronic spectroscopy indicate that $E_{1/2}$ of the reduction of silicon-substituted ketones are markedly lower than those of their carbon analogues ($\Delta E_{Si-C} \cong 250-270$ mV) and that electron-withdrawing substituents at the carbonyl carbon atom have a greater influence on the electrochemical reactivity than substituents at the *para*-position of the aromatic ring.

Phenyl-substituted polysilanes $Ph(SiMe_2)_nMe$ and $Ph(SiMe_2)_nPh$ are reduced in the range of potentials $-3.3 < E_{1/2} < -3.2$ V, which is close to the region of electrical activity of the solvent [$E_{1/2} = -3.26$ V for *p*-bis(trimethylsilyl)benzene and $E_{1/2} = -3.23$ V for *p*-bis(pentamethylsilanyl)benzene *vs* Ag/Ag^+], whereas naphthylpolysilanes exhibit one reversible diffusionally controlled wave ($n = 1$, $i/H^{1/2} = \text{const}$, where H is the height of the mercury column in the dropping-mercury electrode; $i/C = \text{const}$) or two single-electron reduction waves in an accessible range of potentials ($-2.845 \leqslant E_{1/2} \leqslant -2.781$ V *vs* Ag/Ag^+).[130] Since linear permethylpolysilanes $Me(SiMe_2)_nMe$ ($n = 2-5$) are not reduced,[130,150] reduction of polysilylated aryl derivatives, evidently, involves one of the degenerate antibonding orbitals of the Ar group. The decrease in $E_{1/2}$ for silylnaphthenes was interpreted taking into account inductive, σ, π, and $d_\pi - p_\pi$ effects of the silyl substituent; the two former effects increase ε_{LUMO}, while the latter markedly decreases it.[130]

Cyclic permethylpolysilanes $(Me_2Si)_n$ ($n = 5-7$) are reduced in Me_2O/DME (3:1) in the presence of Bu_4NClO_4 to give a radical anion, the EPR spectrum of which recorded at $-120\,^\circ C$ indicates that the unpaired electron is delocalised over all the Si atoms in the ring.[151]

The $Si_6Me_{11}^-$ anion is formed upon electroreduction of Si_6Me_{12} in HMPT at -1.9 V and can react with various electrophiles:[152] for example, its reaction with EtBr affords the corresponding ethylated product.

Tetraaryldisilenes are reduced irreversibly in the THF/Bu_4NPF_6 system at less negative potentials ($E_p = -2.03$ to -2.2 V *vs* SCE) than dialkyldiaryldisilenes ($E_p = -2.6$ V). This is due to the fact that the two aromatic rings and the double bond in the molecules of tetraaryl-derivatives are nearly coplanar; as a consequence, π^* orbitals of the disilene and aromatic fragments are largely mixed and the LUMO energies of the molecules decrease.[153]

In the reduction of iodomethylsilanes,[154,155] the presence of a Me_3Si group also shifts the $E_{1/2}$ potential to less negative values (Table 5); the corresponding polarograms contain two single-electron diffusion waves rather than one two-electron wave as in the case of primary iodoalkanes. The process was assumed to correspond to the E + E + C scheme.

$$R_3SiCH_2I + e \longrightarrow R_3SiCH_2^{\cdot} + I^-,$$

$$R_3SiCH_2^{\cdot} + e \longrightarrow R_3SiCH_2^-,$$

$$R_3SiCH_2^- + H_2O \longrightarrow R_3SiCH_3 + OH^-.$$

In the case of $Et_2SiMeCH_2I$, the slope in the plot for the $E_{1/2}$ potential against the logarithm of the period of dropping in the dropping-mercury electrode (t_1) is $\Delta E^1_{1/2}/\Delta\lg(t_1) \cong 60$ mV, which corresponds to the transfer coefficient $\alpha \cong 0.5$.[154]

Table 5. Characteristics of electroreduction of iodo- and chloromethylsilanes in 57% EtOH/0.09 M KCl (the $E_{1/2}$ potentials are referred to SCE).[154,155]

Halomethylsilane	$-E^1_{1/2}$/ V	$-E^2_{1/2}$/ V
Et_3SiCH_2I	1.54	1.72
$CF_3(CH_2)_2SiMe_2CH_2I$	1.33	1.54
p-$FC_6H_4SiMe_2CH_2I$	1.40	1.53
p-$ClC_6H_4SiMe_2CH_2I$	1.37	1.50
m-$CF_3C_6H_4SiMe_2CH_2I$	1.34	1.45
$Et_2SiMeCH_2I$	1.56	1.70
$Pr_2SiMeCH_2I$	1.60	1.76
$Bu_2SiMeCH_2I$	1.58	1.79
$PhSiMe_2CH_2I$	1.43	1.56
Me_3SiCH_2Cl	1.51[a]	
$ClMe_2SiCH_2Cl$ (**41**)	1.48[a]	

[a] From Ref. 157.

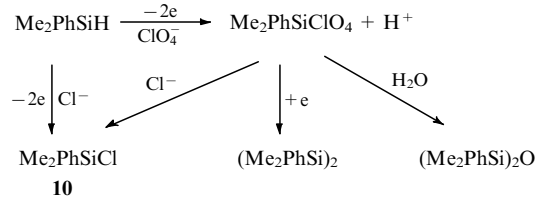
Using the method of homogeneous redox catalysis, it has been shown that the coordinate of the reaction of reduction of $ClCH_2SiMe_3$ **41** contains a point corresponding to the real radical anion.[156,157] This mechanism of reduction, unusual for alkyl chlorides, is due to the fact that the negative charge arising on the α-carbon atom (more precisely, in the σ^* orbital of the C–Cl bond) upon electron transfer is delocalised by silicon, and this decreases the energy of the ground state of the radical anion, which thus becomes lower than the level of the transition state leading to dissociation. Due to the same effect, the E_p potentials of iodo- and chloromethylsilanes are abnormally small.

The reduction of Ph_3SiH and Ph_2MeSiH in the presence of Bu_4NClO_4 in a divided cell does not lead to the replacement of hydrogen by the halogen, as in the case of germanium analogues;[159] instead, it yields disiloxanes. When the electrolysis was carried out in the presence of Bu_4NBF_4, formation of traces of Ph_3SiF was detected by GC/MS analysis, $(Ph_3Si)_2O$ still being the main reaction product.

VI. Electrooxidation of organosilicon compounds

1. Hydrosilanes

Unlike oxidation of some hydrosilanes at metallic electrodes, which is characterised by low potentials (Table 6), oxidation of Me_2PhSiH at a glassy carbon electrode in MeCN/$LiClO_4$ occurs at a high potential§ $E_p = 2.2$ V *vs* SCE.[160] Preparative electrooxidation of Me_2PhSiH in DME/Bu_4NClO_4 in the presence of $CuCl_2$ or CuCl gives rise to a number of products, the formation of which can be described by the following scheme:



Depending on the copper chloride used ($CuCl_2$ or CuCl) and on the amount of electricity passed, the chlorosilane **10** is formed in a yield of 46%–95%. Under the same conditions, Bu^tMe_2SiH and Et_3SiH **42** are converted into the corresponding chlorosilanes

§ Since in the presence of CuCl, chloro-derivatives are also formed in a chemical process without passing the electricity, the high E_p values may be due to oxidation at these potentials of compounds other than hydrides.

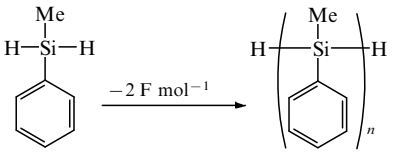
Table 6. Characteristics of electrooxidation of hydrosilanes.

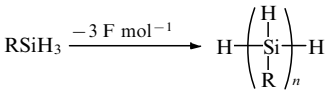
Silane	E_p/ V (*vs* SCE)	Electrode	i_k/i_a (v = 0.5 V s^{-1})	Ref.
Et_3SiH (**42**)	0.23	Pt [a]	0.63	161
$(EtO)_3SiH$	−0.05	Pt [a]	0.61	162
$(EtO)_3SiH$	0.45	Au [a]	0.42	162
$(EtO)_3SiH$	0.30	Hg [a]	0.34	162
$MeCl_2SiH$	−0.28	Pt [b]	0.9	163
$MePh_2SiH$	2.1	GC [b]	irrevers.	160
Me_2PhSiH	2.2	GC [b]	irrevers.	160
$MePhSiH_2$	0.7	Pt [c]		164
$PhSiH_3$	0.7	Pt [c]		164
n-$C_6H_{13}SiH_3$	0.6	Pt [c]		164

[a] $MeCN/Et_4NClO_4$; [b] $MeCN/LiClO_4$; [c] $MeCN/Bu_4NBF_4$.

in 83% and 50% yields, respectively. When the supporting electrolyte is replaced by Bu_4NBF_4, Me_2PhSiF is formed in a yield of 90%, presumably *via* exchange reaction between the chlorosilane formed initially and BF_4^- (*cf.* Refs 27, 35, 71, and 105).

Electrooxidation of hydrosilanes in DME/Bu_4NBF_4 in an undivided cell with Pt electrodes affords polysilanes in overall yields of 32% – 70%.





R = Ph, n-C_6H_{13}, n = 2 – 6.

The oxidation potentials of hydrosilanes[164] are 200 mV smaller than that of the polymer; this prevents the latter from oxidation with rupture of the polysilane chain according to a scheme similar to that described by Diaz *et al.*[165, 166]

The electrically catalysed anodic substitution of hydrogen in the molecule of hydrosilane **42** by an acetoxy-group,[167] like processes of direct anodic substitution, occurs without oxidation of the nucleophile (CH_3COOH), the transferring agent being generated from the electrolytic additive (I^-, Cl^-, NO_3^-). The transferring agent reacts with the hydrosilane **42** by a radical mechanism and at potentials smaller than the potential of oxidation of the acetate anion.

$$X^- \xrightarrow{-e} X^{\bullet},$$

$$Et_3SiH + X^{\bullet} \longrightarrow Et_3Si^{\bullet} + HX,$$

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$$Et_3Si^{\bullet} + X^{\bullet} \longrightarrow Et_3SiX,$$

$$Et_3Si^{\bullet} + HX(X_2) \longrightarrow Et_3SiX + H^{\bullet}(X^{\bullet}),$$

$$Et_3SiX + MeCOOH \longrightarrow Et_3SiOCOMe + HX.$$

X = I, NO_3, ClO_4.

The same process catalysed by bromide ions by a redox mechanism and carried out using $(C_{10}H_{21})_4NBr$ or Et_4NBr as supporting electrolytes and EtOH or PrOH as nucleophiles yields triethylalkoxysilanes in 30% – 95% yields.[168]

Radical cations resulting from electrooxidation of silanes R_3SiH have been identified as adducts with tetracyanoethylene.[169] The lifetime of the radical cation derived from the silane **42** and detected using a rotating disc-ring electrode is equal to 0.003 – 0.006 s.[161, 163] In the absence of radical traps, this radical cation decomposes with the abstraction of a hydrogen atom.

$$Et_3SiH \overset{-e}{\rightleftharpoons} [Et_3SiH]^{+\bullet} \longrightarrow Et_3Si^+ + H.$$

In the presence of cyclohexene, the radical cation [**42**]$^{+\bullet}$ adds to the double bond.[162, 163, 170] The reaction occurs by a chain mechanism, the role of the anode being limited to its initiation (creation of the initial concentration of the radical cations in the solution equal to 10^{-10} M).

$$R_2R'SiH \overset{-e}{\rightleftharpoons} \left[R_2R'SiH\right]^{+\bullet}$$

$$\left[R_2R'SiH\right]^{+\bullet} + \text{⬡} \longrightarrow \left[R_2R'Si-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{CH}}\right]^{+\bullet},$$

$$\left[R_2R'Si-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{CH}}\right]^{+\bullet} + R_2R'SiH \longrightarrow$$

$$\longrightarrow R_2R'Si-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{CH}} + \left[R_2R'SiH\right]^{+\bullet}.$$

R = R′ = EtO; R = Cl, R′ = Me.

2. Di- and poly-silanes

The redox properties of polysilanes resemble those of carbon compounds with conjugated double bonds: the HOMO energy of polysilanes increases with increase in the number of linked silicon atoms (this increase is more pronounced than the decrease in the LUMO energy), which results in an increase in their electrochemical activity in oxidation reactions.

The potentials of oxidation of aliphatic disilanes (Table 7), like potentials E_p of other derivatives containing two identical or different elements of the silicon group, obey a linear correlation with vertical gas-phase ionisation potentials (IP) with a slope of less than unity. The latter has been attributed to the influence of the fast kinetics of decomposition of the radical cation and the solvent on E_p.[171]

In the series of diaryltetraalkyl-, arylpentamethyl- and hexaalkyldisilanes, both types of electron transfer during reduction have been found; stepwise electron transfer was observed in compounds in which a silicon atom carries at least one aromatic substituent and dissociative electron transfer was observed for aliphatic disilanes.[172] An electron-withdrawing NO_2 group in the *para*-position of the aromatic ring destabilises the SOMO of the radical cation so markedly that in the case of bis(*p*-nitrophenyl)tetramethyldisilane, the type of electron transfer changes: the stepwise mechanism is replaced by dissociative mechanism, and the oxidation potential E_p is smaller than that calculated from the IP for reversible electron transfer.

The E_0 values calculated for hexamethyldisilane and $Me(SiMe_2)_3Me$ are approximately 1 V smaller than their effective potentials E_p, which is due to the high energy of reorganisation (38±5 kcal mol^{-1}) for these compounds.[174]

Of the two peaks of oxidation of polysilanes of the composition $[(MeSiFc)(MeSiPh)_n]_x$, where n = 5, 7 and 25, with ferrocenyl (Fc) groups, the one corresponds to the process involving the Fc moiety (+ 0.4 V *vs* SCE), while the other (E_p = 1.15 V) is associated with the oxidation of the polysilane chain.[165]

Polysilane films deposited on a platinum electrode exhibit an irreversible oxidation peak,[166] the potentials of which for alkylpolysilanes lie in the range 1.4 – 1.6 V (*vs* SCE) and depend only slightly on the nature of the alkyl substituent. Conversely, the potentials for arylpolysilanes depend appreciably on the electronic effects of the substituents in the aromatic ring, which is manifested in the anodic shift of E_p by 0.3 – 0.6 V (Table 7). This difference is caused by the marked increase in the relative HOMO

Table 7. Oxidation potentials of linear di- and poly-silanes.

Compound	E_p /V, *vs* SCE	$E_{1/2}$ /V (Ag/$AgClO_4$, GC electrode)	Ref.
$Me_3SiSiMe_3$	1.76 [a]		171
	($v = 0.1$ V s^{-1})		
	1.880		173
	($v = 0.1$ V s^{-1})		
	($E_0 = 0.92$)[b]		174
		1.48 [c]	69
	1.667		172
$Pr_3SiSiPr_3$	1.542		172
$BuMe_2SiSiMe_2Bu$	1.563		172
$Et_3SiSiEt_3$	1.76 [a]		171
p-$MeOC_6H_4SiMe_2SiMe_3$		0.82	94
p-$MeC_6H_4SiMe_2SiMe_3$		0.93	94
p-$NCC_6H_4SiMe_2SiMe_3$	1.632		172
$PhMe_2SiSiMe_3$		1.05	94
$PhCH_2SiMe_2SiMe_3$		1.05	94
(*p*-$MeOC_6H_4SiMe_2)_2$	1.307		172
(*p*-$NCC_6H_4SiMe_2)_2$	1.616		172
(*p*-$O_2NC_6H_4SiMe_2)_2$	1.735		172
$Me_3SiMe_2SiSiMe_3$	1.40 [d]		171
	($v = 0.1$ V s^{-1})		
	1.520		173
	($E_0 = 0.55$)[b]		174
$Me(SiMe_2)_4Me$	1.330		173
$Me(SiMe_2)_5Me$	1.180		173
$Me(SiMe_2)_6Me$	1.075		173
$[MePhSi]_n$	1.0		166
$[(p\text{-}MeOC_6H_4)MeSi]_n$	0.69		166
poly(methyl-β-phenethylsilane)	1.30		166
poly(cyclohexylmethylsilane)	1.42		166
$[n\text{-}C_6H_{13}MeSi]_n$	1.44		166
$[(n\text{-}C_6H_{13})_2Si]_n$	1.60		166
$[Me_2Si]_n$	1.0		166

[a] *vs.* Ag/AgCl; MeCN/Et_4NClO_4, $E_{p/2} = 1.36$ V *vs* Fc/Fc^+ (MeCN/-Bu_4NClO_4, Pt);[175] [b] the E_0 values calculated *vs* SCE are given in parentheses; [c] *vs* Ag/0.1 M $AgNO_3$; [d] *vs* Ag/AgCl; MeCN/Et_4NClO_4, $E_{p/2} = 1.10$ V *vs* Fc/Fc^+ (MeCN/Bu_4NClO_4, Pt).[175]

energy of the polysilane chain due to its interaction with the π orbitals of an aromatic substituent.

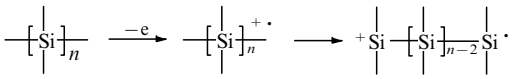
The E_p potentials for linear permethylpolysilanes decrease as the length of the chain increases and are related almost linearly to the ε_{HOMO} value calculated by the Sandorfi method.[173] A scheme including the formation of a silicenium adduct with acetonitrile ($n = 1$ or 2) has been proposed for the two-electron reduction of the disilane **9**.[173]

$$\underset{\mathbf{9}}{Me_3SiSiMe_3} \xrightarrow[MeCN]{-2e} 2Me_3Si^+(NCMe)_n.$$

During reverse scanning, two peaks (−0.25 and −1.0 V *vs* SCE) were detected in the cathodic region; they were attributed to reduction of the adducts with different *n*.

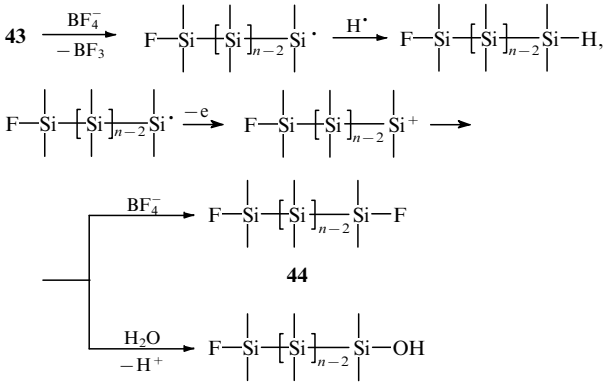
Cyclic polysilanes are oxidised in two steps ($E_p^1 = 1.1-1.4$ V, $E_p^2 = 1.4-1.9$ V *vs* SCE).[176] The potential of the first step also depends on the number of silicon atoms linked to one another.[177] However, the character of this dependence is disturbed by another factor that determines the electrochemical reactivity, namely, by the magnitude of the Si–Si–Si angles, which varies as a function of the size of the ring. For cyclosilanes with $n = 3-7$, the E_p potential diminishes with a decrease in the size of the ring ($7 \approx 6 \approx 5 > 4 > 3$), because the ring becomes more strained. For cyclopolysilanes with $n > 9$ in which the strain of the ring is no longer significant, only a tendency of E_p to decrease, similar to that observed in the series of linear polysilanes, was pointed out; however, the numerical values of the potentials were not reported.[176]

Preparative oxidation of cyclopolysilanes is accompanied by ring opening yielding intermediate **43** in which the charge and spin densities are separated in space.[176, 177]



43

When the process is carried out in the presence of Et_4NBF_4 in CH_2Cl_2/MeCN (4 : 1), α,ω-difluorinated products **44** are formed.[176]



44

It was assumed that ring opening occurs *via* the formation of the intermediate radical cation,[176, 177] although the variation of the E_p potentials in various solvents [177] (MeCN/CH_2Cl_2) indicates that this is rather an electrochemically irreversible process.

3. Disilenes

Sterically hindered disilenes are irreversibly oxidised in THF at a stationary platinum electrode at close potentials (Table 8), which indicates that the HOMO energy levels of these compounds are close to one another.[153] Since the interaction between the occupied π orbitals of the disilene and the aromatic fragments in tetraaryldisilenes is weak due to the substantial difference between their energies, the redox properties and the low oxidation potentials are determined by the π-electrons of the disilene bridge.

Table 8. Potentials of the oxidation peaks of disilenes $R^1R^2Si{=}SiR^1R^2$ in THF/0.1 M Bu_4NPF_6 at a Pt electrode; $v = 0.2$ V s^{-1}.

R^1	R^2	E_p/ V *vs* SCE
Mes	Mes	0.38
2,4-$Me_2C_6H_4$	2,4-$Me_2C_6H_4$	0.47
4-Bu^t-2,6-$Me_2C_6H_3$	4-Bu^t-2,6-$Me_2C_6H_3$	0.48
Mes	Bu^t	0.54
Mes	1-Adamantyl	0.36

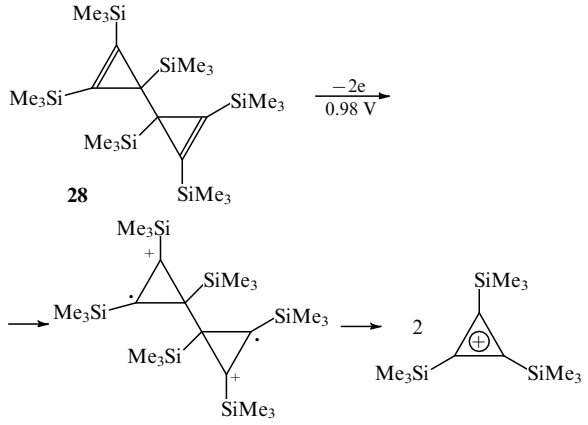
4. Tetraorganosilanes

The potential of oxidation of Et_4Si ($E_p = 2.56$ V *vs* SCE), like potentials of alkyl derivatives of metals (Ge, Sn, Pb, Hg) obey a linear correlation with the gas-phase IP.[178] Since the steric factors have no influence on the linear ratio of free energies, the process is assumed to occur as an outer-sphere electron transfer followed by a fast chemical reaction, the rate of which is higher than the rate of the transfer of an electron to the radical cation; this accounts for the fact that the process as a whole is chemically irreversible.

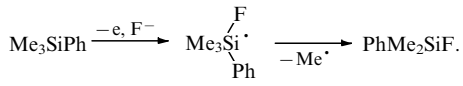
Electrooxidation of Ph_4Si **46** ($E_{1/2} = 2.1$ V *vs* Ag/0.01 M Ag^+), $PhSiMe_3$ and $Ph_2Si(OH)_2$ in $CH_2Cl_2/AlCl_3$ at a Pt electrode results in black polymeric precipitates being formed on the surface

of the electrode; these precipitates have been found to incorporate conjugated aromatic fragments.[179] When $PhSiH_3$ is oxidised at a rotating disc Pt electrode, an oxidation peak (E_p = 2.1 V) associated with the passivation of the electrode can be observed. Preparative electrolysis afforded a black polymer similar to that resulting from oxidation of the silane **46**, because disproportionation of the initial silane in the presence of $AlCl_3$ gives rise to the silane **46** and SiH_4. Oxidation of 2-methyl-2-vinyltetraphenylcyclotrisiloxane gives the same conductive polymer as the oxidation of the silane **46**, since the latter is one of the oxidation products of this phenylcyclotrisiloxane.

Hexakis(trimethylsilyl)-3,3′-bicyclopropenyl **28** undergoes irreversible two-electron oxidation in $MeCN/(C_6H_{13})_4NClO_4$ being thus converted into a biradical dication, which decomposes to give two cyclopropenyl cations.[180]



Oxidation of a number of tetraalkyl- and trialkylaryl-silanes at a controlled potential in the $MeCN/Et_4NF \cdot 3HF$ system at Pt electrodes results in the anodic substitution of fluorine for one of the alkyl groups in the silane (Table 9).[181] In the presence of F^- anions, the oxidation potential of trimethylphenylsilane decreases by 300 mV (+2.6 and +2.3 *vs* Ag/0.1 M $AgNO_3$ with Et_4NClO_4 and $Et_4NF \cdot 3HF$, respectively), which is due to the F^--assisted single-electron oxidation of the organosilane. After the formation of a Si–F bond, the intermediate radical with pentacoordinated silicon eliminates the most stable alkyl radical.



Alkyl radicals with $E_{1/2} > 2.3$ V ($Me^\bullet$) either dimerise or add an $H^\bullet$ atom, whereas the radicals with $E_{1/2} < 2.3$ V ($Et^\bullet$, $PhCH_2^\bullet$) are oxidised at the anode to give the corresponding carbocations.

Silanes with a Si–H bond can also be fluorinated by an electrochemical procedure;[181] however, in the presence of $Et_4NF \cdot 3HF$, catalytic protodesilylation of R_3SiH to give R_3SiF occurs at a Pt electrode, in parallel with the electrochemical process.

Redox processes involving niobocene complexes with silicon-containing cyclopentadienyl rings and the EPR spectra of their cationic forms have been described.[182]

Table 9. Anodic fluorination of organosilanes (Q = 1.2 F mol^{-1}).[181]

Tetraorgano-silane	Fluorosilane	Yield (%)	Products formed from R•
$PhSiMe_3$	$PhSiMe_2F$	80	CH_4, C_2H_6
p-$FC_6H_4SiMe_3$	p-$FC_6H_4SiMe_2F$	80	CH_4, C_2H_6
$PhCH_2SiMe_3$	Me_3SiF	50	PhCHO
$PhCH_2SiEt_3$	Et_3SiF	70	PhCHO
Et_3SiMe	$MeSiEt_2F$ +	45	EtF, $CH_2=CH_2$
	+ Et_3SiF	5	CH_4, C_2H_6

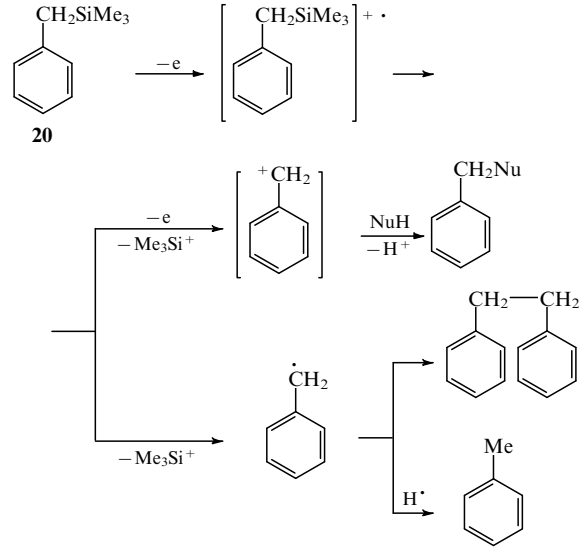
5. Allyl and benzylsilanes

A distinctive feature of compounds containing a silicon-containing substituent in the β-position with respect to the double bond is $\sigma-\pi$-conjugation between the bonding σ orbital of the Si–C bond and π-electrons of the double bond. As a consequence, the energy of the HOMO of the unsaturated fragment increases,[183,184] and, hence, the potentials of electrooxidation of these compounds are markedly lower than the oxidation potentials of compounds that do not contain this fragment (Table 10). Another consequence of the β-effect is that the Si atom in the radical cations derived from benzyl- and allylsilanes becomes more electrophilic. This facilitates cleavage of the C–Si bond (Me_3Si^+ is a 'super-proton') and the occurrence of nucleophilic reactions involving this centre.[185–191]

The oxidation potentials of β-silyl-substituted unsaturated compounds obey a linear correlation with their first IP with a regression slope of less than unity.[195]

In a study of oxidation of a series of benzyltrialkylsilanes substituted in the ring, it has been shown that in the case of p-$MeOC_6H_4CH_2SiPr_3$ and p-$MeOC_6H_4CH_2SiMe_3$, this process involves the formation of a radical cation that was detected by voltammetry.[191] In a non-nucleophilic medium, the potential-determining reaction between the radical cations of benzylsilanes is first order (rupture of the C–Si bond). The reactivity of benzylsilanes is described by a three-parameter model that takes into account the polar effect of the substituent in the aromatic ring and also the inductive and steric effects of the alkyl groups at the Si atom. The relative sensitivity of the potential-determining reaction (ρ_c) to the inductive effect of alkyl substituents is higher than the sensitivity of E_0 (ρ_π), and this accounts for the apparent opposite influence of the $+I$ effect of alkyl groups on the effective potential E_p ($\rho_I < 0$).

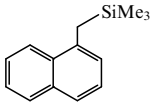
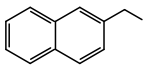
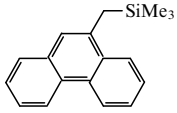
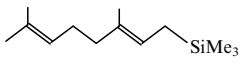
Oxidation of trimethylsilylmethanes with π-electron substituents (benzyl, allyl) in the presence of alcohols, carboxylic acids [189] or water [187] results in the formation of anodic substitution products incorporating C–O bonds. It is assumed that initially, the benzyltrimethylsilyl radical cation is formed; subsequently, it loses the Me_3Si^+ fragment and the resulting radical is oxidised to a benzyl cation.



When the process is carried out at a glassy carbon electrode (which is favourable for the adsorption of aromatic fragments) in the presence of Et_4NOTs (the surface activity of TsO^- is lower than that of ClO_4^-), dibenzyl and toluene resulting from transformations of the benzyl radical are also formed.

In the absence of additional nucleophiles in the solution, an unoxidised benzyltrimethylsilane molecule can act as a nucleophile. For example, oxidation of benzyltrimethylsilane **20** in the

Table 10. Potentials of electrooxidation of β-silyl-substituted π-systems.

Compound	E_p /V (*vs* SCE, υ = 0.1 V s^{-1})	$E_{1/2}$ /V (*vs* Ag/Ag^+)	Ref.
$PhCH_2SiMe_3$	1.38 [a]		189, 192
	1.84 [b]		186
		1.48	188
		1.22 [c]	193
		1.40 [c]	194
	1.627		191
p-$MeC_6H_4CH_2SiMe_3$	1.17 [a,b]		189, 192
	1.56		191
o-$MeC_6H_4CH_2SiMe_3$	1.18 [a]		192
p-$ClC_6H_4CH_2SiMe_3$	1.66		191
m-$Me_3SiCH_2C_6H_4CH_2SiMe_3$	1.60		195
	1.12 [a]		192
		1.14 [d]	196
p-$Me_3SiCH_2C_6H_4CH_2SiMe_3$	1.06 [a]		192
		0.96 [d]	196
o-$Me_3SiCH_2C_6H_4CH_2SiMe_3$	1.13 [a]		192
		1.08 [d]	196
p-$MeOC_6H_4CH_2SiMe_3$	1.20 [a]		192
	1.34		191
m-$MeOC_6H_4CH_2SiMe_3$	1.55		191
o-$MeOC_6H_4CH_2SiMe_3$	1.37 [a]		192
p-$MeC_6H_4CH_2SiEt_3$	1.58		191
p-$MeOC_6H_4CH_2SiPr_3$	1.40		191
$PhC(SiMe_3)_3$	1.70		195
p-$(Me_3Si)_3CC_6H_4C(SiMe_3)_3$	1.36		195
$(Me_3SiCH_2)_2C=C(CH_2SiMe_3)_2$	0.87		195
p-$MeOC_6H_4C(O)SiMe_3$	1.84 [e]		141
p-$Bu^tC_6H_4C(O)SiMe_3$	1.90 [e]		141
m-$MeC_6H_4C(O)SiMe_3$	1.75 [e]		141
$PhC(O)SiMe_3$	1.88 [e]		141
m-$CF_3OC_6H_4C(O)SiMe_3$	2.10 [e]		141
p-$CF_3OC_6H_4C(O)SiMe_3$	2.20 [e]		141
$PhC(O)SiPhMe_2$	2.02 [e]		141
$CH_2=CHCH_2SiMe_3$		1.58	193
		1.70 [d,e]	197
$CH_2=CMeCH_2SiMe_3$		1.28	193
$Me_2C=CHCH_2SiMe_3$		0.92	193
$PhCH=CHCH_2SiMe_3$		0.91 [d]	185
		0.96 [d]	185
		0.96 [d]	185
		0.94 [d]	185
	1.3 [b,e]		187

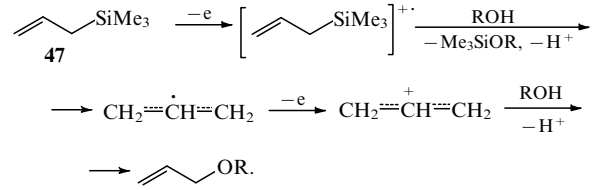
[a] Referred to sat. $Ag/AgNO_3$, $MeCN/Bu_4NBF_4$, Pt; [b] the υ value was not given; [c] calculated from IP_1 *vs* Ag/Ag^+; [d] $E_{p/2}$ /V is given ; [e] *vs* Ag/AgCl.

CH_2Cl_2/Bu_4NClO_4 in a divided cell at a Pt anode gives benzyl(trimethylsilylmethyl)benzene in 30% yield.[189]



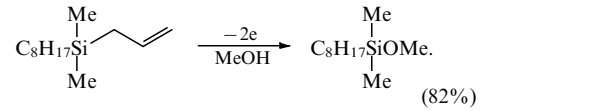
20

Oxidation of allylsilanes, in particular, allyltrimethylsilane **47**, also involves the intermediate formation of a cation, which reacts with a molecule of an O-nucleophile giving the final product.[187]



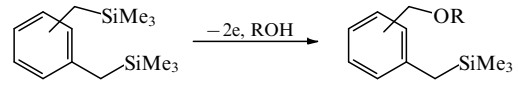
47

The regioselectivity of the formation of products, which does not depend on the nature of the nucleophile but is governed by the substituents at the double bond is evidence supporting the above mechanism. In the only study [187] where the subsequent transformations of the silyl fragment have been followed, it has been shown that alkoxytriorganosilane is formed as the final product.



(82%)

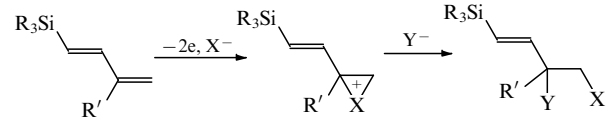
When α,α′-bis(trimethylsilyl)xylenes are oxidised in the presence of alcohols, only one Me_3Si fragment undergoes anodic substitution.[192] No α,α′-dialkoxylated xylenes or products of alkoxylation of the ring are formed. This selectivity of the reaction is due to the fact that the remaining Me_3Si group stabilises the cationic intermediate, and the oxidation potential of the monoalkoxylated product is more positive than that of the initial bis(trimethylsilyl)xylene.



The abstraction of a trimethylsilyl fragment leads to a cation, in which the positive charge is localised on the benzylic carbon atom and does not migrate to the β-position of the ring. This is confirmed by the fact that the reaction products contain no *p*- or *o*-quinodimethanes.[192]

6. 1-Trialkylsilyl-1,3-alkadienes

Oxidation of 1-trialkylsilyl-1,3-alkadienes in solutions of alkali metal chlorides or bromides in water–organic media [198] yields only kinetically and thermodynamically controlled 3,4-adducts.

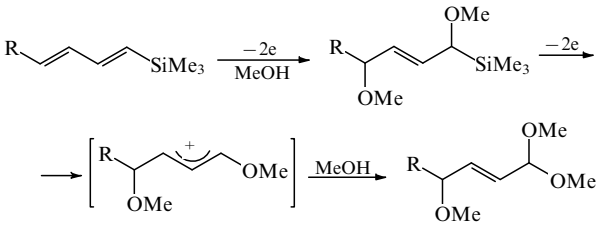


R = Me, Et; R′ = H, Me; X = Cl, Br;
Y = Cl, Br, OH, OMe, OEt, OAc.

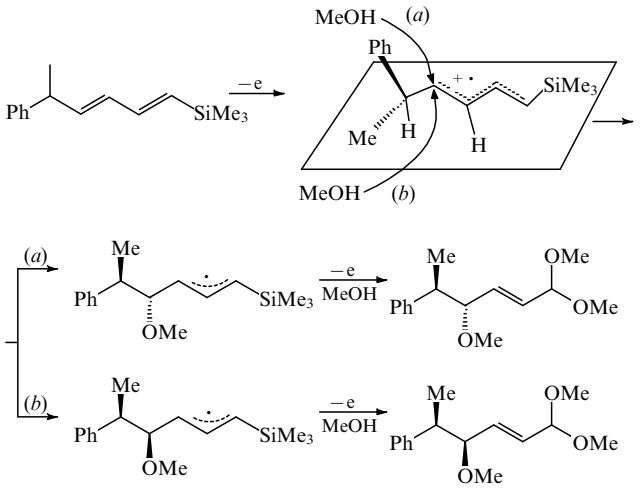
The authors cited explained the high regioselectivity of electrochemical halogenation by the occurrence of single-electron reduction of the unsaturated molecule to give a radical cation, the spin density of which, as shown by extended Hückel quantum-chemical calculations, is mostly localised on the terminal carbon atom of the conjugated system. However, according to the Markovnikov rule, regioselectivity of this addition should apparently be governed by the possibility of resonance stabilisation of the cationic intermediate rather than by the spin density.

Oxidation of 1-trimethylsilyl-1,3-dienes in methanol [199] at a carbon electrode gives rise to α,β-unsaturated 1,1,4-trimethoxy-

alkenes (29% – 76%). The latter are readily hydrolysed with dilute HCl to the corresponding α,β-unsaturated aldehydes.



The overall process requires ~4.2 F of electricity per mole of the diene; the first half of the electricity passed is consumed in the formation of the silylated allylic intermediate, while the rest of the electricity is spent for its further oxidation, similarly to the process described in another study.[187] Only *trans*-products are formed. The diastereoselectivity of the oxidative methoxylation of 5-phenyl-1-trimethylsilyl-1,3-hexadiene is due to the fact that methanol preferably attacks the radical cation from its less sterically hindered side.[199] The overall yield of the stereomers is 53%.

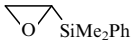
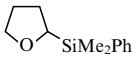
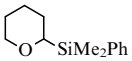
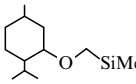
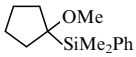
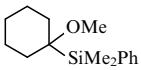
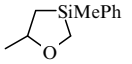
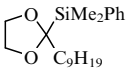
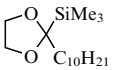
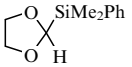
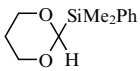


7. β-silyl ethers

The main characteristic feature of compounds containing silicon in the β-position with respect to the heteroatom (O, S, N), so that its *p* orbitals can be involved in conjugation with a π-system (if it is present in the molecule), is that the σ_{C-Si} bonding orbital interacts fairly strongly with the lone electron pair of the heteroatom. Although this effect depends on the nature of the heteroatom and on the mutual arrangement of the interacting orbitals, it usually markedly increases the HOMO energy of the molecule and thus facilitates its electrooxidation (E_{Ox} decreases by 200 – 800 mV). Owing to this effect, the silicon atom becomes more electrophilic, especially after the transfer of an electron; as a result, nucleophilic reactions at this site occur at high rates.

Quantum-chemical calculations of HOMO energies as functions of the Si – C – O – C torsional angle have shown [200] that when this angle is equal to 0° (a configuration with perpendicular arrangement of the C – Si bond with respect to the *p* orbital of oxygen), the HOMO level is relatively low and mostly corresponds to the σ orbital. The energy of the HOMO increases as the torsional angle increases and reaches its maximum at an angle of ~95°. In this configuration, the C – Si bond and the oxygen *p* orbital are nearly parallel and can overlap efficiently with each other. The maximum destabilisation of the HOMO by the silicon atom in this configuration is 0.9 eV. The results of quantum-chemical calculations are in full agreement with the character of variation of the oxidation potentials (E_p) of alkoxysilanes in which rotation around the C – O bond is hindered and the dihedral angle has a fixed magnitude (cyclic silicon-containing ethers in Table 11). The introduction of one more silyl group in the molecule results in further decrease in E_p indicating that the HOMO level becomes even higher. An additional oxygen-containing substituent also decreases the oxidation potential (presumably, owing to an increase in the statistical weight of conformers that are favourable for electron transfer) (Table 11).[200]

Table 11. Oxidation potentials (*vs* Ag/AgCl) of acylsilanes and alkoxysilanes.

Compound	E_p /V	$E_{1/2}$ /V	Ref.
$C_{10}H_{21}C(O)SiMe_3$	1.45		201
		1.62	202
$C_9H_{19}C(O)SiMe_3$		1.37 [a]	203
$C_9H_{19}C(O)SiPhMe_2$		1.38 [a]	203
$C_9H_{19}C(O)SiPh_2Me$		1.40 [a]	203
$C_9H_{19}C(O)SiPh_3$		1.46 [a]	203
$C_8H_{17}CH(OMe)SiMe_3$	1.6		201
$MeOCH_2SiMe_3$	1.9		200
		1.85	202, 204
$MeOCH(SiMe_3)_2$		1.54	202, 204
$Me_3SiCH_2O(CH_2)_2OCH_2SiMe_3$		~1.9	204
$C_7H_{15}CH(SiPhMe_2)OMe$	1.60 [b]		205
$C_7H_{15}CH(SiMe_3)OMe$	1.72 [b]		205
$C_7H_{15}CH(SiPhMe_2)OSiMe_2Bu^t$	1.95 [b]		205
$C_7H_{15}CH(SiPhMe_2)OH$	1.70 [b]		205
$C_8H_{17}CH(SiPhMe_2)OH$	1.70		200
$HOC_6H_4OCH_2SiMe_3$		1.07 [c]	206
$MeOC_6H_4OCH_2SiMe_3$		1.20 [c]	206
$NCC_6H_4OCH_2SiMe_3$		1.02 [c]	206
$O_2NC_6H_4OCH_2SiMe_3$		2.06 [c]	206
$ClO_2SC_6H_4OCH_2SiMe_3$		2.14 [c]	206
	2.15 [b]		205
		1.84	200
	1.67 [b]		205
		1.53	200
	2.08 [b]		205
		1.70	200
		1.83	202, 204
	1.63	1.50	200
	1.45	1.38	200
	1.82		200
$C_{12}H_{25}C(SiMe_3)_2OMe$	1.48		200
$C_{12}H_{25}C(OMe)_2SiMe_3$	1.50		200
	1.47	1.27	200
	1.45	1.36	200
	1.50	1.55	200
	2.0		200

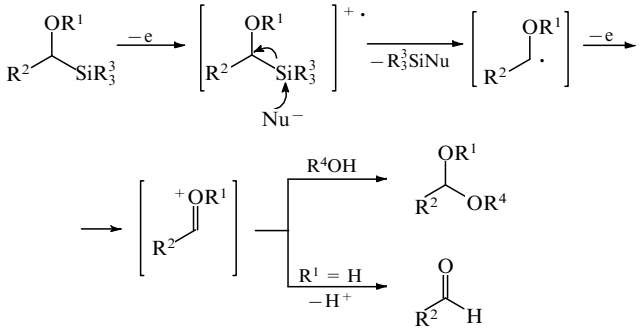
[a] $\upsilon = 10$ mV s^{-1}; [b] $\upsilon = 50$ mV s^{-1}; [c] *vs* SCE.

Anodic processes involving β-silyl ethers are accompanied, as a rule, by oxidative rupture of the C_α – Si bond and by the addition

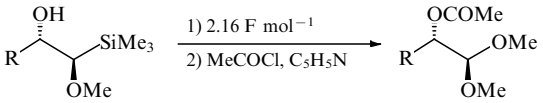
of the nucleophile present in the solution to the resulting carbocation.

Oxidation of alkoxysilanes has been assumed[205] to occur according to Scheme 4.

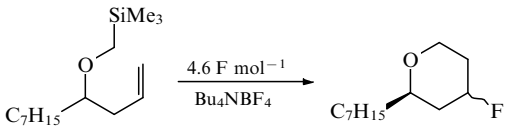
Scheme 4



This process was used as one of the stages in the iteration synthesis of optically active polyols.[206]

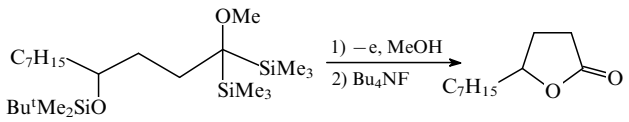


Electrooxidation of unsaturated α-silyl-substituted ethers results in the formation of a new C–C bond with the closure of a ring.[207] This process conducted in the presence of PF_6^- or BF_4^- gives rise to cyclic fluorinated *cis*- and *trans*-derivatives.

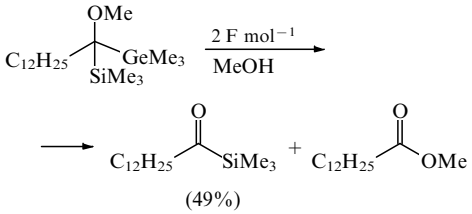


(68%)
cis : *trans* = 1.2 : 1

A β-gem-disilane methoxymethyl group acts as a sort of 'latent carboxyl', which can be activated by electrooxidation.[208] For example, oxidation of gem-disilane containing a protected (as a *tert*-butyldimethylsilyl ether) hydroxyl group is accompanied by cyclisation. This reaction has been used at the final stage of the synthesis of γ-undecalactone.[208–210]



Oxidation of alkoxysilanes containing a trimethylgermyl group, which is more easily eliminated as a carbocation, makes it possible to prepare acylsilanes.[202] Tridecanoyltrimethylsilane is formed (yield 49%) together with some methyl tridecanoate; the latter results from oxidation of the acylsilane itself under galvanostatic conditions and is formed in 96% yield when 5 F mol^{-1} of electricity is passed through the solution.

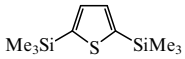
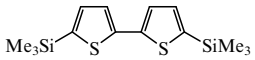
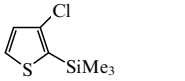
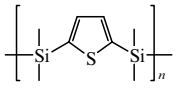


(49%)

8. β-Silyl sulfides

The electronic effects acting in the molecules of ethers are also typical of the molecules of β-silyl sulfides, but in the latter case, they are markedly weaker, because the 3*p* energy level of the S atom is much higher than those of the orbitals forming the C–Si bond, and these orbitals cannot interact as efficiently as those in the molecules of the oxygen analogues. Reactions involving β-silyl sulfides are similar to the corresponding reactions of β-silyl ethers and are determined by the ease of elimination of the trimethylsilyl group as a cation during anodic substitution.

Table 12. Oxidation potentials of β-silyl sulfides and thiophenes.

Compound	E_p /V [a] (*vs* Ag/AgCl)	Ref.
$PhSCH_2SiMe_3$	1.10	200
	(1.15)	194
$MeSCH(Ph)SiMe_3$	0.99 [b]	189
$C_8H_{17}CH(SPh)SiMe_3$	1.10	200
	1.25	210
$C_8H_{17}C(SPh)_2SiMe_3$	1.20	200
$C_8H_{17}C(SiMe_3)_2SPh$	1.10	200
$RHSiMe_3$ [c]	0.99 [d]	211
RBu^tSiMe_3 [c]	0.95 [d]	211
$RPhSiMe_3$ [c]	0.85 [d]	211
$R(SiMe_3)_2$ [c]	0.70 [d]	211
$R(SnMe_3)SiMe_3$ [c]	0.44 [d]	211
	1.92 [e]	212
	1.14 [e]	212
	1.92 [e]	212
	0.85 [e]	212
	2.05 [e]	216

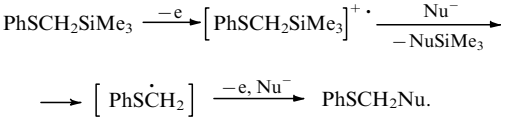
[a] $E_{1/2}$ *vs* SCE are given in parentheses; [b] *vs* $Ag/AgNO_3$ (sat.);

[c] R =  ; [d] *vs.* Ag/0.1 M $AgNO_3$; [e] *vs* SCE.

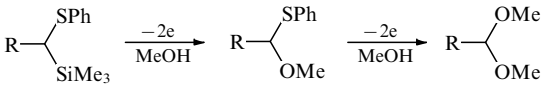
The oxidation potentials of β-silyl-substituted sulfides are somewhat lower than those of unsaturated compounds. The introduction of additional organylthio- or trimethylsilyl groups does not cause further decrease in E_p (Table 12).

Alkoxylation and acetoxylation of β-silyl phenyl sulfides occurs during their anodic oxidation in the presence of alcohols and carboxylic acids (Scheme 5).[189,197,207] The yields of the reaction products vary depending on the nature of the nucleophile (25%–66%).

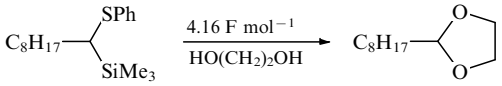
Scheme 5



1-Phenylthio-1-trimethylsilylalkanes are oxidised in the presence of monohydric alcohols (overall, 4 F mol^{-1} of electricity is required) to give the corresponding acetals in high yields (64%–84%).[210] The process includes two stages. Initially, 1-methoxy-1-phenylthioalkane is formed (2 F mol^{-1}); it can be detected during the reaction by chromatography or isolated from the reaction mixture. The subsequent two-electron oxidation of this compound is accompanied by rupture of the C–S bond and affords acetals.

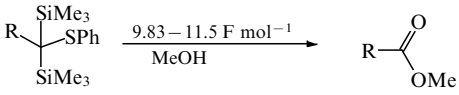


Conduct of the process in the presence of dihydric alcohols makes it possible to synthesise cyclic acetals.[210]

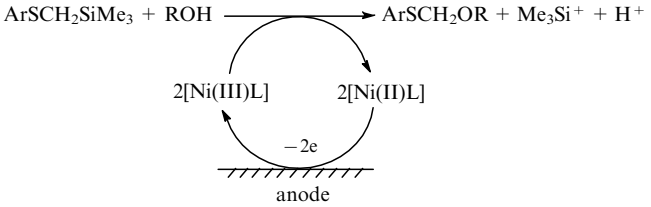


(60%)

Upon electrooxidation in MeOH, 1-phenylthio-1,1-bis(trimethylsilyl)alkanes are converted into the corresponding methyl carboxylates.[209]

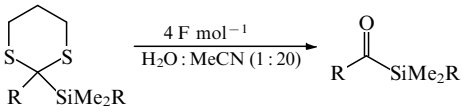


Alkoxylation of β-trimethylsilyl aryl sulfides, similar to the process shown in Scheme 5, has been accomplished using homogeneous redox catalysis by a cyclam complex of Ni(III).[213]



Ar = *p*-Tol, Ph; L is cyclam.

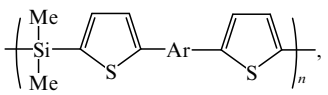
A trimethylsilyl group present at the 2-position of 1,3-dithianes somewhat decreases the potential of their irreversible oxidation but to a lesser extent than an alkyl group (Table 12).[211] The relatively weak effect of the β-Me_3Si group is due to its equatorial position. When two trimethylsilyl groups are attached to the C(2) atom in 1,3-dithianes, the orientation of one of them becomes favourable for interaction of its σ_{C-Si} orbital with the 3*p* orbital of the S atom, which facilitates oxidation of the dithiane. This effect is even more pronounced for a Me_3Sn substituent, because the energy of σ_{C-Sn} bond is closer to that of the 3*p* orbital of the S atom. Oxidation of 2-trialkylsilyl-1,3-dithianes does not involve the C–Si bond; the yields of the corresponding acylsilanes are 70%–96%.[214] If the substituent R contains an unsaturated fragment, the reaction affords α,β-unsaturated acylsilanes.



R = Me, Bu^t.

In the oxidation of aryl trimethylsilylmethyl selenides,[121,217] the β-effect of the Me_3Si group changes in principle the character of the potential-determining reaction of the electrically generated radical cations (E + C_{DIM} + Cl instead of E + Cl + E as for aryl alkyl selenides), despite the fact that this effect is the least pronounced in the series of β-silylated isostructural compounds of Group VIA elements ($\Delta E_{1/2} \cong 50$ mV). Oxidation of aryl trimethylsilylmethyl selenides and sulfides in a non-nucleophilic medium[217] is accompanied by rupture of the Se–C_{sp^3} and S–C_{sp^3} bonds rather than the Si–C_{sp^3} bond (*cf.* Refs 189, 197, 207 and 210).

The voltammetric behaviour of α,α′-silyl-[212] and β-silyl-substituted polythiophenes,[215] polythiophenes based on tetrathienylsilane $(C_4H_3S)_4Si$,[216] polymers with units

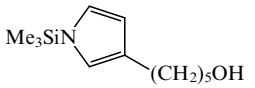
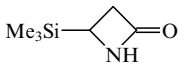


(where Ar are mono- or polynuclear substituted aromatic fragments)[218] and polymers prepared from 2,5-bis(trimethylsilyl)-thiophene, bis(2-thienyl)dimethylsilane, 1,2-bis(2-thienyl)tetramethyldisilane and bis(2-thienyl)diphenylsilane[219] have been reported. Electropolymerisation of silyl-substituted thiophenes, like polymerisation of unsubstituted thiophene, has been carried out by galvanostatic oxidation of the monomers in solution in nitrobenzene.[212,215,216,219]

9. β-Silylamines and carbamates

Based on the voltammetric behaviour of silylated cyclic amines derived from pyrrolidine, piperidine and perhydroazepine,[220] ($n = 1$; $i/v^{1/2}$ = const, the absence of reversibility of the oxidation peak at the sweep rate $v = 1$ V s^{-1} at -35 °C), it has been suggested that a low-stability radical cation is formed. Substituents at the Si atom, the size of the ring and the presence of methyl groups have only a slight influence on E_p (Table 13), whereas in

Table 13. Oxidation potentials of silyl-substituted amines (*vs* SCE).

Compound	E_p/ V	$E_{p/2}$/ V	Ref.
$PhNHCH_2SiMe_3$		0.44 [a]	194
$Ph_2NCH_2SiMe_3$		0.41 [a]	194
$PhNHCH_2SiMe_2Ph$		0.45 [a]	194
$PhNHCH_2SiMeBu_2$		0.48 [a]	194
$PhNHCH_2SiMe_2(C_8H_{17})$		0.48 [a]	194
p-$MeOC_6H_4NHCH_2SiMe_3$		0.26 [a]	194
$Ph_2N(CH_2)_2SiMe_3$		0.74 [a]	194
$PhNH(CH_2)_2SiMe_3$		0.60 [a]	194
$Ph_2N(CH_2)_3SiMe_3$		0.75 [a]	194
$Me(Me_3SiO)_2SiCH_2NC_4H_8$	0.56		220
$Me(Me_3SiO)_2SiCH_2NC_6H_{12}$	0.50		220
$Me(Me_3SiO)_2Si(CH_2)_2NC_4H_8$	0.77		220
$Me(Me_3SiO)_2Si(CH_2)_3NC_6H_{12}$	0.72		220
Me_3SiR [b]	1.00		220
$Me_3SiCH_2NC_5H_{10}$	0.65		220
Me_3SiCH_2R [b]	0.62		220
$Me_3Si(CH_2)_2R$ [b]	0.90		220
$Me_3Si(CH_2)_2R$ [c]	0.90		220
$Me_3Si(CH_2)_3R$ [b]	0.90		220
$Me_3Si(CH_2)_3R$ [c]	0.90		220
$Me_3SiNC_4H_4$	1.35		221
$Me_3SiNC_5H_{10}$	1.00		220
	1.173 [d]		221
$PhNHSiMe_3$		0.73 [d]	194
Et_3SiNEt_2		1.23	222
$Me_2(NC_5H_{10})SiC\equiv CH$		1.29	222
$MeVin(NC_5H_{10})SiC\equiv CH$		1.00	222
$Me_2Si(NEt_2)_2$		1.35	222
$MeVinSi(NEt_2)_2$		1.08	222
$MeSi(NEt_2)_3$		1.12	222
$VinSi(NEt_2)_3$		0.98	222
$Ph(CH_2)_2N(CO_2Me)CH_2SiMe_3$	1.45		200, 223
	1.75 [e]		224
Silatranes	1.4–1.8		225

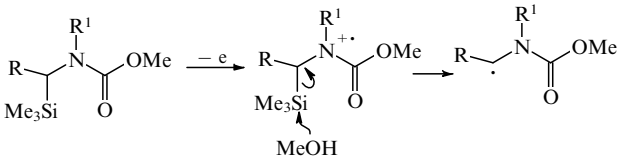
[a] $v = 20$ mV s^{-1}; [b] R = ; [c] R = ; [d] E_0; [e] *vs* Ag/AgCl.

the presence of a CH_2 fragment between the Si and N atoms, the E_p value becomes 1.3–1.4 V lower than those for compounds containing no silyl substituent.

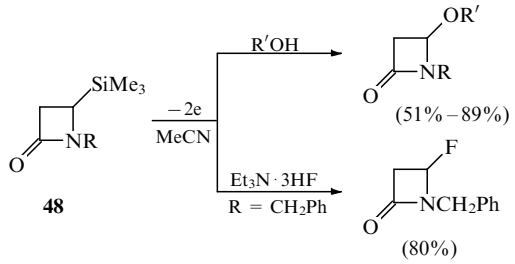
This type of variation of the potentials, which is also typical of aromatic *N*-(trimethylsilylmethyl)amines,[194] is associated with the resonance interaction between the trimethylsilylmethyl group and the cationic centre of the radical cation induced by the charge transfer. This interaction is enhanced on passing from the initial compound to the transition state.

The decrease in the potentials of oxidation of nitrogen-containing compounds following the introduction of a β-trimethylsilyl group is relatively small for amines and is more significant for carbamates.[200] This manifestation of the β-effect is due to the fact that conjugation with the carbonyl group decreases the energy of the *p* orbital of the nitrogen atom in the molecules of carbamates and thus facilitates its more efficient overlap with the bonding σ_{C-Si} orbital.

Preparative processes involving this type of compound are similar to those involving β-silyl ethers and sulfides. They include anodic substitution of an appropriate nucleophile for the trimethylsilyl group. The carbamates activated by a silyl group undergo electrooxidation with cleavage of the C–Si bond and regioselective methoxylation of the α-carbon atom.[223] The corresponding α-methoxycarbamates are obtained in yields of 68%–100%.



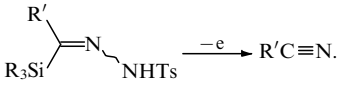
N-Substituted 4-trimethylsilylazetidin-2-ones **48** are also converted into alkoxylated and acyloxylated products. When $Et_3N \cdot 3HF$ is added to the solution of an electrolyte, fluorinated products of anodic substitution are formed.[224]



R = H, $PhCH_2$;
R′ = Ac, Me, CH_2CHMe_2, $CH_2CH=CH_2$, $(CH_2)_2CH=CH_2$, $PhCH_2$.

Oxidation of [(*N*-methylbenzylamino)methyl]trimethylsilane in the presence of MeOH or EtOH is the only example of reaction in which the C–Si bond in a β-silyl-substituted nitrogen-containing compound does not undergo oxidative rupture but, instead, the C–N bond is cleaved.[189] This leads to bis(benzylmethylamino)methane rather than to alkoxylated products.

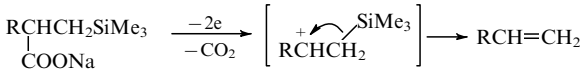
Electrooxidation of tosylhydrazones of acylsilanes in an undivided cell affords the corresponding nitriles.[203] The process requires 3.2–4.4 F mol^{-1} of electricity.



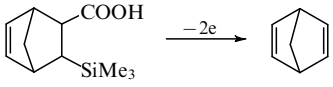
In a divided cell, the formation of nitriles requires a catalytic amount of electricity (Q = 0.26–0.8 F mol^{-1}); the yields of nitriles are markedly higher.

10. β-Silyl-substituted derivatives of carboxylic acids

Anodic oxidation of β-trimethylsilyl-substituted carboxylic acids affords only terminal alkenes as the final products, because at the carbocation stage resulting from oxidative decarboxylation of the initial molecule, the process is controlled by the trimethylsilyl group.[226]

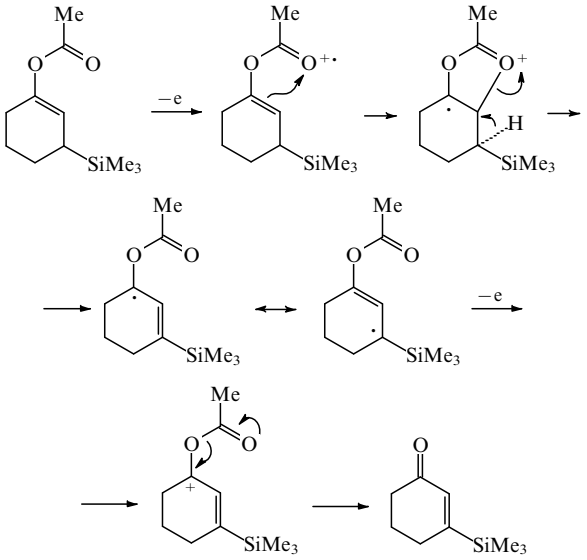


Oxidative decarboxylation–desilylation has been used in the synthesis of 2,5-norbornadiene.[158]



11. β-Silyl-substituted enol acetates

Oxidation of β-silyl-substituted enol acetates yielding α,β-unsaturated β-silylcycloalkenones is the only known reaction in which the trimethylsilyl group does not undergo oxidative elimination from the allylic position.[227]



The process is believed to include cyclisation of the primary radical cation, which is converted by deprotonation into an α-radical stabilised by the silicon atom. This effect, together with the antiparallel arrangement of the C_β–H bond with respect to the C–O^+ bond being cleaved in the oxonium intermediate, results in the rupture of the C_β–H bond instead of the C_β–Si bond which is cleaved in the case of allyl- and benzyl-silanes.

12. Siloxy-derivatives

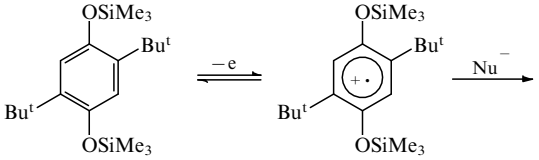
The oxidation potentials of trialkylsiloxybenzenes are virtually determined by the first siloxy-group attached to the aromatic ring. The introduction of the second group of this type changes E_p only slightly [228] (Table 14).

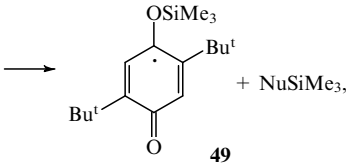
Table 14. Oxidation potentials of trialkylsiloxybenzenes $R^1R^2R^3R^4C_6H_2$ in MeCN/0.1 M $LiClO_4$ (Pt electrode, v = 0.1 V s^{-1}).

R^1	R^2	R^3	R^4	E_p/ V (*vs* SCE)
1-Me_3SiO	4-Me_3SiO	H	H	1.10
1-Me_3SiO	4-Me_3SiO	2-Cl	H	1.25
1-Me_3SiO	4-Me_3SiO	2-Bu^t	5-Bu^t	1.05
1-Bu^tMe_2SiO	4-Bu^tMe_2SiO	2-Bu^t	5-Bu^t	1.07
1-Me_3SiO	4-Me_3SiO	2-MeO	H	1.05
1-Me_3SiO	4-MeO	H	H	1.14
9-Me_3SiO [a]	10-Me_3SiO	H	H	0.78

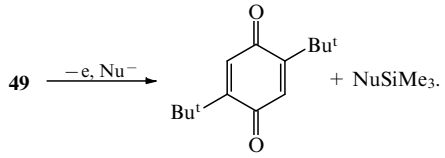
[a] 9,10-Bis(trimethylsiloxy)anthracene.

Trimethylsilyl ethers of hydroquinone lose Me_3Si fragments during oxidation and, *via* the intermediate formation of radicals **49**, they are converted into the corresponding quinones in 65%–92% yields.[228]

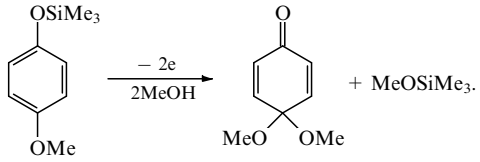




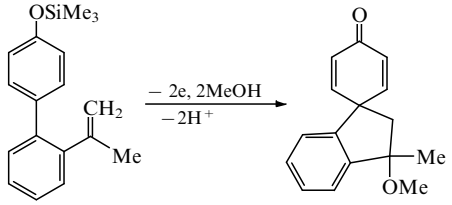
49



Under similar conditions, monosilylated 4-methoxy-1-(trimethylsiloxy)benzene gives rise to 4,4-dimethoxy-2,5-cyclohexadienone (yield 99%).[228]

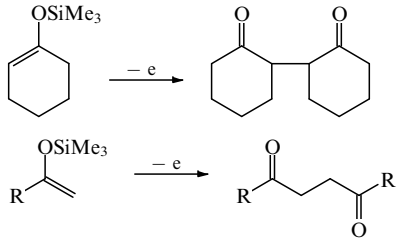


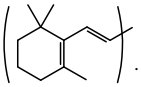
Anodic oxidation of the trimethysilyl ether of 4-(2′-alkenylphenyl)phenol **50** carried out in MeOH (Pt anode, 0–10 °C) is accompanied by the elimination of the trimethylsilyl group and by intramolecular cyclisation involving the double bond of the alkenyl substituent.[229]



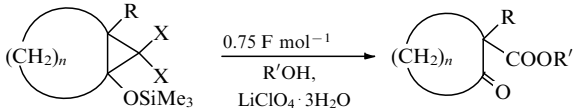
50 (73%)

Silyl ethers of enols undergo electrooxidation to give γ-diketones. The latter result from dimerisation of either the primary radical cations or the radicals arising after the oxidative rupture of the Si–O bond.[230]



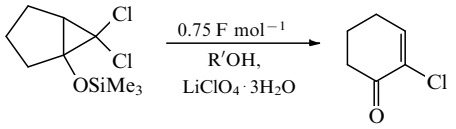
R = .

β-Oxoesters are formed in the electrooxidation of 1-trimethylsilyloxybicyclo[*n*.1.0]alkanes[231] in ethanol in the presence of $Fe(NO_3)_3$ in a divided cell at a Pt electrode.



n = 4, 5, 10; R = H, Me; X = H, Br, Cl.

Under the same conditions, 6,6-dichloro-1-trimethylsilyloxybicyclo[3.1.0]hexane yields only the product of ring expansion.



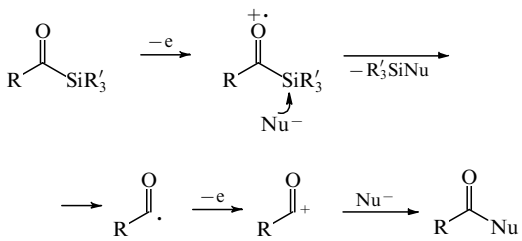
It was noted that the maximum yield of β-oxoesters is observed at −13 to −10 °C, but neither the reason for this effect nor the role of Fe(III) were discussed.

13. α-Silyl esters

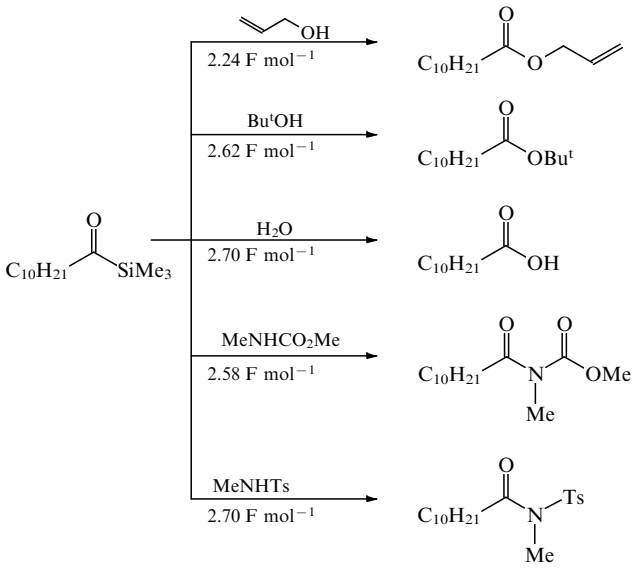
The oxidation potentials of acylsilanes in which the silicon atom is attached to an electron-withdrawing carboxylic group are smaller than the potentials of the corresponding alkoxysilanes (see Table 11).[201,203] In terms of the concept of σ_{C-Si}–p_O conjugation, this is explained by the rigid fixing of the orbitals in the carbonyl compound, which ensures their efficient overlap, and by the possibility of free rotation around the C–O bond in alkoxysilanes, which results in a lower probability of efficient conjugation in the latter case. However, in the case of adiabatic stepwise transfer of an electron during oxidation (which assumes that a primary radical cation is present on the reaction coordinate), stabilisation of the radical cation by the β-effect of the silyl group should be identical for these two types of compound (owing to the free rotation). Therefore, the experimental observation in question is rather associated with the fact that the C = O bond is shorter than C–O. This ensures more efficient overlap of the interacting orbitals, which destabilises the HOMO of the initial molecule and thus decreases the oxidation potential of acylsilanes.

Preparative oxidation of acylsilanes, like the oxidation of allyl- and benzylsilanes, involves rupture of the C–Si bond and affords products of electrophilic reactions of the carbocationic intermediate.[201,203,232] It has been assumed that the carbocation is formed *via* nucleophilic attack on the primary radical cation derived from acylsilane (Scheme 6).

Scheme 6



Electrooxidation of acylsilanes in the presence of a 5–6-fold excess of a nucleophilic reagent gives the corresponding products of anodic substitution in 69%–92% yields.[210]

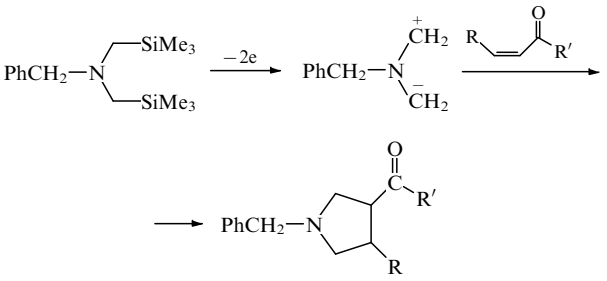


14. α-Silylamines

The appearance of the silyl group at the nitrogen atom in aniline (see Table 13) increases E_{Ox} with respect to that of the unsubstituted compound, which is in agreement with the electron-withdrawing properties of the α-Me_3Si group.[194]

The single-electron reduction of silylamines at a Pt electrode has been considered.[222] In the case of alkyl derivatives, the inductive mechanism of the transfer of electron density predominates, whereas, in the case of vinyl derivatives, the EPR data for the electrically generated radical cation $[MeVinSi(NEt_2)_2]^{+\bullet}$ made it possible to conclude that the positive charge and spin density are delocalised in the N–Si–N group. However, in the latter case, there is no conjugation over the C=C–Si–N system of bonds. The $\varepsilon_{HOMO} - E_{p/2}$ plots for alkyl- and vinyl-substituted silylamines are separate straight lines for each family of compounds, which is due to the differences in the transfer of electronic effects.

Electrooxidation of bis(trimethylsilylmethyl)benzylamine in DMF is a convenient method for generation of 1,3-dipoles, which react with activated alkenes.[233] The yields of the cycloaddition products vary in the range 8%–61% depending on the nature of the substituent in the alkene molecule.

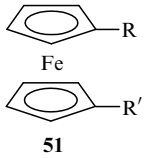


R = H, CO_2Me, Ph; R′ = OMe, OBu^t, H.

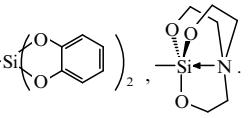
The use of AcONa or KF as a supporting electrolyte is significant for efficient cycloaddition.

15. Compounds of hypervalent silicon

Comparison of the oxidation potentials of mono- and bis-pentacoordinated systems with silatrane ($E_{1/2}$ = −0.07 and +0.21 V *vs* SCE) or silylcatecholate fragments ($E_{1/2}$ = +0.07 and +0.31 V *vs* SCE) with the oxidation potentials of 1,1′-bis-silyl-substituted ferrocene derivatives **51** ($E_{1/2}$ = +0.55 V)[234] has demonstrated an interesting electronic effect: a substantial decrease in the $E_{1/2}$ potential for the reversible Fe(II)/Fe(III) pair is observed in the case of anionic and pentacoordinated compounds, whereas in the case of bis(trimethoxysilyl)ferrocene, a slight increase in this potential has been found [$\Delta E_{1/2}$ for bis(trimethoxysilyl)ferrocene with respect to unsaturated ferrocene is +0.09 V].



51

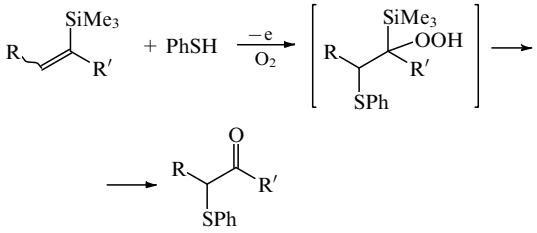


Thus, the coordination number proves to be an important factor determining the electronic properties of organosilicon compounds: tetracoordinated compounds exhibit electron-withdrawing properties, whereas pentacoordinated compounds are characterised by electron-donating properties (irrespective of their geometry). Although this effect has not yet received a clear explanation, it is assumed that the electron density in pentacoordinated organosilicon compounds is delocalised over the surrounding ligands. In this case, silicon acts as a donor of electrons and thus becomes more electrophilic. In the molecules of silatranes, the electron density is markedly displaced from nitrogen to iron through the silicon atom, owing to the bis-apical arrangement of these atoms in the trigonal bipyramid.

Voltammetric curves for R-silatranes (R = Me, Et, Vin, Ph) (υ = 0.2–0.5 V s^{-1}) are practically reversible, and the oxidation potential depends appreciably on the nature of R, which indicates that the N → Si interactions are retained during the electrode process.[225]

VII. Electrochemical processes involving organic derivatives of silicon

Electrooxidation of alkenylsilanes in the presence of PhSH and with molecular oxygen being bubbled through the solution requires a catalytic amount of electricity (Q = 0.16 to 1.19 F mol^{-1}) and is a direct and regiospecific pathway to α-phenylthio-substituted carbonyl compounds.[235] The yields of the products depend appreciably on the nature of the substituents R and R′.



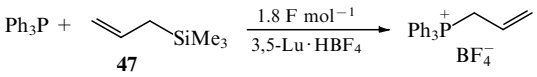
R	R′	Yield (%)
C_6H_{13}	H	12
H	C_8H_{17}	73
H	$C_8H_{17}CH(OH)CH_2$	93
C_4H_9	C_4H_9	13

Oxidation (Q = 0.04–3.77 F mol^{-1}) of 0.5 mmoles of 1-phenylthio-1-(trimethylsilyl)alkenes in the presence of 2–6 equivalents of thiophenol results in the formation of a product with two phenylthio-groups (R′ = SPh) in a yield of 60%–99%.

During the electrochemically initiated oxygenation of 1-phenylthio-1-(trimethylsilyl)alkenes, only the C–Si bond undergoes oxidative rupture, the C–S bond remaining intact. A chain radical mechanism for this process has been proposed; this mechanism includes radical addition of the phenylthio radical to the double bond, reaction of the resulting C-radical with oxygen and abstraction of an H$^{\bullet}$ atom from PhSH by a peroxy radical, which yields hydroperoxide and regenerates the phenylthio radical.

Decomposition of the hydroperoxide with elimination of the Me_3Si fragment affords the final carbonyl compound.

Allylsilanes react with cationic intermediates resulting from the anodic oxidation of triphenylphosphine.[236] In the reaction with the electrically generated $Ph_3P^{+\cdot}$ radical cation, the trimethylsilyl group in allyltrimethylsilane **47** also acts as a 'superproton'.

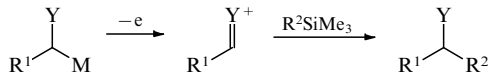


47

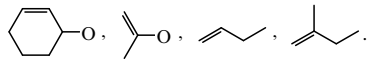
Lu is lutidine.

Allylphosphonium salts were isolated as stable products of this reaction in 21% – 72% yields. The nature of the silicon-containing products was not elucidated.

Electrooxidative coupling of silicon-protected nucleophiles with a number of α-substituted heteroatomic (O, S, N) organostannanes and organosilanes has been accomplished.[197, 237]

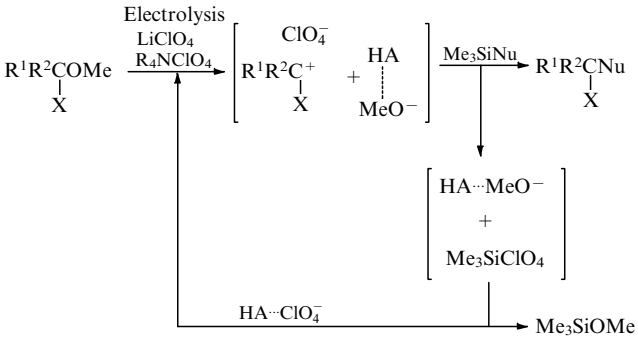


M = $SiMe_3$, $SnBu_3$; Y = OR^3, NR^3_2, CO_2Me, OCO_2Me, SR^3;

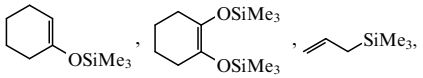
R^2 = 

Numerous reactions of acetals, aldehydes and ketones with compounds of electrophilic silicon catalysed by electrochemically generated acids (HA) have been reported (Scheme 7).[238] Aldol condensation, allylation, cyanation and hydride addition follow a common route that includes activation of the substrate by the acid generated electrically from the perchlorate and the formation of a carbenium ion stabilised by the ClO_4^- anion.

Scheme 7



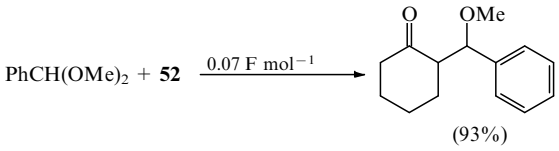
X = OR^3, NR^3R^4;

Me_3SiNu = 

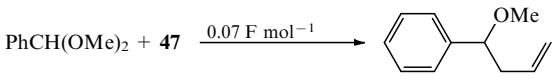
52

Me_3SiCN, Et_3SiH.

The cation easily undergoes a nucleophilic attack by Me_3SiNu present in the solution giving a product with a C – Nu bond. At this stage, Me_3SiClO_4 is assumed to participate in the process; it is rapidly hydrolysed by a methoxide anion giving methoxytrimethylsilane and regenerating HA. The electrochemical efficiency of cyclic processes of this type is quite high (Q = 0.01 – 0.87 F mol^{-1}).

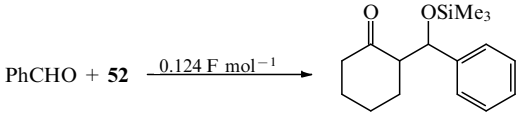


(93%)



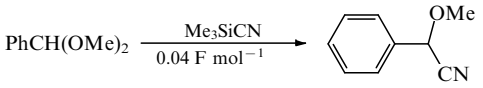
(82%)

The reaction of the silyl ether **52** with aldehydes leads to products of reductive addition.

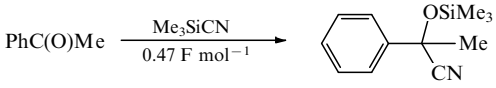


(85%)

Methyl ethers of cyanohydrins are obtained from acetals in the reactions involving trimethylsilylnitrile. Under the same conditions, ketones afford trimethylsilyl ethers of cyanohydrins.

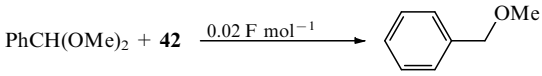


(80%)



(88%)

The reaction of dimethyl acetals with the silane **42** affords the products resulting formally from the replacement of one methoxy-group by a hydride ion.



(88%)

The intermediates of the electrooxidation of $(Me_3Si)_2$ and $(Me_3Si)_2NH$ react with cyclohexene to give cyclohexyltrimethylsilane.[63, 69]

Preparation of Me_4Si with electrochemical regeneration of reactants has been reported.[239] $SiCl_4$ and MeCl are added to an $AlCl_3$/NaCl melt containing suspended aluminium, which serves as the acceptor of the halogen. Tetramethylsilane is formed in a quantitative yield, while Al is regenerated *via* electrochemical reduction of $AlCl_3$.

$$3SiCl_4 + 12MeCl + 8Al \longrightarrow 3Me_4Si + 8AlCl_3,$$

$$2AlCl_3 \longrightarrow 2Al + 3Cl_2.$$

A number of processes of 'direct' electrosynthesis of organic derivatives of silicon based on the use of Si-containing electrodes have been reported. For example, tetraorganosilanes, tetraorganohydroxysilanes and organopolysiloxane liquids have been prepared by the electrolysis of the corresponding halides and alcohols at a silicon anode in the presence of mineral salts (Al, Mg and Li chlorides and bromides).[240]

Tetraethylsilane **45** has been obtained both in cathodic and anodic processes as a result of the radical attack by ethyl radicals (electrically generated by oxidation of EtMgBr or reduction of EtBr) on a silicon atom of the electrodes.[241] When ethyl chloride or acrylonitrile is used in this process, no organosilicon compounds are formed.

Tetraethoxysilane is prepared by oxidation of EtOH in the presence of $(NH_2)_2CO \cdot HCl + (NH_2)_2CO$ or $Et_3N \cdot HCl + Et_3N$ at a ferrosilicon anode.[3, 242–245] Depending on the supporting electrolyte and its concentration and on the current density, the yield of the reaction product ranges from 3.3% to 60% based on the dissolved ferrosilicon.[244]

VIII. Conclusion

The character of silyl substitution (α- or β-substitution) in aromatic or heteroatomic molecules changes their electrochemical reactivity according to the influence of the silyl group on the frontier orbitals. α-Substitution decreases the LUMO energy and facilitates reduction reactions, whereas β-substitution increases the HOMO energy and decreases the IP, which accounts for the easier anodic oxidation of these compounds.

Evidently, electroreduction of chlorosilanes involves the activation type of electron transfer (although the Si–Cl bond is very strong) giving rise to silyl radicals, which are reduced at the potential of formation to silyl anions. For this reason, cathodic processes involving chlorosilanes occur by an ionic mechanism.

The crucial factor determining the behaviour of organosilicon radical-cation intermediates in anodic reactions is that trialkylsilyl groups are eliminated extremely easily in the cationic form. Therefore, organosilicon derivatives are quite attractive for functionalisation of organic compounds in the reactions of anodic substitution.

The publications dealing with the electrochemistry of organosilicon compounds can be clearly divided into two groups. The first group includes theoretical studies in which the electrochemical method is used to obtain characteristics of FMOs and to study orbital interactions, whereas the second group comprises purely preparative studies (synthetic studies based on the electrochemical generation of active intermediates and electrochemical initiation of reactions in the bulk of a solution). The studies of the first group usually deal with potentials of reversible redox pairs (the ion-radical components of which are so stable that they exist in solution over long periods without entering in any reactions), while the studies of the second group occur normally under non-controlled conditions, and potentials are often not used at all to characterise the reactivities of compounds.

It is clear that these two lines of research do not exhaust the potentialities of organic electrochemistry and, therefore, it is quite reasonable to expect that new studies in this field will be published. In particular, one might expect that studies dealing with elementary steps of electrochemical processes, kinetics and thermodynamics of electron transfer and of accompanying chemical reactions will appear, because it is the mechanistic investigations that would create the scientific grounds for controlling the reactivity of intermediates (and, hence, the nature of the final products) as early as at the stage of charge transfer and potential-determining reactions.

References

1. W J Settineri, L D McKeever, in *Technique of Electroorganic Synthesis* (New York: Wiley-Interscience, 1975) p. 398
2. G A Tedoradze *J. Organomet. Chem.* **88** 1 (1975)
3. M Devaud *J. Am. Chem. Soc.* **98** 87 (1976)
4. S G Mairanovskii *Usp. Khim.* **45** 604 (1976) [*Russ. Chem. Rev.* **45** 298 (1976)]
5. A P Tomilov, A V Bukhtiarov *Khim. Promst.* **2** 91 (1978)
6. A J Bard, H Lund *Encyclopedia of Electrochemistry of the Elements* (New York: Marcel Dekker, 1980)
7. E M Genies, A F El Omar *Electrochim. Acta* **28** 541 (1983)
8. A P Tomilov, Yu M Kargin, I N Chernykh *Elektrokhimiya Elementoorganicheskikh Soedinenii* (*Elementy IV, V i VI Grupp Periodicheskoi Sistemy*) [Electrochemistry of Organoelement Compounds (Elements of Group IV, V, and VI of the Periodic System)] (Moscow: Nauka, 1986) p. 6
9. L Walder, in *Organic Electrochemistry* (Ed. H Lund) (New York, 1991) p. 809
10. Yu M Kargin, V V Jouikov, Yu G Budnikova, D S Fattakhova *Elektrokhimiya* **28** 498 (1992) [a]
11. J Yoshida *Kagaku Kogyo* (*Osaka*) **67** 151 (1993); *Chem. Abstr.* **119** 72 640 (1993)
12. N G Connelly *NATO ASI, Ser. C* **385** 317 (1993); *Chem. Abstr.* **120** 40 321h (1994)
13. J Yoshida *Top. Cur. Chem.* 40 (1994)
14. E A Abrahamson, C A Reynolds *Anal. Chem.* **24** 1827 (1952)
15. A L Allred, L W Bush *J. Am. Chem. Soc.* **90** 3352 (1968)
16. W G Boberski, A L Allred *J. Organomet. Chem.* **88** 73 (1975)
17. P Duchek, R Ponec, V Chvalovsky *J. Organomet. Chem.* **271** 101 (1984)
18. P Duchek, R Ponec, V Chvalovsky *Collect. Czech. Chem. Commun.* **51** 967 (1986)
19. T Koizumi, T Fuchigami, T Nonaka *Electrochim. Acta* **33** 1635 (1988)
20. I M Tyurin, V N Flerov, V K Goncharuk *Zh. Obshch. Khim.* **41** 490 (1971) [b]
21. A B Thomas, E G Rochow *J. Am. Chem. Soc.* **79** 1843 (1957)
22. R J P Corriu, G Dabosi, M Martineau *J. Organomet. Chem.* **222** 195 (1981)
23. R J P Corriu, G Dabosi, M Martineau *J. Chem. Soc., Chem. Commun.* 457 (1979)
24. R J P Corriu, G Dabosi, M Martineau *J. Organomet. Chem.* **186** 19 (1980)
25. A L Allred, C Bradley, T H Newman *J. Am. Chem. Soc.* **100** 5081 (1978)
26. M Bordeau, C Biran, P Pons, M-P Leger, J Dunoguès *J. Organomet. Chem.* **382** 21 (1990)
27. C Duprat, Thesis, Univ. Bordeaux I, Bordeaux, 1995
28. T Shono, H Ohmizu, S Kawakami, H Sugiyama *Tetrahedron Lett.* **21** 5029 (1980)
29. T Ishiwata, T Nonaka, M Umezawa *Chem. Lett.* 1631 (1994)
30. V V Jouikov, Y Kargin, in *The VIIIth IUPAC Conference on Organic Synthesis, Helsinki 1990* p. 169
31. V V Jouikov, G Salaheev *Electrochim. Acta* **41** 2623 (1996)
32. R J P Corriu, G Dabosi, M Martineau *J. Organomet. Chem.* **150** 27 (1978)
33. R J P Corriu, G Dabosi, M Martineau *J. Organomet. Chem.* **186** 25 (1980)
34. V V Leshkova, V N Knyazev, B G Vlasova, V A Drozdov *Zh. Obshch. Khim.* **15** 1742 (1973) [b]
35. A Kunai, E Toyoda, T Kawakami, M Ishikawa *Organometallics* **11** 2899 (1992)
36. C Jammegg, S Graschy, E Hengge *Organometallics* **13** 2397 (1994)
37. E Hengge, H Firgo *J. Organomet. Chem.* **212** 155 (1981)
38. A Kunai, T Ueda, E Toyoda, M Ishikawa *Bull. Chem. Soc. Jpn.* **67** 287 (1994)
39. R E Dessy, W Kitching, T Chivers *J. Am. Chem. Soc.* **88** 453 (1966)
40. R J P Corriu, G Dabosi, M Martineau *J. Organomet. Chem.* **188** 63 (1980)
41. C Biran, M Bordeau, P Pons, M-P Leger, J Dunoguès *J. Organomet. Chem.* **382** 17 (1990)
42. M Umezawa, M Takeda, H Ichikava, T Ishikawa, T Nonaka, in *The 40th ISE Meeting, Kyoto, Japan 1989* Vol. II, p. 857
43. E Hengge, G Litscher *Angew. Chem.* **88** 414 (1976)
44. P Boudjouk *J. Am. Chem. Soc.* **104** 4992 (1982)
45. A V Bukhtiarov, E A Chernyshev, O V Kuz'min, B K Kabanov, V N Golyshin, A P Tomilov *Zh. Obshch. Khim.* **54** 2399 (1984) [b]
46. J Gobet, H Tannenberger *J. Electrochem. Soc.* **135** 109 (1988)
47. E D Lavrinenko-Ometsinskaya, V V Pen'kovskii, G S Shapoval, T L Krasnova, E A Chernyshev *Zh. Obshch. Khim.* **46** 734 (1976) [b]
48. E Hengge, G Litscher *Monatsh. Chem.* **109** H5, 1217 (1978)
49. M Bordeau, C Biran, M-P Leger-Lambert, F Sparau, D Deffieux in *Inorganic, Organometallic Polymers II. Advanced Materials, Intermediates* (Eds P Wisian-Neilson, H R Allcock, K J Wynne) (Washington, DC: American Chemical Society, 1994) p. 18

50. T Shono, S Kashimura *J. Electrochem. Soc.* **137** 619 (1990)
51. T Shono, S Kashimura, M Ishifune, R Nishida *J. Chem. Soc., Chem. Commun.* 1160 (1990)
52. T Shono, S Kashimura, R Nishida, in *The 59th National Meeting of Chemical Society of Japan, Yokohama, 1990* p. 3 D710
53. E Hengge, G Litscher *Angew. Chem., Int. Ed. Engl.* **15** 370 (1976)
54. A Kunai, T Kawakami, E Toyoda, M Ishikawa *Organometallics* **10** 893 (1991)
55. A Kunai, T Kawakami, E Toyoda, M Ishikawa *Organometallics* **10** 2001 (1991)
56. T Shono *Kino Zaikyo* **12**/**2** 15 (1992); *Chem. Abstr.* **117** 7964 (1992)
57. C Biran, M Bordeau, M-P Leger in *Inorganic, Organometallic Polymers with Special Properties* (Ed. R M Lain) (Dordrecht, The Netherlands: Kluwer Academic, 1990) p. 79
58. M Umezawa, M Takeda, H Ichikawa, T Ishikawa, T Koizumi, T Fuchigami, T Nonaka *Electrochim. Acta* **35** 1867 (1990)
59. T Shono, Y Matsumura, S Katoh, N Kise *Chem. Lett.* 463 (1985)
60. L A Grigor'eva, V V Jouikov, V Z Latypova, E P Lebedev, V A Baburina, in *IXth Vsesoyuz. Soveshchanie po Polyarografii, Ust'-Kamenogorsk, 1987* (The IXth All-Union Meeting on Polarography, Ust'-Kamenogorsk, 1987) p. 140
61. V V Jouikov, L A Grigor'eva, Yu M Kargin, E P Lebedev, in *Vsesoyuz. Konf. po Elektrokhimii Organicheskikh Soedinenii, Karaganda, 1990* (All-Union Conference on the Electrochemistry of Organic Compounds, Karaganda, 1990) p. 170
62. V V Jouikov, in *Pervyi Kremniiorganicheskii Mikrosimpozium* (The First Organosilicon Microsymposium) (Moscow: GNIIKhTEOS, 1994) p. 2
63. V Jouikov, L Grigorieva *Electrochim. Acta* **41** 2489 (1996)
64. A Kunai, O Ohnishi, T Sakurai, M Ishikawa *Chem. Lett.* 1051 (1995)
65. C Duprat, C Biran, M Bordeau, T Constantieux, K Gil, F Serein-Spirau, in *The IV Journ. GSO* (Toulouse: Univ. Paul Sabatier, 1995) p. C502
66. C Biran, M Bordeau, T Constantieux, P Gerval, J Dunoguès *J. Chem. Soc., Chem. Commun.* 2107 (1995)
67. P. USSR 1 556 081; *Byull. Izobret.* (1990)
68. P. USSR 1 550 896; *Byull. Izobret.* (1990)
69. L A Grigor'eva, Candidate Thesis in Chemical Sciences, Kazan' Institute of Chemical Technology, Kazan', 1990
70. V V Jouikov, V Z Latypova, L A Grigor'eva, E P Lebedev, V A Baburina, in *Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii* (The Structure and Reactivity of Organosilicon Compounds) (Irkutsk: Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, 1989) p. 23
71. A Kunai, E Toyoda, T Kawakami, M Ishikawa *Electrochim. Acta* **39** 2089 (1994)
72. M Umezawa, H Ichikawa, T Ishikawa, T Nonaka *Denki Kagaku* **59** 421 (1991)
73. A L Allred, C A Ernst, M A Ratner, in *Homoatomic Rings, Chains, and Macromolecules of Main Group Elements* (Ed. A L Reinold) (Amsterdam: Elsevier, 1977) p. 307
74. R D Miller, J Michl *Chem. Rev.* **89** 1359 (1989)
75. M Umezawa, M Takeda, H Ichikawa, T Ichikawa, T Koizumi, T Nonaka *Electrochim. Acta* **36** 621 (1991)
76. M Bordeau, C Biran, M-P Leger-Lambert, J Dunoguès *J. Chem. Soc., Chem. Commun.* 1476 (1991)
77. A Watanabe, T Komatsubara, M Matsuda, Y Yoshida, S Tagawa *J. Polym. Sci., Technol.* **5** 545 (1992)
78. Jpn. P. 05 247 217; *Chem. Abstr.* **120** 135 472 (1994)
79. Jpn. P. 05 247 218; *Chem. Abstr.* **120** 135 473 (1994)
80. Jpn. P. 05 247 216; *Chem. Abstr.* **120** 135 471 (1994)
81. Jpn. P. 04 348 128; *Chem. Abstr.* **119** 73 387 (1993)
82. A Watanabe, O Ito, T Miwa *Jpn. J. Appl. Phys. 2, Lett.* **34**/**9A** L1164 (1995)
83. A V Bukhtiarov, A P Tomilov, V P Bud'ko *Elektrokhimiya* **16** 1274 (1980) [a]
84. P Pons, C Biran, M Bordeau, J Dunoguès, S Sibille, J Perichon *J. Organomet. Chem.* **321** C27 (1987)
85. J-I Yoshida, K Muraki, H Funahashi, N Kawabata *J. Organomet. Chem.* **284** C33 (1985)
86. J-I Yoshida, K Muraki, H Funahashi, N Kawabata *J. Org. Chem.* **51** 3996 (1986)
87. S Torii, H Tanaka, T Katoh, K Morisaki *Tetrahedron Lett.* **25** 3207 (1984)
88. T Ohno, H Nakahiro, K Sanemitsu, T Hirashima, I Nishiguchi *Tetrahedron Lett.* **233** 5515 (1992)
89. C Biran, M Bordeau, F Serein-Spirau, M-P Leger-Lambert, J Dunoguès *Synth. Commun.* **23** 1727 (1993)
90. P Pons, C Biran, M Bordeau, J Dunoguès *J. Organomet. Chem.* **358** 31 (1988)
91. P Pons, Thesis, Univ. Bordeaux I, Bordeaux, 1990
92. M Bordeau, C Biran, P Pons, M-P Leger-Lambert, J Dunoguès *J. Org. Chem.* **57** 4705 (1992)
93. Fr. P. 2 681 866; *Chem. Abstr.* **119** 72 833 (1993)
94. Br. P. 2 234 511; *Ref. Zh. Khim.* **2** N 159P (1992)
95. V V Jouikov, V Krasnov *J. Organomet. Chem.* **498** 213 (1995)
96. V V Jouikov, V V Ivkov, Yu M Kargin, in *Konf. po Elektrokhimii Organicheskikh Soedinenii, Tambov (EKhOS-94)* (Conference on the Electrochemistry of Organic Compounds, Tambov (ECOC-94) (Moscow: Institute of Electrochemistry, Russian Academy of Sciences, 1994) p. 25
97. J-P Pillot, M Birot, F Dubondin, M Bordeau, C Biran, J Dunoguès, in *Frontiers of Organosilicon Chemistry* (Eds A R Bassindale, P P Gaspar) (Edinburgh, 1990) p. 40
98. A J Fry, J Touster *J. Org. Chem.* **54** 4829 (1989)
99. C Moreau, F Spirau, C Biran, M Bordeau, in The *IV Journ. GSO* (Toulouse: Univ. Paul Sabatier, 1994) p. P101
100. C Moreau, Thesis, Univ. Bordeaux I, Bordeaux, 1995
101. D Deffieux, Thesis, Univ. Bordeaux I, Bordeaux, 1993
102. C Biran, M Bordeau, D Bonafoux, D Deffieux, C Duprat, C Moreau, F Spirau *J. Electrochim. (Strasbourg)* CT8-1 (1995)
103. A V Bukhtiarov, V N Gol'shin, V A Rodnikov, O V Kuz'min, L N Nekrasov, G R Khomchenko *Elektrokhimiya* **22** 665 (1986) [a]
104. F Aymard, J-Y Nedelec, J Perichon *Tetrahedron Lett.* **35** 8623 (1994)
105. G K S Prakash, D Deffieux, A K Youdin, G A Olah *Synlett.* 1057 (1994)
106. A J Fry, J Touster, U N Sirisoma *J. Electrochem. Soc.* **137**/**3** 521 (1990)
107. A J Fry, J Touster, U N Sirisoma, B Raimundo, in *Electroorganic Synthesis* (Eds R D Little, N L Weinberg) (New York: Marcel Dekker, 1991) p. 99
108. G K S Prakash, H A Buchholz, D Deffieux G A Olah *Synlett* 819 (1994)
109. G K S Prakash, H A Buchholz, D Deffieux G A Olah *J. Org. Chem.* **59** 7532 (1994)
110. T Shono, S Kashimura, H Murase *J. Chem. Soc., Chem. Commun.* 896 (1992)
111. S Kashimura, M Ishifune, H Ishida, T Shono, in *International Symposium on Electroorganic Synthesis, Kurashiki, 1994* p. 114
112. S Kashimura, Y Murai, M Ishifune, H Masuda, H Murase, T Shono *Tetrahedron Lett.* **36** 4805 (1995)
113. S Kashimura, M Ishifune, T Shono, in *International Symposium on Electroorganic Synthesis, Kurashiki, 1994* p. 194
114. T Troll, W Elbe, G W Ollmann *Tetrahedron Lett.* **22** 2961 (1984)
115. T Troll, G W Ollmann *Electrochim. Acta* **29** 467 (1984)
116. N Kise, H Kaneko, N Uemoto, J Yoshida *Tetrahedron Lett.* **36** 8839 (1995)
117. S Grelier, T Constantieux, D Deffieux, M Bordeau, J Dunoguès, J-P Picard, C Palomo, J M Aizpurua *Organometallics* **13** 3711 (1994)
118. D Bonafoux, M Bordeau, C Biran, J Dunoguès *J. Organomet. Chem.* **493** 27 (1995)
119. A V Bukhtiarov, V V Mikheev, A V Lebedev, O V Kuz'min, A P Tomilov *Zh. Obshch. Khim.* **58** 684 (1988)s [b]
120. V V Jouikov, V Z Latypova, L A Grigorieva, V A Baburina, E P Lebedev, in *The IInd International Conference on Heteroatom Chemistry, Albany, NY, 1989* p. 23
121. D S Fattakhova, Candidate Thesis in Chemical Sciences, Kazan' Institute of Chemical Technology, Kazan', 1993
122. V V Jouikov, V Z Latypova, L A Grigor'eva , E P Lebedev, V A Baburina, O G Yakovleva, in *VII Vsesoyuz. Konf. po Elektrokhimii, Chernovtsy, 1988* (The VIIth All-Union Conference on Electrochemistry, Chernovtsy, 1988) Vol. 3, p. 179
123. S Torii, T Inokuchi, N Hasegawa *Chem. Lett.* 639 (1980)

124. V V Jouikov, D S Fattakhova, V V Ivkov, Yu M Kargin *Elektrokhimiya* **32** 297 (1996) [a]
125. V V Jouikov, in *International Symposium on Electroorganic Synthesis*, *Kurashiki, 1994* p. 132
126. V V Jouikov, D S Fattahova, in *The Vth International Conference on New Aspects of Organic Chemistry*, *Kyoto, Japan, 1991* p. 112
127. V V Jouikov, D S Fattahova *J. Electrochim. (Grenoble)* CA 6.36 (1993)
128. V V Jouikov, D S Fattakhova, Yu M Kargin, in *Konf. po Elektrokhimii Organicheskikh Soedinenii, Tambov (EKhOS-94)* (Conference on the Electrochemistry of Organic Compounds, Tambov (ECOC-94) (Moscow: Institute of Electrochemistry, Russian Academy of Sciences, 1994) p. 75
129. V V Jouikov, L Grigorieva *Electrochim. Acta* **40** 325 (1995)
130. G G Pitt, R N Carey, E C Toren *J. Am. Chem. Soc.* **94** 3806 (1972)
131. A N Egorochkin *Usp. Khim.* **61** 1092 (1992) [*Russ. Chem. Rev.* **61** 600 (1992)]
132. M D Curtis, A L Allred *J. Am. Chem. Soc.* **87** 2554 (1965)
133. H Watanabe, M Aoki, H Matsumoto, Y Nagai, T Sato *Bull. Chem. Soc. Jpn.* **50** 1019 (1977)
134. V M Kazakova, I G Makarov, M E Kurek, E A Chernyshev *Zh. Strukt. Khim.* **9** 525 (1968) [c]
135. H Bock, H Alt *Angew. Chem.* **80** 906 (1968)
136. I G Makarov, V M Kazakova, N G Komalenkova *Dokl. Akad. Nauk SSSR* **195** 1368 (1970) [d]
137. F Correa-Duran, A L Allred, D E Glover, D E Smith *J. Organomet. Chem.* **49** 353 (1973)
138. I G Makarov, V M Kazakova *Zh. Strukt. Khim.* **9** 996 (1968) [c]
139. A V Il'yasov, Y A Levin, I D Morozova *J. Mol. Struct.* **19** 671 (1973)
140. A G Evans, B Jerome, N H Rees *J. Chem. Soc., Perkin Trans. 2* 447 (1973)
141. K Mochida *Chem. Lett.* 805 (1986)
142. H Bock, H Alt *Angew. Chem.* **79** 932 (1967)
143. R A Benkeser, C A Tincher *J. Organomet. Chem.* **13** 139 (1968)
144. C Eaborn, R A Jackson *J. Chem. Soc., Perkin Trans. 1* 2055 (1974)
145. S Kashimura, M Ishifune, Y Murai, N Moriyoshi, T Shono *Tetrahedron Lett.* **36** 5041 (1995)
146. H Bock, H Alt *Chem. Ber.* **103** 1784 (1970)
147. H Bock, H Seidl *J. Am. Chem. Soc.* **90** 5694 (1968)
148. I G Makarov, V M Kazakova, N G Tolstikova, E A Chernyshev *Zh. Strukt. Khim.* **10** 595 (1969) [c]
149. H Bock, H Alt, H Seidl *J. Am. Chem. Soc.* **91** 355 (1969)
150. R E Dessy, L A Bares *Acc. Chem. Res.* **5** 415 (1972)
151. E Carberry, R West, G E Glass *J. Am. Chem. Soc.* **91** 5446 (1969)
152. A L Allred, R T Smart, D A Van Beek *Organometallics* **11** 4225 (1992)
153. B D Shepherd, R West *Chem. Lett.* 183 (1988)
154. S G Mairanovskii, V A Ponomarenko, N V Barashkova *Izv. Akad. Nauk SSSR, Ser. Khim.* 1951 (1964) [e]
155. S G Mairanovskii, V A Ponomarenko, N V Barashkova, A D Snegova *Dokl. Akad. Nauk SSSR* **134** 387 (1960) [d]
156. D S Fattakhova, E A Avvakumova, V V Jouikov, in *Konf. po Elektrokhimii Organicheskikh Soedinenii, Tambov (EKhOS-94)* (Conference on the Electrochemistry of Organic Compounds, Tambov (ECOC-94) (Moscow: Institute of Electrochemistry, Russian Academy of Sciences, 1994) p. 15
157. V V Jouikov, C Biran, M Bordeau, J Dunoguès *Zh. Obshch. Khim.* (1997) (in the press) [b]
158. H Schäfer, D Hermeling *Angew. Chem.* **96** 338 (1984)
159. M Okano, K Mochida *Bull. Chem. Soc. Jpn.* **64** 1381 (1991)
160. A Kunai, T Kawakami, E Toyoda, T Sakurai, M Ishikawa *Chem. Lett.* 1945 (1993)
161. N T Berberova, O Yu Okhlobystin *Zh. Obshch. Khim.* **51** 224 (1981) [b]
162. A A Khapicheva, N T Berberova, E S Klimov, O Yu Okhlobystin *Zh. Obshch. Khim.* **55** 1533 (1985) [b]
163. N T Berberova, Author's Abstract of Doctoral Thesis in Chemical Sciences, Rostov State University, Rostov on Don, 1991
164. Y Kimata, H Suzuki, S Satoh, A Kuriyama *Organometallics* **14** 2506 (1995)
165. A Diaz, M Seymour, K H Pannell, J M Rozell *J. Electrochem. Soc.* **137** 503 (1990)
166. A Diaz, R D Miller *J. Electrochem. Soc.* **132** 834 (1985)
167. G T Fedorova, N P Kharitonov *Zh. Obshch. Khim.* **51** 834 (1981) [b]
168. N P Kharitonov, B P Nechaev, G T Fedorova *Zh. Obshch. Khim.* **39** 824 (1969) [b]
169. R J Klingler *J. Am. Chem. Soc.* **101** 6626 (1979)
170. O Yu Okhlobystin, N T Berberova *Dokl. Akad. Nauk SSSR* **332** 599 (1993) [d]
171. K Mochida, A Itani, M Yokoyama, T Tsuchiva, S Worley, J Kochi *Bull. Chem. Soc. Jpn.* **58** 2149 (1985)
172. V V Jouikov *Zh. Obshch. Khim.* (1997) (in the press) [b]
173. W G Boberski, A L Allred *J. Organomet. Chem.* **88** 65 (1975)
174. S Fukuzumi, T Kitano, K Mochida *Chem. Lett.* 1741 (1990)
175. M Okano, K Mochida *Chem. Lett.* 701 (1990)
176. J Y Becker, E Shakkour, R West *Tetrahedron Lett.* **33** 5633 (1992)
177. H Watanabe, K Yoshizumi, T Muraoka, M Kato, Y Nagai, T Sato *Chem. Lett.* 1683 (1985)
178. R J Klingler, J K Kochi *J. Am. Chem. Soc.* **102** 4790 (1980)
179. E M Genies, A F El Omar *Electrochim. Acta* **28** 547 (1983)
180. G K S Prakash, S Quaiser, H A Buchholz, J Casanova, G A Olah *Synlett.* 113 (1994)
181. I Y Alyev, I N Rozhkov, I L Knunyants *Tetrahedron Lett.* **28** 2469 (1976)
182. D Lucas, Y Mugnier, A Antinolo, A Otero, M Fajardo *J. Organomet. Chem.* **435** C3 (1992)
183. H Bock, H Alt *Angew. Chem.* **79** 934 (1967)
184. H Bock, W Kaim *J. Am. Chem. Soc.* **102** 4429 (1980)
185. K Mizuno, M Yasueda, Y Otsuji *Chem. Lett.* 229 (1988)
186. E Baciocchi, T D Giacco, C Rol, G V Sebastiani *Tetrahedron Lett.* **30** 3573 (1989)
187. J-I Yoshida, T Murata, S Isoe *Tetrahedron Lett.* **27** 3373 (1986)
188. K Ohga, P S Mariano *J. Am. Chem. Soc.* **104** 617 (1982)
189. T Koizumi, T Fuchigami, T Nonaka *Bull. Chem. Soc. Jpn.* **62** 219 (1989)
190. G Distefano, A Ricci, R Danieli, A Foffani, G Innorta, S Torroni *J. Organomet. Chem.* **65** 205 (1974)
191. V V Jouikov *Zh. Obshch. Khim.* (1997) (in the press) [b]
192. T Koizumi, T Fuchigami, T Nonaka *Electrochim. Acta* **33** 1635 (1988)
193. K Mizuno, M Ikeda, Y Otsuji *Tetrahedron Lett.* **26** 461 (1985)
194. B E Cooper, W J Owen *J. Organomet. Chem.* **29** 33 (1971)
195. H Bock, V Lechner-Knoblauch *J. Organomet. Chem.* **294** 295 (1985)
196. K Mizuno, Y Ishii, T Ohshika, Y Otsuji, in *International Symposium on Electroorganic Synthesis, Kurashiki, 1994* p. 184
197. J-I Yoshida, M Itoh, S Isoe *J. Chem. Soc., Chem. Commun.* 547 (1993)
198. V I Koshutin, L N Maksimova *Elektrokhimiya* **15** 280 (1979)
199. J-I Yoshida, T Murata, S Isoe *Tetrahedron Lett.* **28** 211 (1987)
200. J-I Yoshida, T Maekawa, T Murata, S-I Matsunaga, S Isoe *J. Am. Chem. Soc.* **112** 1962 (1990)
201. J-I Yoshida, S-I Matsunaga, S Isoe *Tetrahedron Lett.* **30** 5293 (1989)
202. J-I Yoshida, Y Morita, M Itoh, Y Ishichi, S Isoe *Synlett.* 843 (1992)
203. J-I Yoshida, M Itoh, S-I Matsunaga, S Isoe *J. Org. Chem.* **57** 4877 (1992)
204. J-I Yoshida, Y Ishichi, K Nishiwaki, S Shiozawa, S Isoe *Tetrahedron Lett.* **33** 2599 (1992)
205. J-I Yoshida, T Murata, S Isoe *J. Organomet. Chem.* **345** 23 (1988)
206. J-I Yoshida, T Maekawa, Y Morita, S Isoe *J. Org. Chem.* **57** 1321 (1992)
207. J-I Yoshida, Y Ishichi, S Isoe *J. Am. Chem. Soc.* **114** 7594 (1992)
208. J-I Yoshida, S-I Matsunaga, T Murata, S Isoe *Tetrahedron* **47** 615 (1991)
209. J-I Yoshida, S-I Matsunaga, S Isoe *Tetrahedron Lett.* **30** 219 (1989)
210. J-I Yoshida, S Isoe *Chem. Lett.* 631 (1987)
211. R Glass, A Radspinner, W Pal Singh *J. Am. Chem. Soc.* **114** 4921 (1992)
212. M Lemair, W Buchner, R Garreau, H A Hoa, A Guy, J Roncali *J. Electroanal. Chem.* **281** 293 (1990)
213. T Takiguchi, T Nonaka *Chem. Lett.* 1217 (1987)
214. K Suda *Tetrahedron Lett.* **33** 1355 (1992)
215. D Adebimpe *J. Electroanal. Chem.* **348** 447 (1993)
216. J Roncali, A Guy, M Lemaire, R Garreau, H A Hoa *J. Electroanal. Chem.* **312** 277 (1991)

217. V V Jouikov, D S Fattakhova *Zh. Obshch. Khim.* **66** 1931 (1996) [b]
218. S-H Yi, S Ohashi, K Ogino, H Sato, H Nomori *Synth. Met.* **61** 247 (1993)
219. H Masuda, Y Taniki, K Kaeriyama *Synth. Met.* **55** 1246 (1993)
220. K Broka, J P Stridins, I Sleiksa, E Lukevics *Latv. Khim. Zh.* **5** 575 (1992)
221. C P Andrieux, P Audebert, P Hapiot, J M Saveant, in *Proceedings of J Heyrovsky Centennial Congress on Polarography. The 41st Organic Joint Meeting ISE, Prague, 1990*, Vol. 2, p. C.Th 2
222. Yu V Kolodyazhnyi, A P Sadimenko, L P Sadimenko, K I Tkachenko, A I Prokof'ev, M M Morgunova, O A Osipov *Zh. Obshch. Khim.* **47** 230 (1977) [b]
223. J-I Yoshida, S Isoe *Tetrahedron Lett.* **28** 6621 (1987)
224. K Suda, K Hotoda, T Takanami, in *International Symposium on Electroorganic Synthesis, Kurashiki, 1994* p. 130
225. K Broka, V Glezer, J Stradins, in *Proceedings of J Heyrovsky Centennial Congress on Polarography. The 41st Organic Joint Meeting ISE, Prague, 1990*, Vol. 2, p. C.Th 14
226. T Shono, H Ohmizu, N Kise *Chem. Lett.* 1517 (1980)
227. L C Lin, L L Chueh, S C Tsay, J R Hwu *Tetrahedron Lett.* **36** 4093 (1995)
228. R T Stewart *J. Am. Chem. Soc.* **102** 4999 (1980)
229. J Swenton, K Carpenter, Y Chen, M Kerns, G Morrow *J. Org. Chem.* **58** 3308 (1993)
230. H J Schäfer *Angew. Chem., Int. Ed. Engl.* **20** 911 (1981)
231. S Torii, T Okamoto N Ueno *J. Chem. Soc., Chem. Commun.* 293 (1978)
232. J-I Yoshida, S -I Matsunaga, T Maekawa, S Isoe *J. Electrochem. Soc.* **137**/**3** 624 (1990)
233. S Torii, H Okamoto, in *International Symposium on Electroorganic Synthesis, Kurashiki, 1994* p. 133
234. G Cerveau, C Chuit, E Colomer, R J P Corriu, C Reye *Organometallics* **9** 2415 (1990)
235. S Nakatani, J-I Yoshida, S Isoe *Tetrahedron* **49** 2011 (1993)
236. T Takanami, K Suda, H Ohmori, M Masui *Chem. Lett.* 1335 (1987)
237. J-I Yoshida, Y Morita, Y Ishichi, S Isoe *Tetrahedron Lett.* 5247 (1994)
238. S Torii, T Inokuchi, S Takagishi, H Horike, H Kuroda, K Uneyama *Bull. Chem. Soc. Jpn.* **60** 2173 (1987)
239. W Sundermeyer, W Verbeek *Angew. Chem., Int. Ed. Engl.* **5** 1 (1966)
240. USSR P. 112 928; *Byull. Izobret.* (5) 36 (1958)
241. V V Zhuikov, Yu M Kargin *Izv. Akad. Nauk, Ser. Khim.* 379 (1995)
242. A V Bukhtiarov, M N Lukanin, A P Tomilov, in *Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii* (The Structure and Reactivity of Organosilicon Compounds) (Irkutsk: Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, 1977) p. 158
243. A V Bukhtiarov, A P Tomilov, M N Lukanin *Elektrokhimiya* **14** 809 (1978) [a]
244. A V Bukhtiarov, A P Tomilov, M N Lukanin, V P Bud'ko *Zh. Prikl. Khim.* **52** 880 (1979) [f]
245. USSR P. 642 313; *Ref. Zh. Khim.* **1** L 298P (1980)

[a] — *Russ. J. Electrochem. (Engl. Transl.)*
[b] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[c] — *J. Struct. Chem. (Engl. Transl.)*
[d] — *Dokl. Chem. (Engl. Transl.)*
[e] — *Russ. Chem. Bull. (Engl. Transl.)*
[f] — *Russ. J. Appl. Chem. (Engl. Transl.)*