

Electrochemical synthesis of fluoro-organosilanes

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Abstract

The electrochemical reduction of some fluorohalocarbons in the presence of trimethylchlorosilane is followed by formation of the corresponding fluoroalkyltrimethylsilanes. CF_3SiMe_3 , $\text{CFCl}_2\text{SiMe}_3$, $\text{CF}_3\text{CCl}_2\text{SiMe}_3$ and $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{SiMe}_3$ were obtained with current efficiency 20–50%. Voltammetric data are presented. © 1997 Elsevier Science S.A.

Keywords: Fluoro-organosilanes; Fluorohydrocarbons; Fluoroalkylation; Silylation; Electrochemical reduction

1. Introduction

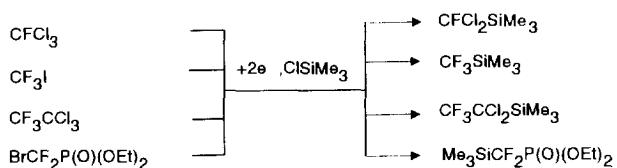
Fluoroalkyltrimethylsilanes are useful reagents for introduction of the fluoroalkyl substituents into organic molecules [1].

Traditional methods of their synthesis include the reaction with non-readily available tris-dialkylamidophosphites [2]. At the same time the electrochemical reduction (ECR) of carbon tetrachloride and chloroform in the presence of trimethylchlorosilane (TMCS) enables di- and trichloromethylsilane formation [3]. Trifluorobromomethane under analogous conditions reacts with the solvent [4], although the authors observed the “silylated” products if a large excess of TMCS was used. Recently electrochemical synthesis of CF_3SiMe_3 has been described [5].

It was our purpose to expand the direct method of electrochemical synthesis of fluoroalkyltrimethylsilanes with various fluoroalkyl substituents.

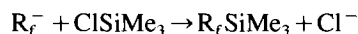
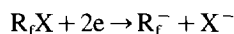
2. Results and discussion

The preparative electrolysis of some fluorocarbons in DMF on a stainless steel cathode with a sacrificial Zn anode in the presence of TMCS excess was established to produce the corresponding haloalkylsilanes:



The results of electroreduction are presented in Table 1. The produced silanes have been identified by ¹⁹F-NMR, chromatography-mass spectra and GLC. Silanes IX, XI, XII are identical to authentic samples [2,6,7]. ECR of difluorodibromomethane (VI) under the same conditions does not afford $\text{Me}_3\text{SiCF}_2\text{Br}$. Trifluorotrichloroethane (VII) undergoes more complicated transformations, which are now under study.

We did not observe the reduction of trimethylchlorosilane at up to -2.7 V by voltammetry (DMF, Et_4NBF_4 , SCE, glassy carbon). The sole peak (-2.14 V) on the voltammogram, being unaffected by water addition, might be related to HCl reduction, produced by trimethylchlorosilane hydrolysis. So the reaction scheme seems to be as follows.



Generation of the fluoroalkyl carbanion is a fast two-electron irreversible process, the silylation stage is more slow, and for reduction of carbon tetrachloride in the presence of trimethylchlorosilane $\text{CCl}_3\text{SiMe}_3$ was observed as a peak on the voltammogram ($E_p - 2.3$ V) at low scan rates (0.1 – 0.5 V s^{-1}). At the scan rate 50 V s^{-1} this peak is absent.

Reduction potentials of silanes IX and X are also about -2.4 V and, in galvanostatic conditions of electrolysis, they are also partially reduced. On reduction of trifluorotrichloroethane (III), besides the main product, the following compounds were detected:

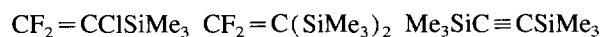


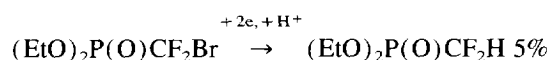
Table 1
Electrochemical silylation of fluorohalogen compounds

Compound	$-E_p$ (V) ^a	Product	Current efficiency (%) ^b
CCl ₄ (I)	1.49	CCl ₃ SiMe ₃	[3]
CFCl ₃ (II)	1.82	CFCl ₂ SiMe ₃ (IX)	50
CF ₃ CCl ₃ (III)	1.61	CF ₃ CCl ₂ SiMe ₃ (X)	18
CF ₂ CBr ₂ (IV)	1.51	–	–
CF ₃ I (V)	1.72	CF ₃ SiMe ₃ (XI)	32
CF ₃ Br (VI)	1.92	(XI)	[5]
CF ₂ ClCFCl ₂ (VII)	2.04	–	–
BrCF ₂ P(O)(OEt) ₂ (VIII)	1.87	(EtO) ₂ P(O)CF ₂ SiMe ₃ (XII)	40

^a Reduction potentials were obtained on a stationary glassy carbon electrode in DMF solution with 0.1 M Et₄NBF₄ as supporting electrolyte, vs. SCE.

^b At two electron process.

Silanes **XI** and **XII** are not electroactive under electrolysis conditions, and difluorophosphonate, formed as a by-product in the silane **XII** synthesis, arises from the concurrent reaction of the intermediate anion with solvent:



We also tried to realise the chemical synthesis of fluorodichloro- and trichloro-methyltrimethylsilanes in conditions close to that of electrolysis. The reaction of Zn powder with trichlorofluoromethane or carbon tetrachloride in dimethylformamide or *N*-methylpyrrolidone in the presence of trimethylchlorosilane appeared to produce the desirable silanes in high yields at very low (<5%) conversion. The conversion increase leads to a sharp decrease of the yield, probably caused by the further reduction of the silane.

3. Experimental

¹⁹F-NMR spectra were recorded on a Bruker AC-200 utilising trifluoroacetic acid as an external standard. Chromatograms were obtained on a "VGMS 70-70 E" instrument. Dimethylformamide was distilled from phosphorus pentoxide at reduced pressure, trimethylchlorosilane in an inert atmosphere from Mg powder. Voltammetry measurements were made with polarographic analyzer PA-2 (Praha), preparative electrolysis was made with potentiostat P-5827M in an atmosphere of dry argon.

3.1. General procedure

The mixture of 50 ml DMF, 15 ml TMCS and 0.2 g Et₄NBF₄ was placed in an undivided electrochemical cell, equipped with a stainless steel cathode (50 cm²), a Zn anode (8 mm diameter rod) and a magnetic stirrer, and pre-electrolysis was carried out at a current of 100 mA during 1 h. Then 0.01–0.08 M of fluorohalocarbon was added and electrolysed with 2.1 F current consumption at a current density of 10 mA cm⁻². Electrolyte was extracted with an ether–

pentane 1:1 mixture, washed with saturated NaCl water solution, dried and distilled.

3.1.1. Fluorodichloromethyltrimethylsilane (IX)

Yield 50%; b.p. 131 °C; ¹⁹F-NMR (without solvent): δ_F –0.9 ppm (s). Lit. [2].

3.1.2. 2,2,2-Trifluoro-1,1-dichloroethyltrimethylsilane (X)

Yield 18%; ¹⁹F-NMR (without solvent): δ_F –4.6 ppm (s). *m/z*: 151 (C₂F₃Cl₂⁺), 73 (Me₃Si⁺). Lit. [8].

3.1.3. Trifluoromethyltrimethylsilane (XI)

Yield 32% b.p.; 45 °C; ¹⁹F-NMR (without solvent): δ_F –11.0 ppm (s). Lit. [6].

3.1.4. Trimethylsilyldifluoromethanephosphonic acid diethyl ester (XII)

Yield 40%; ¹⁹F-NMR (without solvent): δ_F 52.3 ppm (d, *J*_{P-F} = 95 Hz). Lit. [7].

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