

Journal of Fluorine Chemistry 85 (1997) 127-128



Electrochemical synthesis of fluoro-organosilanes

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Received 12 December 1996; accepted 7 April 1997

Abstract

The electrochemical reduction of some fluorohalocarbons in the presence of trimethylchlorosilane is followed by formation of the corresponding fluoroalkyltrimethylsilanes. CF_3SiMe_3 , $CFcl_2SiMe_3$, $CF_3CCl_2SiMe_3$ and $(EtO)_2P(O)CF_2SiMe_3$ 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 CF₃SiMe₃ 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:



0022-1139/97/\$17.00 © 1997 Elsevier Science S.A. All rights reserved *PII* S0022-1139(97)00073-0 The results of electroreduction are presented in Table 1. The produced silanes have been identified by ¹⁹F-NMR, chromato-mass spectra and GLC. Silanes **IX**, **XI**, **XII** are identical to authentic samples [2,6,7]. ECR of diffuorodibromomethane (**VI**) under the same conditions does not afford Me₃SiCF₂Br. Triffuorotrichloroethane (**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, Et₄NBF₄, 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.

$$R_{f}X + 2e \rightarrow R_{f}^{-} + X^{-}$$
$$R_{f}^{-} + ClSiMe_{3} \rightarrow R_{f}SiMe_{3} + Cl^{-}$$

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 trimethychlorosilane CCl₃SiMe₃ 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:

 $CF_2 = CClSiMe_3 CF_2 = C(SiMe_3)_2 Me_3SiC \equiv CSiMe_3$

Compound	$-E_{\rm p}$ (V) ^a	Product	Current efficiency (%) ^b
$\operatorname{CCl}_{4}(\mathbf{I})$	1.49	CCl ₃ SiMe ₃	[3]
CFCl ₃ (II)	1.82	$CFCl_{3}SiMe_{3}(IX)$	50
CF ₃ CCl ₃ (III)	1.61	$CF_3CCl_2SiMe_3(X)$	18
$CF_2CBr_2(IV)$	1.51	-	_
$CF_{4}I(\mathbf{V})$	1.72	CF_3SiMe_3 (XI)	32
$CF_{3}Br(VI)$	1.92	(\mathbf{XI})	[5]
CF ₂ ClCFCl ₂ (VII)	2.04	<u> </u>	
$BrCF_2P(O)(OEt)_2(VIII)$	1.87	$(EtO)_2P(O)CF_2SiMe_3(XII)$	40

Table 1 Electrochemical silylation of fluorohalogen compounds

^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:

$$(\text{EtO})_2 P(O) CF_2 Br \xrightarrow{+2e, +H^+} (\text{EtO})_2 P(O) CF_2 H 5\%$$

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. Chromatomass spectra 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 Et_4NBF_4 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): $\delta_{\rm F} = 0.9$ ppm (s). Lit. [2].

3.1.2. 2,2,2-Trifluoro-1,1-dichhloroethyltrimethylsilane (X) Yield 18%; ¹⁹F-NMR (without solvent): $\delta_{\rm F}$ -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): $\delta_{\rm F} - 11.0$ 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].

Acknowledgements

We wish to thank the International Science and Technology Center (ISTC project No 136-94) for financial support of this research.

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