

(Fluorovinyl)trimethylsilanes from the Electrochemical Silylation of Fluoroalkenes in the Presence of Chlorotrimethylsilane

Boris I. Martynov

State Research Institute of Organic Chemistry and Technology, 23, Shosse Entuziastov, Moscow, 111024 Russia.

Andrei A. Stepanov*

A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 Vavilov Str., Moscow, 117813 Russia.

D. Vaughan Griffiths

Department of Biological and Chemical Sciences, University of Essex, Wivenhoe Park, Colchester C04 3SQ, UK.

Received 14 October 1997; revised 28 October 1997; accepted 30 October 1997

Abstract: The synthesis of the 2-substituted (1,2-difluorovinyl)trimethylsilanes **3** (R = F, Cl and CF₃) has been investigated by the electrochemical reduction of an appropriate fluoroalkene in the presence of chlorotrimethylsilane (TmsCl) in an undivided cell using a sacrificial anode. While the vinylsilanes **3** (R = F and Cl) were produced in good yield from trifluorobromoethene and 1,2-difluoro-1,2-dichloroethene, respectively, the production of **3** (R = CF₃) from hexafluoropropene was only achieved in low yield. Voltammetry data are presented.

© 1997 Elsevier Science Ltd. All rights reserved.

The value of organosilicon compounds as useful synthetic intermediates is well established.¹ Fluorinated vinylsilanes, like the analogous fluoroalkylsilanes, are of interest because of their potential for introducing fluorinated hydrocarbon units into organic molecules.² Fluorovinylsilanes have generally been prepared either by the silylation of lithium fluoroalkenes, which are available from several sources,^{3,4,5} or *via* a route which initially involves the irradiation of a mixture of the perfluoroalkene and bis(trimethylsilyl)mercury.⁶ In this latter method, the mercury compound is first added across the carbon-carbon double bond of the fluoroalkene to give a saturated system which then eliminates mercury and fluorotrimethylsilane to give the required (fluorovinyl)silane. A route involving the use of hexaethyl phosphorous triamide to couple chlorotrimethylsilane to bromotrifluoroethene has also been reported⁷ although chlorotrifluoroethene proved unreactive under these conditions.

Since the electrochemical silylation of fluorohalocarbons has proved to be a convenient method for the synthesis of certain (fluoroalkyl)trimethylsilanes,⁸ it was of interest to investigate whether a similar approach could be used for synthesis of (fluorovinyl)trimethylsilanes.

RESULTS AND DISCUSSION

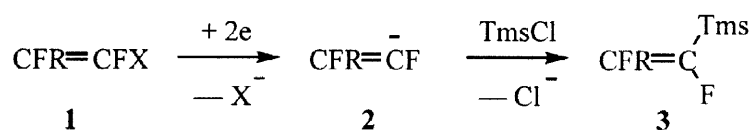
The electrochemical reduction of several fluoroalkenes **1**, exhibiting reduction potentials less negative than -2.7 V,⁹ has been investigated in the presence of excess chlorotrimethylsilane (TmsCl) in an appropriate organic solvent and shown to lead to the formation of the corresponding (fluorovinyl)trimethylsilanes **3** (see Table 1).

Table 1. Electrochemical Silylation of Fluoroalkenes.⁹

Fluoroalkene	E _p V	Product	Current efficiency, %
CFCI=CFCI	-2.63	CFCI=CFTms	20 — 40
CF ₂ =CFBr	-1.90	CF ₂ =CFTms	28 ^{a,b}
CF ₃ CF=CF ₂	-2.14	CF ₃ CF=CFTms	<10 ^{a,c}

^a Using a stainless steel cathode and a sacrificial zinc anode; ^b Solvent DMF; ^c Solvent MeCN.

Since we have recently reported¹⁰ that the reduction potential of chlorotrimethylsilane would be more negative than -2.7 V under these conditions, it is reasonable to assume that the reaction process being observed in the presence of both the fluoroalkenes **1** and chlorotrimethylsilane involves the initial generation of the vinylic carbanion **2** which then undergoes silylation by the chlorotrimethylsilane as shown in Scheme 1.



Scheme 1

The preparative scale electrochemical reduction of 1,2-difluoro-1,2-dichloroethene **1** (R = X = Cl) in the presence of a two- to three-fold molar excess of chlorotrimethylsilane was investigated in a variety of aprotic solvents, including acetonitrile, dimethylformamide, and hexamethyl phosphoric triamide (HMPT). The reductions were carried out at constant current in an undivided cell using either a stainless steel (SS) or nickel cathode and a sacrificial zinc or aluminium anode. The results are summarised in Table 2.

Table 2. Electrochemical Silylation of **1** (R = X = Cl) to give **3** (R = Cl).

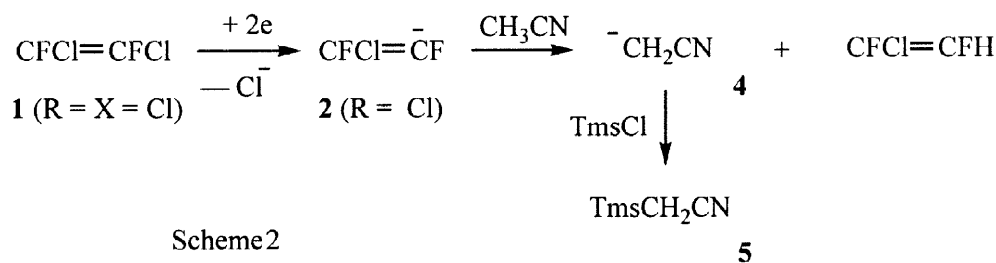
Solvent	Cathode	Anode	Current density, mA/cm ²	Current efficiency, %	E:Z isomer ratio [†]
DMF	SS	Zn	20	19	3:1
DMF	SS	Zn	15	19	5:1
DMF + TMEDA	SS	Zn	20	36	3:1
DMF + bipy-Ni	SS	Zn	12	25	1.6:1
TmsCl:HMPT 4:1	SS	Al	7.5	42	6:1
MeCN	SS	Al	15	40	2.8:1
MeCN	SS	Al	7.5	41	3.1:1
MeCN	Ni	Al	15	40	3:1
DMF	SS	Al	10	-	-

[†] E:Z isomer ratios for **3** (R = Cl) were determined by GLC

The use of a zinc anode for the silylation of **1** (R = X = Cl) resulted in a low yield of the silane **3** (R = Cl) and zinc deposition on the cathode was also observed. However, when tetramethylethylenediamine

(TMEDA) was added to the reaction mixture, to prevent zinc deposition, the current efficiency for the production of **3** (R = Cl) was increased to 36%. The addition of tris(bipyridyl)nickel tetrafluoroborate (bipy-Ni) to the reaction mixture was also investigated. However, while the combination of a sacrificial zinc anode, together with a catalytic quantity of tris(bipyridyl)nickel tetrafluoroborate, has been shown to facilitate the electroreductive coupling of organic halides to some electrophiles^{11,12} via the *in situ* formation of Ni(0), this combination produced little improvement in the electroreductive coupling of **1** (R = X = Cl) to chlorotrimethylsilane. In contrast, the use of a sacrificial aluminium anode allowed the electrolysis of 1,2-difluoro-1,2-dichloroethene **1** (R = X = Cl) to proceed at higher cathodic potentials, except when the silylation was attempted in dimethylformamide (DMF) when only tar was obtained. Interestingly, the combination of DMF as solvent and a sacrificial aluminium electrode was not selected for the electrochemical formation of trimethyl(trifluoromethyl)silane from bromotrifluoromethane⁸ due to the possibility of trifluoroacetaldehyde formation.¹³ The highest current efficiency for the formation of **3** (R = Cl) was achieved in a solvent mixture of chlorotrimethylsilane (80%) and HMPT (20%) using stainless steel and aluminium electrodes. However, the low conductivity of this solution and the precipitation of an aluminium chloride—HMPT complex hindered product formation and separation. The most convenient system for the preparation of **3** (R = Cl), from the point of view of product isolation, was found to be that with acetonitrile as the solvent and aluminium as the sacrificial anode. Under these conditions the current efficiency was about 40% regardless of whether a stainless steel or nickel cathode was used.

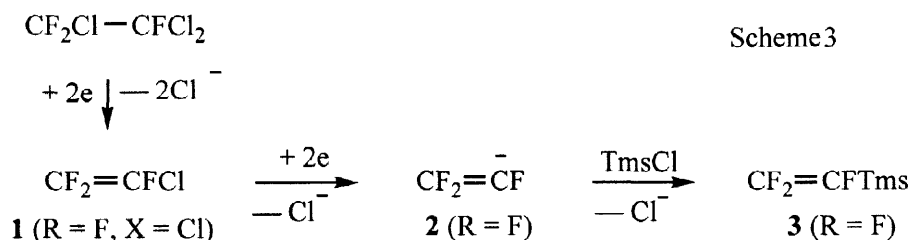
The yield of the (fluorovinyl)silane **3** (R = Cl) via the electroreductive coupling approach is significantly higher than that produced via the bis(trimethylsilyl)mercury route,⁶ although lower than that claimed for the production of trimethyl(trifluoromethyl)silane by the electrochemical trimethylsilylation of bromotrifluoromethane.⁸ The lower yield of the (fluorovinyl)silane is probably due to two factors; firstly, the high reduction potential of **1** (R = X = Cl) which means that side reactions involving the supporting electrolyte tend to take place and, secondly, the high reactivity of the intermediate vinylic carbanion **2** (R = Cl) which is initially formed. Thus, for example, trimethylsilylacetonitrile **5** was observed amongst the products of the electrolysis of **1** (R = X = Cl) in acetonitrile. This suggests the involvement of the cyanomethyl carbanion **4** which would be formed by hydrogen abstraction from the acetonitrile by the vinylic carbanion **2** (R = Cl) (see Scheme 2).



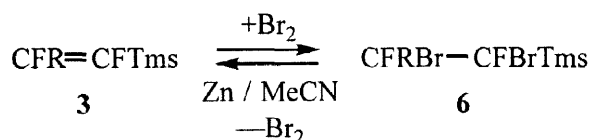
It is also interesting to note that, while the E to Z isomer ratio in the starting alkene **1** (R = X = Cl) was 1:1, the proportion of the E isomer present in the product **3** (R = Cl) was higher (see Table 2). This may be caused either by isomerisation of an intermediate such as the radical precursor of the carbanionic intermediate **2** (R = Cl),¹⁴ or by small differences in the reduction potentials of the E and Z isomers of the alkene **1** (R = X = Cl). The observation that the isomer ratio in the product **3** (R = Cl) is dependent on the current density

used during the electrochemical reduction, with selectivity increasing as the current density is reduced (see Table 2), points to the latter explanation being the more likely.

The electrochemical silylation of trifluorobromoethene **1** (R = F, X = Br) was also investigated and here the reaction was successfully carried out in DMF with a stainless steel cathode and a sacrificial zinc anode to facilitate the isolation of the vinylsilane **3** (R = F). Although these conditions resulted in some zinc deposition, the yield of the vinylsilane **3** (R = F) was still about 60%, based on the quantity of starting material consumed, comparable to the yield obtained when the anion **2** (R = F) was generated by the action of methyl lithium on the bromoalkene **1** (R = F, X = Br).³



It is interesting to note that traces of the vinylsilane **3** (R = F) were also observed following the electrochemical reduction of 1,1,2-trichloro-1,2,2-trifluoroethane in the presence of chlorotrimethylsilane. It seems probably that under these conditions some chlorotrifluoroethene **1** (R = F, X = Cl) is initially produced which is then able to undergo reduction to vinylic carbanion **2** (R = F) before being silylated (see Scheme 3). However, it should be noted, that reduction of chlorotrifluoroethene **1** (R = F, X = Cl) is not observed by voltammetry under these same conditions. This suggests that if chlorotrifluoroethene is produced from the 1,1,2-trichloro-1,2,2-trifluoroethane it probably remains associated with the electrode in some way prior to its reduction.



Scheme 4

Although it has been shown previously that the trifluoromethylation of dialkyl fluorophosphonates can be carried out in essentially quantitative yield with trimethyl(trifluoromethyl)silane in the presence of a catalytic quantity of fluoride ion,¹⁵ the analogous reaction did not occur when attempts were made to react the silane **3** (R = F) with diisopropyl fluorophosphonate and diethyl chlorophosphonate in the presence of caesium fluoride. Both the vinylsilanes **3** (R = Cl) and **3** (R = F) could, however, be quantitatively brominated by the addition of bromine. The *erythro*- and *threo*- isomer ratio in the dibromo compound **6** (R = Cl) was found to be the same as in the starting silane **3** (R = Cl), and both silanes **6** (R = Cl) and **6** (R = F) were readily debrominated by heating with zinc powder in acetonitrile. This bromination/debromination procedure (Scheme 4) provides a convenient method for the purification of **3** (R = Cl).

Although the electrosilylation of hexafluoropropene **1** (R = CF₃, X = F) in acetonitrile resulted in the formation of some 1,2,3,3,3-pentafluoro-1-(trimethylsilyl)propene,^{4,16} yields were low (see Table 1) and the product isolated was found to have exclusively the E-configuration. While this may be due to the preferential destruction of the Z isomer under the reaction conditions, it is interesting to note that earlier workers¹⁶ also

reported the formation of only one isomer from the reactions of the anion **2** ($R = CF_3$), which they attributed to isomerisation of this anionic intermediate. Later workers,⁴ however, observed the formation of both isomeric products and could find no evidence for significant isomerisation of the anion **2** ($R = CF_3$).

EXPERIMENTAL

¹⁹F NMR spectra were recorded on a Bruker AC-200 spectrometer using neat trifluoroacetic acid as the external standard. GC-mass spectra were obtained on a VGMS 70-70E instrument. DMF was purified by distillation from phosphorus pentoxide at reduced pressure. Chlorotrimethylsilane was purified by distillation from Mg-powder in an inert atmosphere. Acetonitrile was twice distilled from phosphorus pentoxide and then from calcium hydride. Voltammetry measurements were made using a polarographic analyzer PA-2 (Praha). Preparative electrolyses were achieved with a P-5827M potentiostat in an atmosphere of dry argon.

General procedure for electrolysis.

The electrochemical cell used was equipped with a stainless steel or nickel grid cathode (20 cm²), a zinc or aluminium rod anode (Ø 6 mm), a water-cooling jacket, magnetic stirrer and inert gas inlet. The solvent (30 cm³) (see Tables 1 and 2), tetraethylammonium fluoroborate (0.1 g) and chlorotrimethylsilane (6 cm³) were added and pre-electrolysis was carried out at constant current (50 mA) for 30 min. The fluoroalkene (20 mmol) was added and electrolysis continued at a current density of 7.5 — 20 mA/cm² until 2 F had been consumed. For the cases **3** ($R = Cl$) and **3** ($R = CF_3$), the resulting electrolyte was poured onto ice and then extracted with diethyl ether (2 × 20 cm³). The extracts were washed with water, dried over anhydrous MgSO₄ and then distilled to obtain the pure product. In the case of **3** ($R = F$), the product was distilled from the electrolyte to a cold trap under reduced pressure and then dissolved in octane. The resulting octane solution was then washed with water, dried, and finally distilled to obtain the pure product.

(2-Chloro-1,2-difluorovinyl)trimethylsilane, 3 (R = Cl). This material was isolated as a colourless liquid as a mixture of two isomers (see Table 2 for isomer ratios), bp 83—87 °C; (E isomer) δ_F 40.5 (1F, d, J_{FF} 134 Hz, F-2), 83.5 (1F, d, J_{FF} 134 Hz, F-1); (Z isomer) δ_F 9.5 (1F, d, J_{FF} 6 Hz, F-2), 69.2 (1F, d, J_{FF} 6 Hz, F-1).⁶

Trifluorovinyltrimethylsilane, 3 (R = F). This material was isolated as a colourless liquid, bp 64—66 °C (lit.,⁵ 65 °C, ³ 67 °C at 760 mmHg); δ_F 11.5(1F, dd, J_{FF} 25 and 71 Hz, F-2a), 40.6(1F, dd, J_{FF} 71 and 116 Hz, F-2b), 122.1(1F, dd, J_{FF} 25 and 116 Hz, F-1).¹⁷

Bromination of the (fluorovinyl)silanes 3 (R = Cl) and 3 (R = F).

A solution of bromine (20 mmol) in pentane (10 cm³) was added to a solution of the (fluorovinyl)silane (10 mmol) in pentane (5 cm³) at 20 — 25 °C. After 0.5 h the mixture was washed with a 5% aqueous sodium carbonate solution and then dried (anhydrous MgSO₄). The dibromo compounds were formed in essentially quantitative yield and isolated by distillation under reduced pressure.

(1,2-Dibromo-2-chloro-1,2-difluoroethyl)trimethylsilane, 6 (R = Cl). This material was isolated as a colourless liquid, bp 72 — 74 °C at 10 mmHg; δ_F —23.8 (1F, d, J_{FF} 27 Hz, F-2), 50.6 (1F, d, J_{FF} 27 Hz,

F-1); δ_{F} —21.7 (1F, d, J_{FF} 32 Hz, F-2), 52.7 (1F, d, J_{FF} 32 Hz, F-1); (Found: C, 18.23; H, 2.73; F, 11.52; Si, 8.37. Calc. for $\text{C}_5\text{H}_9\text{F}_2\text{ClBr}_2\text{Si}$: C, 18.17; H, 2.75; F, 11.50; Si, 8.50%).

(1,2-Dibromo-1,2,2-trifluoroethyl)trimethylsilane, **6** ($R = \text{F}$). This material was isolated as a colourless liquid, bp 63 °C at 30 mmHg; δ_{F} —27.2 (1F, dd, J_{FF} 18 and 171 Hz, F-2a), 22.8 (1F, dd, J_{FF} 27 and 171 Hz, F-2b), 64.5 (1F, dd, J_{FF} 18 and 27 Hz, F-1); (Found: C, 19.20; H, 3.11; F, 17.97. Calc. for $\text{C}_5\text{H}_9\text{F}_3\text{Br}_2\text{Si}$: C, 19.12; H, 2.89; F, 18.15%).

Debromination of **6** ($R = \text{Cl}$)

The silane **6** ($R = \text{Cl}$) (1.6 g, 5 mmol), acetonitrile (2 cm³) and zinc powder (1 g) were heated at 50 °C for 1 h. Ether (15 cm³) was then added and the mixture filtered. The diethyl ether solution was then washed with water and then dried (anhydrous MgSO_4). Distillation resulted in the isolation of the silane **3** ($R = \text{Cl}$) (0.6 g, 70%) together with a quantity (0.1 g) of the unreacted starting material **6** ($R = \text{Cl}$).

ACKNOWLEDGEMENTS

The authors are grateful to the International Science and Technology Center (ISTC project 136-94) for their financial support of this work.

REFERENCES AND NOTES

- Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*, Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Eds.; Pergamon Press: Oxford, 1982; vol. 7, pp. 515-659; Fleming, I. In *Comprehensive Organic Chemistry*, Barton, D. H. R.; Ollis, W. D. Eds.; Pergamon Press: Oxford, 1979; vol. 3, pp. 541-686.
- Petrov, V. A.; Shevchenko, N. V.; Grinevskaya, V. K.; Parnes, Z. N.; Bardin, V. V.; Furin, G. G.; German, L. S.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 2826-31.
- Tarrant, P.; Oliver, W. H. *J. Org. Chem.* **1966**, 31, 1143-46.
- Hahnfeld, J. L.; Burton, D. J. *Tetrahedron Lett.*, **1975**, 773-76.
- Seyferth, D.; Welch, D. E.; Raab, G. *J. Amer. Chem. Soc.* **1962**, 84, 4266-69.
- Fields, R.; Haszeldine, R. N.; Hubbard, A.F. *J. Chem. Soc. Perkin Trans. 1*, **1972**, 847-49.
- Bardin, V. V.; Pressman L. S.; Cherstkov, V. F. *Synth. Commun.* **1995**, 25, 2425-33.
- Surya, G. K.; Deffieux, D.; Yudin A. K.; Olah, G. A. *Synlett.* **1994**, 1057-58.
- Reduction potentials were obtained on a stationary glassy carbon electrode in a solution of Et_4NBF_4 in acetonitrile (0.1 M) vs SCE.
- Martynov, B. I.; Stepanov, A. A. *J. Fluor. Chem.* in the press.
- Conan, A.; Sibille S.; Périchon, J. *J. Org. Chem.* **1991**, 56, 2018-24.
- Mcharek, S.; Sibille, S.; Nédélec, J-Y; Périchon, J. *J. Organomet. Chem.* **1991**, 401, 211-15.
- Sibille, S.; Périchon J.; Chaussard, J. *Synth. Commun.* **1989**, 19, 2449-52.
- Yoshida, J.; Muraki, K.; Funahashi, H.; Kawabata, N. *J. Org. Chem.* **1986**, 51, 3996-4000.
- Semchenko, F. M.; Eremin, O. G.; Martynov, B. I. *Zh. Obshch. Khim.* **1992**, 62, 473-74.
- Tarrant, P.; Whitfield Jr., R. W.; Summerville, R. H. *J. Fluor. Chem.* **1971**, 1, 31-40.
- Moreland, C. G.; Brey Jr., W. S. *J. Chem. Phys.* **1966**, 45, 803-808.