

Journal of Fluorine Chemistry 114 (2002) 225-228



www.elsevier.com/locate/jfluchem

Organoelement compounds in the electrochemical synthesis of fluoroorganics

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Abstract

Electrochemical generation of organic anion-radicals in the presence of fluoroorganosilanes causes the chain addition reaction. Adducts of CFCl₂SiMe₃, CFCl=CFSiMe₃ and CF₃SiMe₃ with benzaldehyde were obtained with conversion efficiency up to 8000%.

Electroreduction of bis-(trifluoromethyl)mercury (II) was established to be the route for the intermediate formation of trifluoromethyl anion, which was trapped by the reactions with benzaldehyde, Me₃SiCl and bromobenzonitrile.

The use of *salen* Ni(II) complex as mediator allows the electrochemical reduction of polyfluoroalkylchlorides at the potentials more than 1 V higher than their reduction potentials. O 2002 Published by Elsevier Science B.V.

Keywords: Electrochemistry; Reduction; Organofluoro compounds; Organosilicon compounds; Organomercury compounds

1. Introduction

The use of organoelement compounds gives many possibilities for the synthesis of fluoroorganics. Organofluorotrialkylsilanes and polyfluoro oganometallics (Zn, Cd, Cu, etc.) are convenient reagents for the synthesis of partially fluorinated compounds. Transition metal complexes are effective catalysts in the addition reactions of fluoroalkylhalides. Here will be considered some examples of the application of elementoorganic compounds in preparative organic electrochemistry for synthesis of fluororganics.

2. Results and discussion

2.1. Organosilicon compounds

The perfluoroalkylation of carbonyl compounds by fluoroorganotrimethylsilanes proceeds under catalysis with nucleophilic initiators (usually fluoride ion). We have found that the electrochemically generated anion-radical of a carbonyl compound causes the same reaction:

$$\sum C=O + e \longrightarrow \left[\begin{array}{c} \dot{C} \cdot O \end{array} \right] \xrightarrow{R_{f} \cdot Ims} \quad \dot{C} \cdot OTms + \\ + R_{f}^{-} \xrightarrow{C=O} R_{f} \cdot \dot{C} \cdot O^{-} \xrightarrow{R_{f} \cdot Tms} R_{f} \cdot \dot{C} \cdot OTms + R_{f}^{-} \\ \qquad Tms = SiMe_{3} \end{array}$$

0022-1139/02/\$ – see front matter O 2002 Published by Elsevier Science B.V. PII: S0022-1139(02)00041-6

Starting from 5–10 mM of silane, this reaction is completed in 1–2 h and charge consumption is 0.02-0.33 F mol⁻¹ (i.e. conversion efficiency is 300–8000%) relative to the starting silane (Table 1), and depends mainly on the impurities in the electrolyte (traces of moisture and oxygen).

The isomer ratio in the diffuorochlorovinylsilane addition product (entry 4) does not change in comparison with that in the starting silane (E:Z = 1.5).

Zinc powder in dimethylformamide may induce the same reactions. Addition of fluorodichloromethyltrimethylsilane (I) to trifluoroacetophenone proceeds exothermically and the product was isolated in about 60% yield.

The yields from the Zn induced reaction of benzaldehyde with (I), strongly depend on the quality of the Zn powder (30-70%). The reduction potential of benzaldehyde (-1.83 V vs SCE) is about 0.3 V lower than that of trifluor-oacetophenone (-1.57 V vs SCE), so if the Zn powder is not active enough, the generation of the anion-radical occurs slowly, and the following reaction takes place

$$CFCl_2Tms \xrightarrow{Zn, DMF} Tms-F (95\%)$$

Destruction of (I) by Zn in DMF is the reason for the failure of our earlier attempts [1] to prepare this silane by the reaction of $CFCl_3$ with Zn in the presence of chlorotrimethylsilane—obviously, the rates of silane formation and destruction are similar.

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Table 1									
Electrochemically	induced	addition	of	fluoroalkyltrimethylsilanes	to				
carbonyl compounds: $RR'C=O + R_fTms \rightarrow R_fRR'C-OTms$									

Entry	R	R′	R _f	Substance yield (%)	$F \text{ mol}^{-1}$ (×10 ²)	
1	Ph	Н	CFCl ₂	62	1.9	
2	Ph	CF_3	CFCl ₂	50	1.5	
3	Ph	Н	CF ₃	84	1.2	
4	Ph	Н	CFCl=CF	49	32	

Stainless steel cathode, Al anode, in 10–20 ml DMF, 5–10 mM silane and carbonyl compound 5–10% excess, constant current 5–20 mA.

Contrary to the electrochemical process, where the presence of moisture only decreases the current efficiency, in the reduction of (I) by Zn, it results in the formation of fluorodichloromethane.

Unfortunately, our attempts at the electrochemically induced trifluoromethylation of ethylmethacrylate and acrylonitrile by trifluoromethyltrimethylsilane failed; as with the fluoride ion initiated reaction [2], only polymeric materials, containing according to the NMR data, no fluorine were obtained.

Reaction of nitrobenzene with fluorodichloromethyl- and trifluoromethyltrimethylsilanes was completed (disappearance of the silane) after consumption of less than 0.005 F per one electron process. The following Scheme 1 may be suggested.

The dimerization of fluorinated radicals and hydrogen capture are the main process. Fluoromethylation of nitrobenzene was observed only in traces. Similar results were obtained for the reaction of *m*-dinitrobenzene with CF₃Tms under electroreduction conditions, and the yields of fluoroalkylated aromatics were also very low.

2.2. Organomercury compounds

Trifluoromethylhalides (bromides and iodides) are excellent sources of the trifluoromethylanion, both in organic and electroorganic [3,4] syntheses. In the latter case, their low boiling points are substantial inconvenience, because the special electrochemical equipment for working under pressure is not readily available. We have suggested that bis-(trifluoromethyl)mercury (II) or trifluoromethylmercury trifluoroacetate, when electrochemically reduced, may be



Fig. 1. Voltammogram of $Hg(CF_3)_2$ (DMF, 0.1 M Et₄NBF₄, glassy carbon electrode, SCE, 100 mV s⁻¹).

precursors of the trifluoromethyl anion. These substances are available by pyrolysis of mercury trifluoroacatate with near quantitative yields. They possess very high boiling points. The voltammetry of bis -(trifluoromethyl)mercury (II) shows a very complicated process (Fig. 1), nevertheless, the reduction takes place already at the available potential -1.5 V.

Preparative electrolysis of (II) in the presence of benzaldehyde, chlorotrimethylsilane and *p*-bromobenzonitrile allows the preparation of corresponding tifluoromethylated products (Scheme 2):

The yields in these reactions are 40–50% and the conversion of starting mercury compound was about 50%. The reason of low current efficiency was that the electrolyses were carried out in a one compartment cell with a sacrificial anode. The copper anode was acceptable only, because standard zinc or Al anodes, even positively polarized, caused the decomposition of the starting mercurial (II). For this reason, a side reaction was the cathodic deposition of copper, arising from the anodic process. Trifluoromethylmercury trifluoroacetate was used in these reactions with approximately the same result.



Scheme 1. Reaction of electrochemically induced anion-radical of nitrobenzene with organofluorotrimethylsilane.



Scheme 2. Electroreductive reactions of bis-(trifluoromethyl)mercury (II).

2.3. Organometallic mediators

Polyfluoroalkyl chlorides are less expensive than corresponding bromides and iodides, but they were not used in electrochemical synthesis because of their low reduction potential. We find out that the *salen* Ni(II) complex is an effective mediator for reduction of CF_3CH_2Cl (reduction potential is more negative than -2.7 V) and $H(CF_2)_6Cl$ (reduction potential, -2.65 V). Voltammetry of *salen* Ni(II) complex (Fig. 1, curve 1) shows one electron reversible reduction at -1.65 V. The addition of the polyfluoroalkyl



Fig. 2. Voltammogram of *salen* Ni(II) complex (acetonitrile, 0.1 M Et₄NBF₄, glassy carbon, SCE, 100 mV s⁻¹). Curve 1, 2×10^{-3} M; curve 2, 2×10^{-3} *salen* Ni(II) complex and 2.8×10^{-3} M of H(CF₂)Cl.

chloride to the electrolyte, causes an irreversible process and the peak current increases by five times (Fig. 2, curve 2), the molar ratio chloride: complex being 1.4. It should be noted that the catalytic effect on the fluorinated alkylchlorides is very high. In the case of non-fluorinated species, the addition of even a 10-fold excess of halide is followed by the increase of the peak current up to 1.5 times [5]. Preparative electrolysis of CF₃CH₂Cl in acetonitrile on a platinum cathode in the presence of catalytic amounts of *salen* Ni(II) complex at -1.6 V results in 1,1-difluoroethene formation. On the addition of benzaldehyde (reduction potential -1.8 V) to the electrolyte, a low yield mixture of trifluoroethylated aromatics, forming

obviously, both via trifluoroethyl radical and anion, was also observed.

Preparative electroreduction of $H(CF_2)_6Cl$ in acetonitrile $(pK_a = 25)$, using the *salen* Ni(II) complex leads to hydrogenolysis of the carbon–chlorine bond and $H(CF_2)_6H$ was obtained with 50% current efficiency. So, as the conversion of starting material was lower than 100%, the substance yield is apparently higher. In dimethylformamide $(pK_a = 32)$ solution, proton abstraction is hindered and defluorination product 6-H-perfluorohexene-1 also forms.

3. Experimental

Electrochemically induced addition of fluoroorganosilanes to carbonyl compounds were carried out in a 30 ml glass cell, equipped with cooling jacket, magnetic stirrer, inert gas inlet, stainless steel cathode (20 cm^2), and Al anode (6 mm diameter rod). The cell was charged with 20 ml DMF, 0.2 g of Et₄NBF₄, 5–10 mM silane and carbonyl compound, 5–10% excess, and electrolyzed under intensiostatic conditions with current density 0.25–1 mA/cm², till the silane disappearance (controlled by GLC). The electrolyte was poured into 20 ml of water and extracted with ether (3 × 15 ml), dried over MgSO₄. The pure silyl esters were obtained by the column chromatography (Al₂O₃, hexane). The silyl esters were transferred by acidic hydrolysis into corresponding alkohols and identified by comparison with authentic samples [6].

Fluoroorganomercurials were reduced in the same cell, using copper anode (6 mm diameter rod). The cell was charged with 20 ml DMF, 6 ml of tetramethylethylenediamine, 0.2 g of Et_4NBF_4 , 10 mM of (II) and 20–30 mM of substrate (chlorotrimethylsilane or benzaldehyde). After consumption of 2 F charge, 5 mM of starting organomercury compound and 2–2.5 mM of corresponding trifluoromethylation product were detected by NMR.

Trifluoromethylation of bromobenzonitrile was carried out by the procedure described in [4], using (II) instead of bromotrifluoromethane.

Reduction of polyfluoroakyl chlorides mediated by *salen* Ni(II) complex was performed in the glass cell with divided anodic and cathodic compartments on platinum cathode under potentiostatic conditions [7].

Acknowledgements

Author thanks the French Ministry of National Education and ESFC-13 Organizing Committee for the financial support of this presentation.

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