

**FLUORIDE ION PROMOTED ANODIC SUBSTITUTIONS OF CHALCOGENO COMPOUNDS.2.1)  
REGIOSELECTIVE ANODIC METHOXYLATION OF 1,1-DIHYDRO-  
PERFLUOROALKYL AND CYANOMETHYL SELENIDES.**

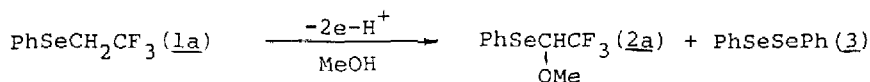
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**Abstract:** Anodic methoxylation of 1,1-dihydroperfluoroalkyl and cyanomethyl selenides was achieved in the presence of Et<sub>3</sub>N·3HF as a supporting electrolyte.

Anodic  $\alpha$ -functionalization of amines and arenes is well-established.<sup>3,4)</sup> However, such functionalization of other heteroatom compounds has been undeveloped. Recently, we have found that anodic  $\alpha$ -methoxylation of sulfides was markedly promoted by strong electron-withdrawing groups such as perfluoroalkyl groups.<sup>5-7)</sup> The reaction is noticeable because nucleophilic substitution at the position  $\alpha$  to the perfluoroalkyl group is usually quite difficult to achieve.<sup>8)</sup> These facts prompted us to attempt anodic  $\alpha$ -methoxylation of 1,1-dihydroperfluoroalkyl phenyl selenides to provide perfluoroalkylated selenoacetals. So far, no paper has been reported on anodic  $\alpha$ -substitution of organic selenium compounds. In addition, only few papers have appeared describing the preparation of simple alkyl and aryl selenoacetals.<sup>9)</sup>

First, we carried out anodic oxidation of phenyl 2,2,2-trifluoroethyl selenide (**1a**) in methanol using Et<sub>4</sub>NOTs as a supporting electrolyte in a manner similar to that of anodic methoxylation of fluoroalkyl sulfides.<sup>6,7)</sup> However, the desired  $\alpha$ -methoxylated selenide **2a** was obtained in extremely low yield and diphenyl diselenide (**3**) was formed considerably. Then, the anodic methoxylation was investigated using various supporting electrolytes. The results are summarized in Table 1. It was found that the methoxylation was remarkably promoted in the presence of fluoride ions: Et<sub>3</sub>N·3HF was much more effective than Bu<sub>4</sub>NF·3H<sub>2</sub>O since the former gave higher yield of the methoxylated product **2a** and suppressed the formation of diselenide **3**. Contrary to these cases, other halogen ions such as chloride and bromide did not promote the methoxylation at all. Therefore, fluoride ions are quite specific.

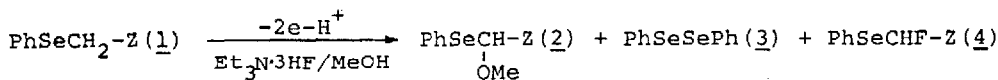
Table 1. Effect of Supporting Electrolytes on Anodic Methoxylation of PhSeCH<sub>2</sub>CF<sub>3</sub> (1a)

Supporting electrolyte	Electricity passed (F/mol)	Con-version (%)	Product yield (%) <sup>a)</sup>	
			<u>2a</u>	<u>3</u>
Et <sub>4</sub> NOTs	10	87	3	15
MeONa	10	20	5	6
Et <sub>4</sub> NCl	10	82	0	0
Et <sub>4</sub> NBr	10	38	0	0
Bu <sub>4</sub> NF·3H <sub>2</sub> O	10	48	33	24
Et <sub>3</sub> N·3HF	17	87	64	1

a) Based on consumed 1a.

Next, we extended this novel fluoride ion promoted anodic methoxylation to selenides bearing other perfluoroalkyl groups and a cyano group.<sup>10)</sup> The results are summarized in Table 2.

Table 2. Anodic Methoxylation of Selenides in the Presence of Fluoride Ions



Selenide No.	Z	Electricity passed (F/mol)	Con-version (%)	Product yield (%) <sup>a)</sup>		
				<u>2</u>	<u>3</u>	<u>4</u>
<u>1a</u>	CF <sub>3</sub>	17	87	64 (3)	1 (15)	trace
<u>1b</u>	C <sub>2</sub> F <sub>5</sub>	10	75	75 (15)	2 (2)	trace
<u>1c</u>	C <sub>3</sub> F <sub>7</sub>	10	65	74 (13)	0 (trace)	trace
<u>1d</u>	CN	8	94	50 (0)	16 (27)	10
<u>1e</u>	H	7	30	0 (0)	0 (0)	trace

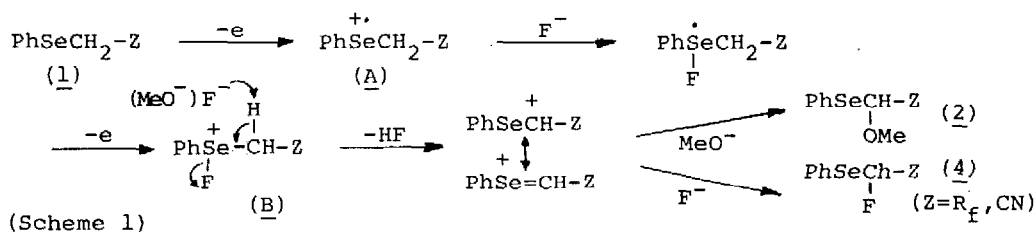
a) Based on consumed 1. Figures in parentheses are yields obtained by the electrolysis using Et<sub>4</sub>NOTs.

Perfluoroalkylated selenides 1b–1c similarly underwent anodic methoxylation very efficiently in the presence of Et<sub>3</sub>N·3HF. Such fluoride ion promoted anodic methoxylation also took place in the case of  $\alpha$ -cyanoselenide 1d although 1d failed to give a methoxylated product under conventional conditions using Et<sub>4</sub>NOTs.<sup>11)</sup> It is noticed that the anodic methoxylation took place selectively at the position  $\alpha$  to the electron-withdrawing groups and ring-methoxylation was not observed at all.

Therefore, this anodic methoxylation is highly regioselective.

Next, we applied this system to a simple alkyl phenyl selenide **1a**. However, the selenide **1a** did not give any methoxylated product. These results indicate that even in the presence of fluoride ions, anodic methoxylation of selenides does not proceed unless they have an electron-withdrawing group.

It should be noticeable that  $\alpha$ -fluorinated selenides **4** were always formed beside the methoxylated products **2**, particularly the selenide bearing cyano group **1d** provided  $\alpha$ -fluorinated product **4d** considerably. We have already found that anodic  $\alpha$ -fluorination of **1d** took place efficiently in acetonitrile containing  $\text{Et}_3\text{N}\cdot 3\text{HF}$ .<sup>12)</sup> The current-potential curves of the selenides in the presence of fluoride ions suggest that the anodic methoxylation is initiated by the direct oxidation of a selenide. In addition, it is known that selenides easily form hypervalent selenium compounds.<sup>13)</sup> From these results and facts, this novel methoxylation may proceed via fluoro-selenonium cation **B** in a Pummerer-type mechanism (Scheme 1).



In this mechanism, the cation radical **A** of the selenide is trapped by a fluoride ion and this step should suppress side reactions from the cation radical **A** (such as C-Se bond cleavage and nucleophilic attack on the aromatic ring).<sup>14)</sup> Since fluoride ions are much weaker nucleophiles compared to methoxide ions, it is reasonable that the methoxylation predominated in methanol.

Contrary to our case, Takaki et al. reported that chloroselenonium ions derived from selenides and *N*-chlorosuccinimide can be used for selective oxidation of alcohols.<sup>15)</sup> However, they have never observed the formation of alkoxyated selenides. In fact, in our experiments, chloride and bromide ions other than fluoride ions did not promote the methoxylation at all (Table I).

The methoxylated products are  $\alpha$ -perfluoroalkyl selenoacetals, which seem to be highly useful fluoro building blocks similar to those of sulfur analogues reported before.<sup>6,16)</sup>

Thus, this work illustrates the first successful example of anodic nucleophilic substitution of organo selenium compounds.

**Acknowledgement.** We are grateful to the UNESCO and the Japanese Ministry of Education, Science, and Culture for making possible Dr. Surowiec's participation to this project.

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