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# Competitive fluorination on methyl-group and benzene-ring during the anodic fluorination of fluorotoluenes in $Et_4NF \cdot mHF$

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# Abstract

Electrochemical fluorinations of 2-fluorotoluene (2a), 3-fluorotoluene (3a) and 4-fluorotoluene (4a) in neat  $Et_4NF \cdot mHF$  ( $Et = C_2H_5$ , m=3.5 or 4.0) were carried out on a platinum anode. The fluorination of 2a, 3a and 4a occurred competitively both on the side-chain (formation of monofluoromethylfluorobenzenes) and on the benzene-ring (formation of methyltrifluoro-1,4-cyclohexadienes). These results are explained by the facility of proton elimination from the methyl groups of the radical cations which have been formed by the anodic one-electron transfer reactions of 2a, 3a and 4a. A cyclic voltammogram of 4a showed three anodic current peaks which correspond to the oxidation of 4a, 1-fluoromethyl-4-fluorobenzene (4b) and 1-difluoromethyl-4-fluorobenzene (4c). On the other hand, voltammograms of 2a and 3a showed two anodic current peaks and no difluoromethylfluorobenzenes was obtained during the fluorination of 2a and 3a.  $\mathbb{C}$  1998 Elsevier Science S.A.

Keywords: Anodic fluorination; Fluorotoluene; Fluoromethylfluorobenzenes; Methyltrifluoro-1,4-cyclohexadienes; Tetraethylammonium fluoride-poly(hydrogen fluoride) electrolytes

# 1. Introduction

The anodic oxidation processes of toluene (1a) and the derivatives have been studied by a few research groups using acetonitrile (MeCN) solution containing a tetraethylammonium fluoride tris(hydrogen fluoride) ( $Et_4NF \cdot 3HF$  ( $Et = C_2H_5$ )) as the supporting electrolyte and the fluorine source [1-4]. However, no fluorinated products was detected from the anodic oxidation of **1a** or fluorotoluenes, but acetoamidated products were mainly obtained.

In a previous paper [5], we succeeded in fluorinating 1a, fluoromethylbenzene (1b) and difluoromethylbenzene (1c) anodically with high yields using neat tetraethylammonium fluoride poly(hydrogen fluoride) ( $Et_4NF \cdot mHF$ ) electrolytes. The anodic fluorination of 1a produced exclusively 1b as the primary product. The fluorination of 1b occurred competitively both on the side-chain (formation of 1c) and on the benzene-ring (formation of 1-monofluoromethyl-2-fluorobenzene (2b) and 1-monofluoromethyl-4-fluorobenzene (4b)). However, further fluorination of 1c occurred only on the benzene-ring, and 1-difluoromethyl-2-fluorobenzene (2c), 1-difluoromethyl-3-fluorobenzene (3c) and 1-difluor

romethyl-4-fluorobenzene (4c) were obtained as the primary products.

In this paper, we describe the identification of main- and by-products, and discuss probable reaction modes for the fluorination of fluorotoluenes.

# 2. Experimental

# 2.1. Preparation of materials

The electrolytes,  $Et_4NF \cdot mHF$  (m=3.5 and 4.0) and  $Me_4NF \cdot 4HF$  were prepared by the same method as described in a previous paper [6]. The substrate compounds **2a**, **3a** and **4a** were synthesized by Schiemann reaction [7] and were purified up to 99% assay by fractional distillation under the atmospheric pressure.

# 2.2. Electrochemical method

A beaker-cell made of fluoro-resins which is the same as that used previously [8]. The components were a pair of smooth platinum (Pt) sheets  $(30 \times 20 \text{ mm}^2)$  as the anode and the cathode, a probe electrode  $(1 \text{ mm } \emptyset - 10 \text{ mm Pt wire})$ 

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for cyclic voltammetry and a reference electrode (Ag/AgClO<sub>4</sub> (0.01 mol dm<sup>-3</sup>; M) in MeCN containing Et<sub>4</sub>NBF<sub>4</sub> (0.1 M) as the supporting electrolyte). In this paper, for convenience, the quantity of electricity passed will be indicated as *F* (Faraday = 96 485 C) per mol of the substrate (F mol<sup>-1</sup>). Each electrolysis was conducted potentiostatically (vs. Ag/Ag<sup>+</sup> (0.01 M)) with the solution being stirred.

The electrolyte solutions contained 0.4 M of the substrate material. During the electrolysis, the variations in the amounts of the substrate and the products were monitored by gas chromatography (GC; Shimadzu gas chromatograph; GC-14A, Chromatopac; CR-4A) with G-450 column (trifluoropropyl methylsilicone 1  $\mu$ m/DC-QF-1; 1.2 mm Ø–40 m; Kagakuhin Kensa Kyoukai) using a similar method as described in our previous paper [6].

Cyclic voltammetry was carried out using the probe electrode as the working electrode without stirring the solution.

# 2.3. Analysis of fluorinated products

A preparative GC (GC-14 with a 6 mm<sup>ID</sup> $\times$ 3 m or a 10 mm<sup>ID</sup> $\times$ 5 m stainless steel column packed with Silicon DC550) was used for the separation of the fluorinated products. The fluorine-containing products were characterized by gas chromatography-mass spectrometry (GC-MS; Shimadzu QP-1000) and <sup>1</sup>H and <sup>19</sup>F NMR spectrometry (Hitachi R-90F, 90 MHz for <sup>1</sup>H NMR and 84.68 MHz for <sup>19</sup>F NMR, using tetramethylsilane (TMS) for <sup>1</sup>H NMR and hexafluorobenzene (HFB) for <sup>19</sup>F NMR as internal standards.

# 3. Results and discussion

# 3.1. Cyclic voltammetry

Fig. 1 shows the cyclic voltammograms for a Pt wire electrode (1 mm  $\emptyset$ –10 mm) in Me<sub>4</sub>NF·4HF containing 0.01 M of **2a** (a), **3a** (b) and **4a** (c) at 0°C. The potential was scanned in a potential range from 0 to 3.0 V with a scan rate of 100 mV s<sup>-1</sup>. The voltammograms obtained in the solutions containing **2a** and **3a** (Fig. 1a and b) showed two anodic peaks,  $E_p1$  (1.83 V vs. Ag/Ag<sup>+</sup> (0.01 M)) and  $E_p2$  (2.00 V), or  $E_p3$  (1.87 V) and  $E_p4$  (2.03 V). In the solution of **4a**, three anodic peaks,  $E_p5$  (1.74 V),  $E_p6$  (1.98 V) and  $E_p7$  (2.23 V) were observed.

In a study of anodic fluorination of 1a, **1b** and **1c** [5], we concluded that the oxidation potential of fluorinated toluenes is influenced by the number of fluorine atoms on methyl group and is little influenced by that on benzene ring. The oxidation potential shifts anodically in the order toluene or fluorotoluenes (ca. 1.8 V) < fluoromethylbenzenes (ca. 2.0 V) < diffuoromethylbenzenes (ca. 2.2 V) < fluorocyclohexadienes. The anodic current peaks at  $E_{\rm p}1$ ,  $E_{\rm p}3$  and  $E_{\rm p}5$  correspond to the anodic oxidation of fluorotoluenes, those at  $E_{\rm p}2$ ,  $E_{\rm p}4$  and  $E_{\rm p}6$  are based on the anodic oxidation of fluoromethylbenzenes, and the current at  $E_{\rm p}7$  is the oxidation of



Fig. 1. Cyclic voltammograms for a Pt wire electrode in Me<sub>4</sub>NF  $\cdot$  4HF containing 0.01 M of **2a** (a), **3a** (b) and **4a** (c) at 0°C: Scan rate 100 mV s<sup>-1</sup>.



Fig. 2. Cyclic voltammograms for a Pt wire electrode in  $Et_4NF \cdot 4HF$  containing 0.05, 0.1, 0.2 and 0.4 M of **2a**: Scan rate 100 mV s<sup>-1</sup>.

difluoromethylbenzenes. It is suggested that the difluoromethylbenzenes are formed only by the fluorination of 4a.

Cyclic voltammograms in  $Et_4NF \cdot 4HF$  solutions containing 0.05, 0.1, 0.2 and 0.4 M of **2a** at room temperature are shown in Fig. 2. The variations in the peak currents at  $E_p1$  $(I_p1)$  with the concentration of **2a** is also shown in Fig. 2. In this concentration range,  $I_p1$  increased linearly with an increase in the concentration of **2a**. This result suggests that the fluorination of **2a** will proceed effectively even at high concentration of **2a** in this electrolyte system. In the case of **3a**, the peak current at  $E_p3$   $(I_p3)$  increased linearly with the concentration of **3a**, which is similar to the result for **2a**.

Fig. 3 shows cyclic voltammograms in Et<sub>4</sub>NF  $\cdot$  3.5HF solutions containing 0.05, 0.1, 0.2, and 0.4 M of **4a** at room temperature. The variation in the currents ( $I_p$ 5) with the concentration of **4a** is not linear. Judging from these data, the fluorination of **4a** would be difficult, compared with those of **2a** and **3a**. Among the electrolyzed solutions of **2a**, **3a** and **4a**, only the solution of **4a** changed markedly in color (brown). Further, the total yield of fluorination products in the solution of **4a** was lower than those of **2a** and **3a**.

# 3.2. Anodic fluorination of fluorotoluenes

## 3.2.1. Fluorination of 2-fluorotoluene (2a)

The results for the electrochemical fluorination of 2a in Et<sub>4</sub>NF · 3.5HF and Et<sub>4</sub>NF · 4HF are summarized in Table 1. 1-Fluoromethyl-2-fluorobenzene (**2b**), 1-methyl-3,6,6-tri-



Fig. 3. Cyclic voltammograms for a Pt wire electrode in  $Et_4NF \cdot 4HF$  containing 0.05, 0.1, 0.2 and 0.4 M of **4a**: Scan rate 100 mV s<sup>-1</sup>.

fluoro-1,4-cyclohexadiene (2d), 2,5-difluorotoluene (5a) and 1-methyl-3,3,6,6-tetrafluoro-1,4-cyclohexadiene (5d) were obtained as the products. The others in Table 1 involved further fluorinated compounds from 2b, from the mass-spectrum.

Fig. 4 shows the variations in the conversion of **2a** and the yields of the major products during the electrolysis of **2a** at 2.3 V in Et<sub>4</sub>NF·4HF (Run 1 in Table 1). The current fell to 50 mA at 3 F mol<sup>-1</sup> passed and small amounts of electroactive compounds **2a** and **5a** remained at this point. In this electrolysis conditions, **2b** ( $E_p2 = 2.00$  V) is unstable for the anodic oxidation, but the oxidation rate is very slow compared with those of fluorotoluenes (**2a** and **5a**). Therefore, only small amounts of **2b** was fluorinated during the reaction of **2a** under this electrolysis conditions.

The primary products of the anodic fluorination of **2a** were apparently **2b** and **2d**. It means that the fluorination of **2a** proceeded both on the methyl group (formation of **2b**) and on the benzene-ring (formation of **2d**), which is similar to the case of the anodic fluorination of **1b** [5]. The chemical instability is expected for **2d** that had saturated C-H bonds [6,9,10]. Significant amounts of the dehydrofluorinated product (**5a**) and further fluorinated product **5d** from **5a** were detected during the electrolysis. However, the dehydrofluorination rate for **2a** was estimated to be slow from a dehydrofluorination test of **5a** extracted with CCl<sub>4</sub> in a 5 N KOH

 Table 1

 Results for the anodic fluorination of 2-fluorotoluene (2a)



Fig. 4. Variations in the conversion of 2a and the yields of products during the electrolysis of 2a at 2.3 V in Et<sub>4</sub>NF · 4HF at room temperature (Run 1); (•) 2a, ( $\bigcirc$ ) 2b, ( $\square$ ) 2d, ( $\triangle$ ) 5a and ( $\neg$ ) 5d.

aqueous solution [10]. Consequently, about one third of the amount of **2d** remained without dehydrofluorination during the electrolysis.

#### 3.2.2. Fluorination of 3-fluorotoluene (3a)

The variations in the conversion of **3a** and the yields of the major products during the electrolysis of **3a** at 2.3 V in  $Et_4NF \cdot 4HF$  are shown in Fig. 5. The current fell to its background level (ca. 30 mA) at 4 F mol<sup>-1</sup>, and both 1-fluoromethyl-3-fluorobenzene (**3b**) and **5d** were obtained as the major final products. The yield of **5a** showed a maximum value (ca. 10%) at the 2 F mol<sup>-1</sup> passage, which is the same as the case in Fig. 4. As small amount of 1-methyl-3,3,6-trifluoro-1,4-cyclohexadiene (**3d**) was detected in the electrolyte solution, the precursor of **5a** is considered to be **3d**. Lower chemical stability of **3d** than **2d** is responsible for this result, according to the experimental data that 3,3,6-trifluoro-1,4-cyclohexadienes are less stable for the dehydrofluorination compared with 3,6,6-trifluoro-1,4-cyclohexadienes [9,11,12].

The major processes for the anodic fluorinations of 2a (to 2b, 5a and 5d) and 3a (to 3b, 5a and 5d) in Et<sub>4</sub>NF·*m*HF are summarized in Scheme 1.

# 3.2.3. Fluorination of 4-fluorotoluene (4a)

The results for the electrochemical fluorination of **4a** in  $Et_4NF \cdot 3.5HF$  and  $Et_4NF \cdot 4HF$  are summarized in Table 2. Two kinds of fluorotoluenes, 1-fluoromethyl-4-fluoroben-

Run	Electrolyte	Anode potential (V vs. Ag/Ag <sup>+</sup> )	Q/F (F mol <sup>-1</sup> )	Conversion of <b>2a</b>	Yield of product/%					
					2b	2d	5a	5d	Others	
1	Et <sub>4</sub> NF · 4HF	2.3	2.0	72.2	15.1	21.8	14.8	16.5	2.0	
			3.0	94.7	20.6	23.1	9,5	29.6	3.7	
2	$Et_4NF \cdot 4HF$	2.5	2.0	73.1	14.7	22.6	13.9	16.7	2.8	
			3.0	92.8	17.5	24.3	10.1	30.5	5.2	
3	$Et_4NF \cdot 3.5HF$	2.3	2.0	71.1	15.2	21.3	14.5	15.8	1.9	

 Table 2

 Results for the anodic fluorination of 4-fluorotoluene (4a)

Run	Electrolyte	Anode potential (V vs. Ag/Ag <sup>+</sup> )	Q/F (F mol <sup>-1</sup> )	Conversion of 4a	Yield of product/%				
					4b	4c	4d	4e	Others
5	Et₄NF·3.5HF	2.5	2.0	75.2	26.1	2.7	19.2	3.8	3.0
			2.7	96.2	27.4	5.3	22.7	6.8	4,6
6	Et₄NF · 3.5HF	2.3	2.0	74.8	26.7	1.8	18.5	2.2	2.2
7	Et <sub>4</sub> NF · 4HF	2.5	2.0	75.8	25.3	2.4	18.9	3.7	3.6



Fig. 5. Variations in the conversion of **3a** and the yields of products during the electrolysis of **3a** at 2.3 V in Et<sub>4</sub>NF · 4HF at room temperature; ( $\bullet$ ) **3a**, ( $\bigcirc$ ) **3b**, ( $\triangle$ ) **5a** and ( $\bigtriangledown$ ) **5d**.



zene (4b), 1-difluoromethyl-4-fluorobenzene (4c), and three kinds of fluoro-1,4-cyclohexacienes, 3-methyl-3,6,6trifluoro-1,4-cyclohexadiene (4d), 3-fluoromethyl-3,6,6-trifluoro-1,4-cyclohexadiene (4e) and 3-difluoromethyl-3,6,6trifluoro-1,4-cyclohexadiene (4f) were obtained as the products. The fluoro-1,4-cyclohexadienes were quite stable both chemically and electrochemically. The others in Table 2 were mainly composed of further fluorinated compounds from 4b and 4c, judging from the mass-spectrum.

Fig. 6 shows the variations in the conversion of 4a and the yields of the major products during the electrolysis of 4a at 2.3 V in  $Et_4NF \cdot 3.5HF$ . The formation of 4c and 4e were



Fig. 6. Variations in the conversion of **4a** and the yields of products during the electrolysis of **4a** at 2.5 V in Et<sub>4</sub>NF  $\cdot$  3.5HF at room temperature (Run 5); (**●**) **4a**, (**○**) **4b**, (**□**) **4c**, (**△**) **4d** and (**▽**) **4e**.



detected after  $1 \text{ F mol}^{-1}$  passed because they were yielded as the results of the fluorination of **4b**. The process for the anodic fluorination of **4a** to **4b**, **4c**, **4d**, **4e** and **4f** is summarized in Scheme 2.

## 3.2.4. Proton elimination from radical cations

The fluorinations of **2a**, **3a** and **4a** proceeded competitively both on the side chain (formation of fluoromethylfluorobenzenes, **2b**, **3b** and **4b**, respectively) and on the benzene-ring (formation of fluorocyclohexadienes, **2d**, **3d** and **4d**).

Scheme 3 shows presumed reaction paths (an ECEC mechanism) for the anodic fluorination of fluorotoluenes. Path A is the addition of fluoride to radical cations and path B is the elimination of proton from radical cations. The fluorinations of **2a**, **3a** and **4a** proceed via both path A and path B. In a previous paper [5], we described that the fluorinations of **1a** and **1c** take different path, path B for **1a** or path A for



**1c**, while the fluorination of **1b** proceeds through both paths A and B. This difference in the reaction path comes from the differences in the ability of proton elimination from the intermediate radical cations. The probability of proton elimination from the radical cation was estimated by C–H bond order calculated by MO method [5]. We concluded that the elimination of proton from the radical cation scarcely occurs when the C–H bond order of the radical cation is higher than 0.95. The proton elimination proceeds with a significant rate when the C–H bond order is lower than 0.90.

Scheme 4 summarizes the C-H bond orders and charge densities on carbon atoms for the radical cations,  $2a^{+}$ ,  $3a^{+}$ ,  $4a^{+}$  and  $5a^{+}$  calculated by MOPAC version 6.0 PM3.

Fig. 7 shows the ratio of path A plotted against the C-H bond orders in CH<sub>3</sub> of  $1a^{++}$ ,  $2a^{++}$ ,  $3a^{++}$ ,  $4a^{++}$  and  $5a^{++}$ , CH<sub>2</sub>F of  $1b^{++}$  and CHF<sub>2</sub> of  $1c^{++}$ . The ratio of path A to path B was calculated from the products yields during the electrolysis. The solid line shows the results obtained in this work and the broken line shows the data of  $1a^{++}$ ,  $1b^{++}$ ,  $1c^{++}$ reported previously [5]. The data of  $3a^{++}$  is apart from the solid line. This is because of the limitation in the MO calculation for *m*-substituted benzenes. The shift of solid line from the broken line as shown in Fig. 7, will be explained by high positive charges on the carbon atoms bonded to fluorine atoms as shown in Scheme 4.

## 3.3. Spectral information

**2a**: MS m/e (%); 111 (M+1, 2), 110 (M<sup>+</sup>, 48), 109 (M-H, 100), 107 (3), 83 (15), <sup>19</sup>F NMR;  $\sigma$  (HFB); 44.1

ppm (F, 2-F, m), <sup>1</sup>H NMR; σ (TMS); 2.24 ppm (3H, 1',1',1'-H, m), 7.01 ppm (2H, 4,5-H, m), 7.16 ppm (2H, 3,6-H, m).

**2b**: MS m/e (%); 129 (M+1, 2), 128 (M<sup>+</sup>, 46), 127 (M-H, 100), 109 (M-F, 8), 107 (4), 101 (6), <sup>19</sup>F NMR;  $\sigma$  (HFB); -52.3 ppm (F, 1'-F, t, 49.6 Hz), 43.2 ppm (F, 2-F, m), <sup>1</sup>H NMR;  $\sigma$  (TMS); 5.43 ppm (2H, 1',1'-H, d, 49.6 Hz).

**2d**: MS m/e (%); 149 (M+1, 3), 148 (M<sup>+</sup>, 57), 147 (M–H, 3), 145 (6), 134 (5), 133 (M–CH<sub>3</sub>, 100), 132 (5), 129 (M–F, 12), 128 (M–HF, 27), 127 (M–HF–H, 72), <sup>19</sup>F NMR;  $\sigma$  (HFB); –15.5 ppm (F, 3-F, d, 45.1 Hz), 65.8 ppm (F, 6-F, AB, 315 Hz), 71.7 ppm (F, 6-F, AB, 315 Hz), <sup>1</sup>H NMR;  $\sigma$  (TMS); 1.56 ppm (3H, 1',1',1'-H, d, m, 20.8 Hz), 5.22 ppm (H, 3-H, d, m, 45.1 Hz), 6.33 ppm (H, 2-H, m), 6.12 ppm (2H, 4,5-H, m).

**3a**: MS m/e (%); 111 (M+1, 3), 110 (M<sup>+</sup>, 49), 109 (M–H, 100), 107 (4), 83 (17), 81 (4), <sup>19</sup>F NMR;  $\sigma$  (HFB); 47.6 ppm (F, 3-F, m), <sup>1</sup>H NMR;  $\sigma$  (TMS); 2.38 ppm (3H, 1',1',1'-H, s), 6.89 ppm (2H, 5,6-H, m), 6.97 ppm (H, 2-H, d, 7.8 Hz), 7.23 ppm (H, 4-H, m).

**3b**: MS m/e (%); 129 (M+1, 4), 128 (M<sup>+</sup>, 58), 127 (M-H, 100), 109 (M-F, 8), 107 (7), 101 (10), <sup>19</sup>F NMR;  $\sigma$  (HFB) – 48.9 ppm (F, 1'-F, t, 49.6 Hz), 49.5 ppm (F, 3-F, m), <sup>1</sup>H NMR;  $\sigma$  (TMS) 5.35 ppm (2H, 1',1'-H, d, 49.6 Hz), 7.08 ppm (3H, 4,5,6-H, m), 7.34 ppm (H, 2-H, m).

**3d**: MS m/e (%); 149 (M+1, 3), 148 (M<sup>+</sup>, 44), 147 (M-H, 5), 133 (M-CH<sub>3</sub>, 45), 129 (M-F, 10), 128 (M-HF, 36), 127 (M-HF-H, 100).

**4a**: MS m/e (%); 111 (M+1, 3), 110 (M<sup>+</sup>, 60), 109 (M-H, 100), 108 (7), 107 (3), 83 (14), <sup>19</sup>F NMR;  $\sigma$  (HFB) 43.7 ppm (F, 4-F, m), <sup>1</sup>H NMR;  $\sigma$  (TMS) 2.26 ppm (3H, 1',1',1'-H, s), 6.89 ppm (2H, 3,5-H, d, d, 8.6 Hz, 8.6 Hz), 7.05 ppm (2H, 2,6-H, d, 8.6 Hz).

**4b**: MS m/e (%); 129 (M+1, 3), 128 (M<sup>+</sup>, 46), 127 (M–H, 100), 125 (5), 109 (9), 107 (7), 101 (9). <sup>19</sup>F NMR;  $\sigma$  (HFB) 49.2 ppm (F, 4-F, m), 43.1 ppm (F, 1'-F, t, 48.2 Hz). <sup>1</sup>H NMR;  $\sigma$  (TMS) 5.32 ppm (2H, 1',1'-H, d, 48.2 Hz), 7.07 ppm (2H, 3,5-H, d, d, 8.54 Hz, 8.58 Hz), 7.35 ppm (2H, 2,6-H, m).





Fig. 7. The ratio of path A plotted against the C-H bond orders in CH<sub>3</sub> of  $1a^{++}$ ,  $2a^{++}$ ,  $3a^{++}$ ,  $4a^{++}$  and  $5a^{++}$ ,  $CH_2F$  of  $1b^{++}$  and  $CHF_2$  of  $1c^{++}$ .

**4c**: MS m/e (%); 147 (M+1, 4), 146 (M<sup>+</sup>,61), 145 (M-H, 100), 133 (9), 127 (25), 125 (8), 101 (8), 96 (58), 95 (16), 75 (25), <sup>19</sup>F NMR;  $\sigma$  (HFB) 52.1 ppm (2F, 1',1'-F, d, 56.4 Hz), 5.30 ppm (F, 4-F, m), <sup>1</sup>H NMR;  $\sigma$  (TMS) 6.60 ppm (H, 1'-H, t, 56.4 Hz), 7.50 ppm (4H, 2,3,5,6-H, m).

**4d**: MS m/e (%); 149 (M+1, 1), 148 (M<sup>+</sup>, 21), 147 (M-H, 1), 134 (4), 133 (M-CH<sub>3</sub>, 100), 132 (4), 129 (M-F, 6), 128 (M-HF, 13), 127 (M-HF-H, 29), <sup>19</sup>F NMR;  $\sigma$  (HFB); 19.8 ppm (F, 1'-F, d, 20.8 Hz), 70.8 ppm (F, 3-F, AB, 320 Hz), 74.5 ppm (F, 3-F, AB, 320 Hz), <sup>1</sup>H NMR;  $\sigma$  (TMS); 1.51 ppm (3H, 1',1',1'-H, d, 20.8 Hz), 6.03 ppm (2H, 3,5-H, d, 10.1 Hz), 6.26 ppm (2H, 2,6-H, d, d, 10.1 Hz, 5.9 Hz).

**4e**: MS m/e (%); 166 (M<sup>+</sup>, 0.5), 133 (M – CH<sub>2</sub>F, 100), 127 (7), <sup>19</sup>F NMR;  $\sigma$  (HFB) – 66.8 ppm (F, 3'-F, t, 49.3 Hz), 3.3 ppm (F, 3-F, m), 69.9 ppm (F, 6-F, AB, m, 325 Hz), 74.3 ppm (F, 6-F, AB, m, 320 Hz), <sup>1</sup>H NMR;  $\sigma$  (TMS) 4.52 ppm (2H, 1',1'-H, d, d, 49.3 Hz, 19.2 Hz), 6.43 ppm (4H, 1,2,4,5-H, m).

**4f**: MS m/e (%); 184 (M<sup>+</sup>, 0.5), 133 (M – CHF<sub>2</sub>, 100), 114 (12), 113 (25), <sup>19</sup>F NMR;  $\sigma$  (HFB) – 4.47 ppm (F, 3-F, m), 31.57 ppm (2F, 3',3'-F, d, d, 54.1 Hz, 14.7 Hz), 68.5 ppm (F, 6-F, AB, m, 330 Hz), 72.6 ppm (F, 6-F, AB, m, 330 Hz), <sup>1</sup>H NMR,  $\sigma$  (TMS) 6.31 ppm (4H, 1,2,4,5-H, m), 5.67 ppm (H, 3'-H, t, d, 54.2 Hz, 5.9 Hz).

**5a**: MS m/e (%); 129 (M+1, 3), 128 (M<sup>+</sup>, 50), 127 (M-H, 100), 125 (3), 109 (9), 107 (6), 101 (11),  $^{19}F$ 

NMR; σ (HFB); 38.1 ppm (F, 2-F, m), 41.8 ppm (F, 5-F, m), <sup>1</sup>H NMR; σ (TMS); 2.22 ppm (3H, 1',1',1'-H, s), 6.8–7.0 ppm (2H, 4,5-H, m), 7.05–7.2 ppm (H, 2-H, m).

**5d**: MS m/e (%); 167 (M+1, 2), 166 (M<sup>+</sup>, 39), 165 (M-H, 3), 151 (M-CH<sub>3</sub>, 13), 147 (M-F, 15), 145 (22), 116 (5), 115 (M-CHF<sub>2</sub>, 25), 102 (9), 101 (19), 97 (M-CF<sub>3</sub>, 100), 96 (14), 95 (14), <sup>19</sup>F NMR;  $\sigma$  (HFB); 61.3 ppm (2F, 6,6-F, s), 68.3 ppm (2F, 3,3-F, s), <sup>1</sup>H NMR;  $\sigma$  (TMS); 1.98 ppm (3H, 1',1',1'-H, m), 5.99 ppm (H, 2-H, m), 6.31 ppm (2H, 4,5-H, m).

## 4. Summary

The reaction paths during the electrochemical fluorination of fluorotoluenes, 2a, 3a and 4a in Et<sub>4</sub>NF·*m*HF were made clear. The fluorinations occurred competitively both on the side-chain and on the benzene-ring. On the whole, these results are explained from the facility of the proton elimination from the methyl groups of radical cations,  $2a^{+}$ ,  $3a^{+}$  and  $4a^{+}$ .

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