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Synthesis of fluorocyclohexadienes by the electrochemical fluorination of *p*-difluorobenzenes on a preparative scale

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Fluorine containing-cyclohexadienes (FCHDs), 3,3,6,6,-tetrafluoro-1,4-cyclohexadiene (**1a**), 1-chloro-3,3,6,6-tetrafluoro-1,4-cyclohexadiene (**3a**) and 1-bromo-3,3,6,6-tetrafluoro-1,4-cyclohexadiene (**4a**), were isolated in pure states with high yields (ca. 80%) by the preparative scale electrochemical fluorination of 1,4-difluorobenzene (**1**), 1-chloro-2,5-difluorobenzene (**3**) and 1-bromo-2,5-difluorobenzene (**4**), respectively, in $Et_4NF \cdot mHF$ ($Et = C_2H_5$: $m = 4.0$, 4.45 and 4.7) at a platinum anode, followed by extraction and fractional distillation. The electrochemical fluorination of 1,2,4-trifluorobenzene (**2**) yielded both 1,3,3,6,6-pentafluoro-1,4-cyclohexadiene (**2a**) and 2,5,5,6,6-pentafluoro-1,3-cyclohexadiene (**2b**) with high yield (ca. 90%). Some of (**2a**) was also isolated in a pure state by fractional distillation. Each substrate compound (**1–4**) was fluorinated to the corresponding FCHDs with an almost quantitative yield when 2.0–2.1 faraday (per mol of substrate) of electricity was passed.

1. Introduction

Earlier papers have described the formation of fluorocyclohexadienes (FCHDs) using both chemical and electrochemical methods. Small amounts of FCHDs were obtained by chemical fluorination of aromatic compounds with high valency metal fluorides, e.g. cobalt trifluoride (CoF_3) [1], cerium tetrafluoride (CeF_4) [2], potassium tetrafluorocobaltate(III) ($KCoF_4$) [3], potassium hexafluoronickelate(IV) (K_2NiF_6) [4], at 240–500 °C, where the main products were fluorocyclohexanes and fluorocyclohexenes. Zweig and coworkers [5] carried out the fluorination of benzene, fluorobenzene, chlorobenzene, 1,2-difluorobenzene, 1,4-difluorobenzene and 1,4-dichlorobenzene using a fine powder of silver difluoride (AgF_2) dispersed in *n*-hexane at room temperature. These authors obtained several kinds of FCHDs with considerable yields produced by addition of two fluorine atoms to substrate compounds. Recently, Mears and Eilenberg [6] reported the formation of some FCHDs with fluorinated aromatic compounds during the electrochemical fluorination of benzene, chlorobenzene and phenol in neat triethylamine-tris(hydrogen fluoride) ($Et_3N \cdot 3HF$). However, they did not isolate the FCHDs. Therefore, no chemical and physical properties of the FCHDs have been reported. Some ^{19}F NMR data [5, 7] and mass spectra [8] of FCHDs produced by fluorination using high valency metal fluorides have been reported.

We have found a series of new useful electrolytes, tetraalkylammonium fluoride-poly(hydrogen fluoride) ($R_4NF \cdot mHF$, R = Me, Et or Pr, $Me = CH_3$, $Et = C_2H_5$, $Pr = C_3H_7$, $m > 3.5$), and studied the electrochemical fluorination of aromatic compounds [9–14] in these electrolytes. As the salts are low-viscous liquids at room temperature, they can be used as the electrolyte without solvent. These molten salt type electrolytes have high conductivities and high anodic stabilities compared with electrolytes containing conventional organic solvents [9, 15].

From the results of the electrochemical fluorination

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of benzene [9], fluorobenzenes [9–11], chlorobenzenes [12], bromobenzenes [13] and trifluoromethybenzenes [14] using these salts, the reaction mechanism and the paths to the fluorinated products have been clarified. Further, it was found that some FCHDs were obtained with very small amounts of by-products through the electrochemical fluorination of 1,4-difluorobenzene [9] and substituted *p*-difluorobenzenes, i.e. 1,2,4-trifluoro-benzene [10], tetra, penta and hexa-fluorobenzenes [11], 1-chloro-2,5-difluorobenzene [12] and 1-bromo-2,5-difluorobenzene [13].

In the present paper, the results of the electrochemical fluorination of 1,4-difluorobenzene and three kinds of substituted *p*-difluorobenzenes (0.2 mol scale) are described. Further, FCHDs (four kinds of 3,3,6,6-tetrafluoro-1,4-cyclohexadienes) were isolated in pure states by extraction and fractional distillation.

2. Experimental details

2.1. *Materials*

The electrolytes, $Et_4NF \cdot m HF$ ($m = 4.0$, 4.45 or 4.7) were synthesized by the reaction of Et_4NBr with an excess of anhydrous HF using a pilot scale plant, in a similar manner as described previously [15]. Solvents *m*-xylene and 3,4-dichlorotoluene for extraction were reagent grade chemicals from Wako Pure Chemical. The substrates, 1,4-difluorobenzene (**1**) and 1,2,4-trifluorobenzene (**2**), were prepared by Schiemann reactions [16] of 4-fluoroaniline and 2,5-difluoroaniline (Morita Chemical), respectively. Both 1-chloro-2,5-difluorobenzene (**3**) and 1-bromo-2,5-difluorobenzene (**4**) were synthesized in house by Sandmayer reactions [17] of 2,5-difluoroaniline. The substrate compounds (**1**)–(**4**) were purified up to 98% assay by fractional distillation under a normal (for (**1**) and (**2**)) or a reduced (for (**3**) and (**4**)) pressure.

2.2. *Method*

The cell components and electrodes for the macro-electrolysis of *p*-difluorobenzenes are shown in Figs 1 and 2. These were essentially the same as those used for the electrolyses of aromatic compounds [9–14], except for a larger cell size (300 cm^3) and higher platinum sheet area (50 × 60 mm^2, 0.2 mm in thickness) as the anode and cathode. A smooth platinum wire (1 mm diam., 10 mm in length; 0.32 cm^2) was used as a probe electrode for cyclic voltammetry (CV) and was placed between two platinum sheet electrodes.

The reference electrode was a $Ag/AgClO_4$ (0.01 M) in acetonitrile containing Et_4NBF_4 (0.1 M) as the supporting electrolyte. The electrolyte $Et_4NF \cdot m HF$ without substrate compound was used as a salt bridge. For the CV experiments, the potential was scanned with $v = 100\,mV\,s^{-1}$ by means of a function generator (Hokuto Denko, HB-104) connected with a potentio/galvanostat (Hokuto Denko, HA-501).

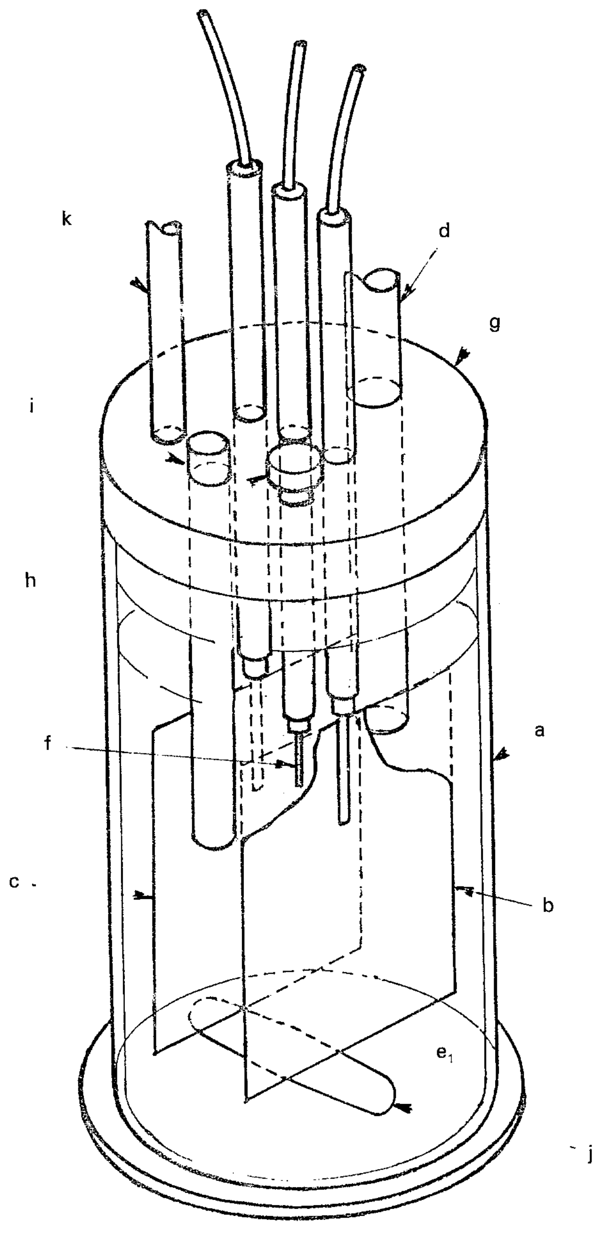


Fig. 1. The schematic diagram of the beaker-type PFA cell (300 cm^3). (a) PFA cell case, (b) anode (Pt, 50 × 60 mm^2), (c) cathode (Pt, 50 × 60 mm^2), (d) reference electrode (Ag/Ag^+), (e_1) electrolyte, (f) CV probe (Pt wire), (g) PTFE cap, (h) PTFE plug, (i) thermometer shell, (j) PTFE coated magnetic stirring bar, and (k) gas outlet.

The voltammograms were recorded on an X–Y recorder (Yokogawa Electrics; 3025–23).

The cell was constructed in a glove box filled with dry nitrogen gas, and then 230 cm^3 of $Et_4NF \cdot m HF$ was charged. After the CV for the electrolyte solution without substrate (background), 0.2 mol of substrate compound was introduced into the cell through a sampling hole ((h) in Fig. 1). The CV of the electrolyte solutions before and after the electrolysis were also measured. The electrolysis was carried out under constant current conditions (usually, 500 mA) at room temperature. The solution was continuously stirred with a polytetrafluoroethylene (PTFE) coated magnetic bar. The anode potential and the cell voltage against time were recorded on the X–Y recorder.

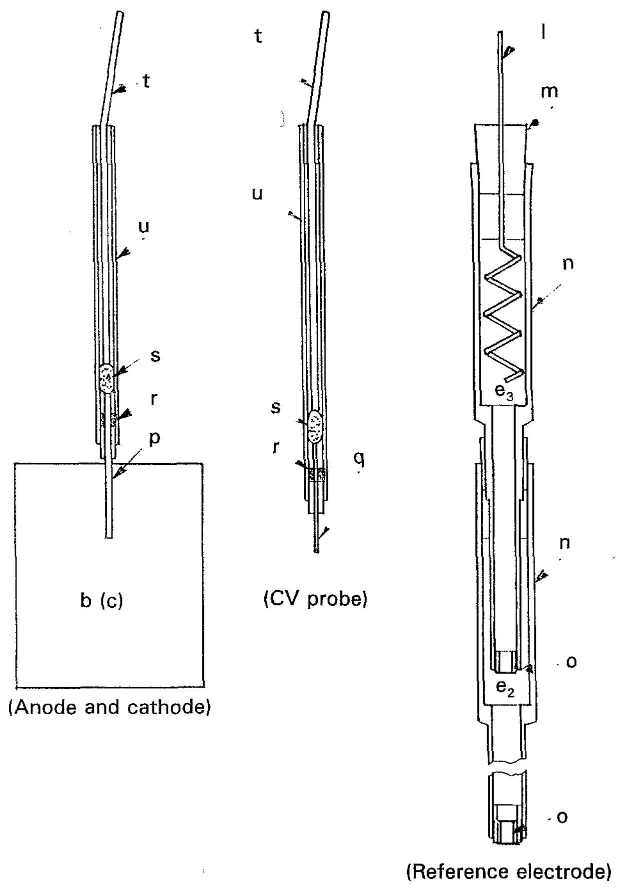


Fig. 2. The schematic diagrams of the electrodes. (e_2) Salt bridge, (e_3) 0.01 M-$AgClO_4$ + 0.1 M-Et_4BF_4/CH_3CN, (l) Ag wire (1 mm diam.), (m) silicone rubber cap, (n) PFA shell, (o) PTFE diaphragm, (p) Pt wire (2 mm diam.), (q) Pt wire (1 mm diam.), (r) epoxy-resin, (s) solder, (t) Cu wire (2 mm diam.) and (u) PFA tube (6 mm outside diam.).

For convenience, the quantity of electricity passed in this paper will be indicated as F ($1\,F = 96\,485\,C\,mol^{-1}$) per mol of the substrate (i.e., $F\,mol^{-1}$). A small amount of the electrolyte solution (ca. 0.1 g) was sampled for each $0.5\,F\,mol^{-1}$ passage during the electrolysis to monitor the variations in the amounts of substrate and products in the electrolyte solution. After treatment [9] with water and tetrachloromethane containing a prescribed amount of chlorobenzene as an internal standard, the sample was analyzed by gas chromatography (GC, Shimadzu, gas chromatograph GC-14A) with G-450 column (1.2 mm internal diameter –40 m; Kagakuhin Kensa Kyoukai) and GC-mass spectrometry (GC-MS, Shimadzu, GCMS-QP1000).

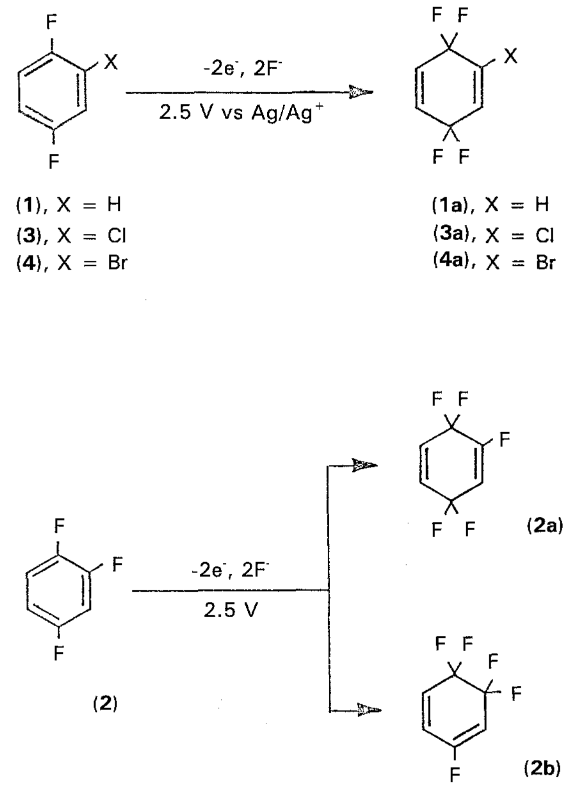
After the electrolysis, 250 cm^3 of water was added to the electrolyte solution, and the products were extracted with three portions of *m*-xylene or 3,4-dichlorotoluene (20 cm^3 each). The sum of the resulting extract was dried over anhydrous magnesium sulfate ($MgSO_4$), followed by fractional distillation under a normal or a reduced pressure through a semimicro distilling column (10 mm inside diam. × 200 mm in length; packed with heripack). Each fraction was analysed by GC-MS, ^1H and ^{19}F-NMR spectrometry. The NMR spectra were obtained on a Hitachi R-90F (84.68 MHz) spectrometer using tetramethylsilane for ^1H-NMR and hexafluorobenzene for ^{19}F-NMR as internal standards.

3. Results and discussion

3.1. *Electrolysis*

From previous results for potentiostatic electrolyses on a smaller scale (30 cm^3 of $Et_4NF \cdot m HF$ electrolyte containing 0.0123 mol of substrate compound), the electrochemical fluorination of (**1**) [9], (**3**) [12] and (**4**) [13] in $Et_4NF \cdot m HF$ gave the corresponding FCHDs that were formed by 1,4-addition of two fluoride anions through an ECEC mechanism as shown in Scheme 1. On the other hand, in the electrochemical fluorination of (**2**), both 1,3,3,6,6-pentafluoro-1,4-cyclohexadiene (**2a**) and 2,5,5,6,6-pentafluoro-1,3-cyclohexadiene (**2b**) were obtained as the major products [10].

Table 1 summarizes the results of the electrochemical fluorination of (**1**)–(**4**) with constant-current electrolyses in $Et_4NF \cdot m HF$. In all cases, the substrate compounds were almost completely fluorinated to the corresponding FCHDs above $2.0\,F\,mol^{-1}$ (theoretical charge passed). The yield of FCHDs and the conversion of the substrate compounds were varied linearly with the quantity of electricity passed. As an instance, the variations in the yield of (**4a**) and the conversion of (**4**) during the fluorination of (**4**) in $Et_4NF \cdot 4.7HF$ (run 7) is shown in Fig. 3. Other compounds were obtained with very low yields during the electrolyses. These were mainly fluorocyclohexadienes and fluorocyclohexenes judging from the mass spectra. However, two kinds of



Scheme 1.

Table 1. Results for the electrochemical fluorination of 1,4-difluorobenzene (**1**), *1,2,4-trifluorobenzene* (**2**), *1-chloro-2,5-difluorobenzene* (**3**) *and 1-bromo-2,5-difluorobenzene* (**4**)*

Run	*Substrate*	*Electrolyte*	*Q* /F mol^{-1}	*Conversion of substrate*	*Main products* (Yield)
1	(**1**)	$Et_4NF \cdot 4.0HF$	2.1	100%	(**1a**), 91.1%
2	(**1**)	$Et_4NF \cdot 4.45HF$	2.1	100%	(**1a**), 91.3%
3	(**1**)	$Et_4NF \cdot 4.7HF$	2.1	100%	(**1a**), 92.8%
4	(**2**)	$Et_4NF \cdot 4.7HF$	2.0	94.7%	(**2a**), 71.2%; (**2b**), 21.4%
5	(**3**)	$Et_4NF \cdot 4.7HF$	2.0	97.3%	(**3a**), 93.7%
6	(**4**)	$Et_4NF \cdot 4.7HF$	2.0	96.5%	(**4a**), 93.2%
7	(**4**)	$Et_4NF \cdot 4.7HF$	2.0†	99.2%	(**4a**), 95.7%
8	(**4**)	$Et_4NF \cdot 4.7HF$	2.1†	100%	(**4a**), 96.1%

* Constant current electrolysis with 500 mA except for runs 7 and 8.

† Current was decreased step by step (500 → 300 → 100 mA) owing to the anode potential kept below 2.5 V vs Ag/Ag$^+$.

trifluoromethylpentadienes, which may be produced by inter molecular rearrangement of (**2a**) and (**2b**), were obtained with low yields (1.3% and 1.6%) in the electrolysis of (**2**). High yields and current efficiencies for the main products mean that the substrates (**1**)–(**4**) were almost quantitatively fluorinated to the corresponding FCHDs.

The yield of (**1a**) increased slightly with increase in the *m* value of $Et_4NF \cdot m HF$, which is the same as the case in previous work under potentiostatic conditions [9]. Further, the cell voltage of run 3 during the electrolysis was lower than those of runs 1 and 2 owing to smaller polarization of the cathode.

In runs 7 and 8, the current was decreased step-by-step (500 → 300 → 100 mA) to keep the anode potential below 2.5 V. This procedure improved both the conversion of (**4**) and the yield of (**4a**).

Figure 4 shows the variations in the anode potentials with the quantity of electricity passed for the galvanostatic electrolyses (500 mA) of (**1**)–(**4**) in $Et_4NF \cdot 4.7HF$ (runs 3–6). The anode potential generally shifted positively with decrease in the concentration of electroactive compound. The profile of curves (b) (the electrolysis of (**2**), run 4 in Table 1) and (d) ((**4**), run 6) differed from the others ((**1**) and (**3**)). The curves (b) and (d) showed plateaux of ca. 2.7 V and 2.85 V, respectively, at 2.0 F mol^{-1}, suggesting further anodic oxidation of electrochemically active products.

The CV in the electrolytes and the electrolyte solutions before and after electrolyses gave useful information regarding the plateau of curves (b) and (d) in Fig. 4. Figure 5 shows voltammograms in (a) $Et_4NF \cdot 4.7HF$ (background), (b) $Et_4NF \cdot 4.7HF$ containing 0.8 mol dm^{-3} of (**1**) and (c) $Et_4NF \cdot 4.7HF$ containing (**1**) after the electrolysis (2.1 F mol^{-1} passed). Curve (b) shows the anodic current of (**1**) at 1.8 V or above. Curves (a) and (c) show that $Et_4NF \cdot 4.7HF$ and the electrolysed solution are fully stable for anodic oxidation up to 3.0 V vs Ag/Ag$^+$ (0.01 M). That is, the product (**1a**) is inert for the anodic oxidation at 3.0 V. In the electrolysis of (**3**), the electrolysed solution was also stable up to 3.0 V. Figures 6 and 7 show the voltammograms of backgrounds (curves (a)) and those in the electrolyte solution before (curves (b)) and after (2.0 F mol^{-1}; curves (c)) the electrolyses of compounds (**2**) and (**4**), respectively. Curves (b) in Figs 6 and 7 showed anodic currents at 1.8 V or above owing to the oxidation

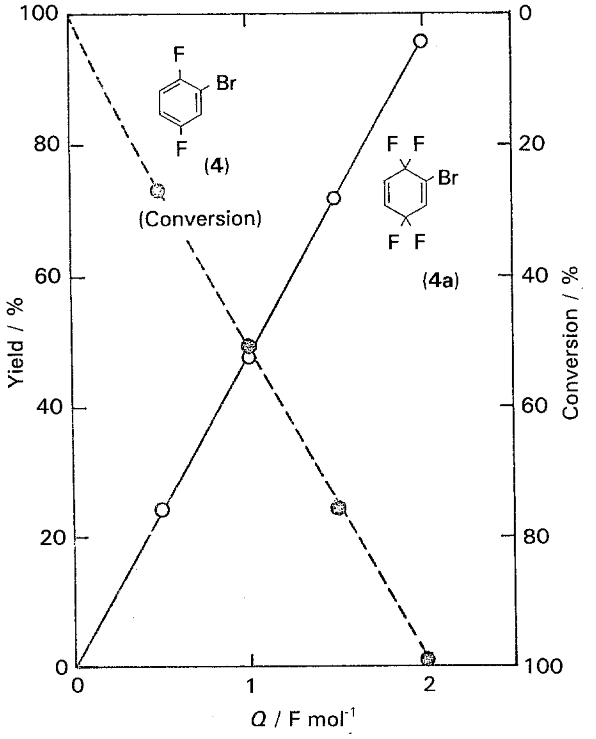


Fig. 3. Variations in the yield of (**4a**) (○) and the conversion of (**4**) (●) during electrolysis (4) in $Et_4NF \cdot 4.7HF$ (run 7).

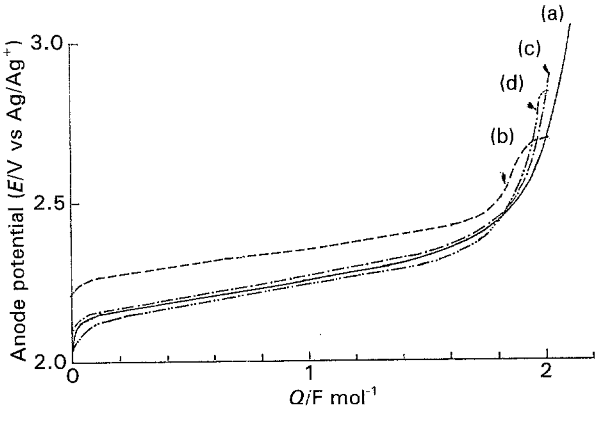


Fig. 4. Variations in the anode potential with quantity of electricity passed during galvanostatic electrolyses (500 mA) of (**1**) (curve a), (**2**) (curve b), (**3**) (curve c) and (**4**) (curve d) in $Et_4NF \cdot 4.7HF$.

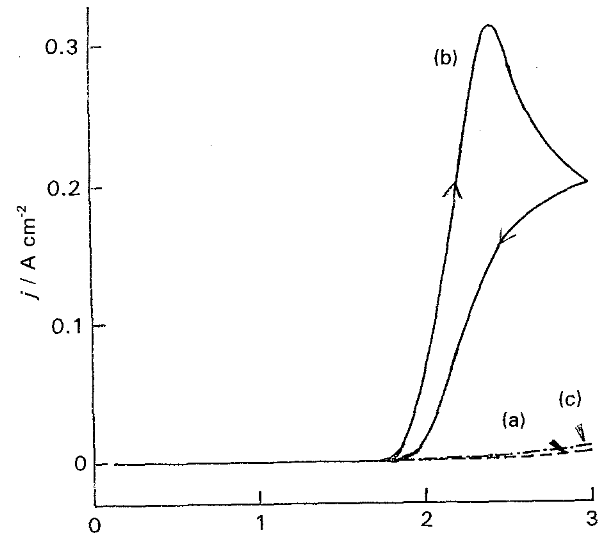


Fig. 5. Voltammograms in $Et_4NF \cdot 4.7NF$ without substrate (curve a; background), and in $Et_4NF \cdot 4.7HF$ containing 0.8 M of (**1**) (before electrolysis (b); and after electrolysis, 2.1 F mol^{-1}, (c); run 3); scan rate 100 mV s^{-1}.

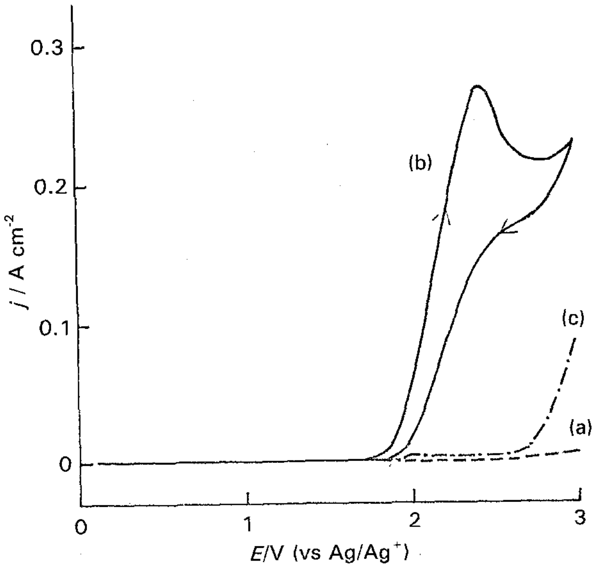


Fig. 7. Voltammograms in $Et_4HF \cdot 4.7HF$ without substrate (curve a; background), and in $Et_4HF \cdot 4.7HF$ containing 0.8 M of (**4**) (before electrolysis (b) and after electrolysis, 2.0 F mol^{-1}, (c); run 6); scan rate 100 mV s^{-1}.

of (**2**) and (**4**), respectively. The anodic current (peak potential is about 2.8 V) of curve (c) in Fig. 6 is based on the electrochemical fluorination of (**2b**) to corresponding fluorohexenes. The products, (**1a**), (**2a**) and (**3a**) isolated in pure states were not oxidized until 3.0 V on the CVs.

It is presumed that the oxidation potentials of fluoro-1,3-cyclohexadienes that are conjugated dienes are more negative than those of the corresponding fluoro-1,4-cyclohexadienes. As shown in the previous paper [12], the oxidation potentials of the substrates (aromatic compounds, A), the fluoro-1,3-cyclohexadienes (B) and fluoro-1,4-cyclohexadienes (C) produced by electrochemical fluorination of A were in the order A < B < C. During the potentiostatic electrolysis (2.5 V vs Ag/Ag$^+$ (0.01 M) of trifluoromethylbenzene, the products fluoro-1,3-cyclohexadienes, i.e. 1-trifluoromethyl-5,5,6-trifluoro-1,3-cyclohexadiene, 1-trifluoromethyl-5,6,6-trifluoro-1,3-cyclohexadiene and 2-trifluoromethyl-5,6,6-trifluoro-1,3-cyclohexadiene, were further fluorinated to the corresponding fluorocyclohexenes electrochemically [14]. On the other hand, the products fluoro-1,4-cyclohexadienes, i.e. 1-trifluoromethyl-3,3,6-trifluoro-1,4-cyclohexadiene, 1-trifluoromethyl-3,6,6-trifluoro-1,4-cyclohexadiene and 1-trifluoromethyl-3,3,6,6,-tetrafluoro-1,4-cyclohexadiene, did not react under these electrolyses conditions (2.5 or 2.7 V). No visible anodic currents were observed for these fluoro-1,4-cyclohexadienes on the CVs. Similar results were obtained in the anodic fluorination of chlorobenzenes [12].

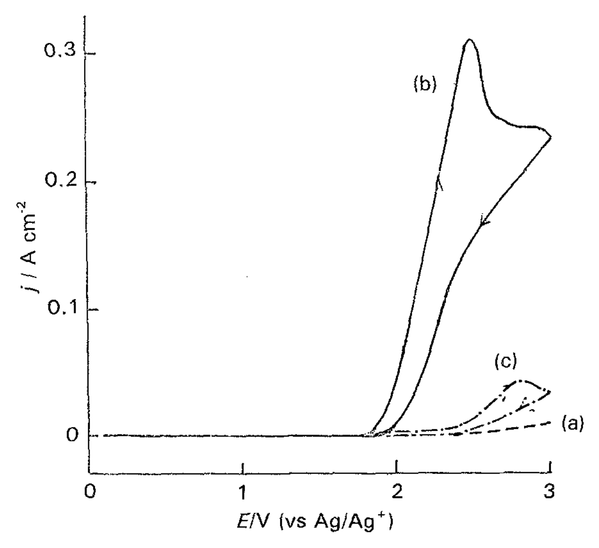


Fig. 6. Voltammograms in $Et_4HF \cdot 4.7HF$ without substrate (curve a; background), and in $Et_4HF \cdot 4.7HF$ containing 0.8 M of (**2**) (before electrolysis (b) and after electrolysis, 2.0 F mol^{-1}, (c); run 4); scan rate 100 mV s^{-1}.

In Fig. 7, anodic current based on the oxidation of (**4a**) was observed around 2.8 V or above (curve (c)). Brominated fluoro-1,4-cyclohexadienes, 3-bromo-3,6,6-trifluoro-1,4-cyclohexadiene and 1-bromo-3,6,6-trifluoro-1,4-cyclohexadiene), were oxidized at 2.6 V or above judging from the CVs [18]. Therefore, the plateaux of curves (b) and (d), observed around

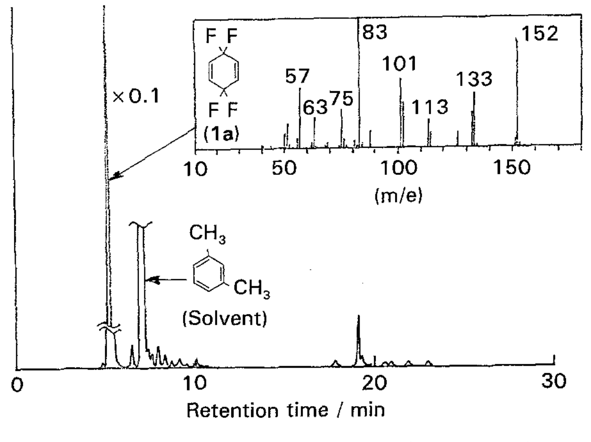


Fig. 8. Gas chromatogram of the extracted solution after electrolysis of (**1**) (run 3) and mass spectrum of (**1a**). Column temp. 50 °C (0 min) → 5 °C min^{-1} → 180 °C (10 min), He: 20 cm^3 min^{-1}.

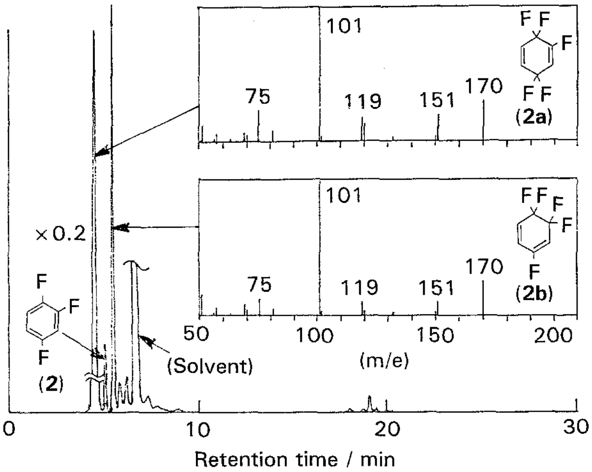


Fig. 9. Gas chromatogram of the extracted solution after electrolysis of (**2**) (run 4) and mass spectra of (**2a**) and (**2b**).

2.0 F mol^{-1} in Fig. 2, are attributable to the electrochemical oxidation of (**2b**) and (**4a**), respectively.

3.2. *Isolation of FCHDs*

After the electrolysis, 250 cm^3 of water was added to the electrolyte solution, and the products were extracted with *m*-xylene (in the cases of the electrolyses of (**1**) and (**2**)) or 3,4-dichlorotoluene (the electrolyses of (**3**) and (**4**)). Figures 8–11, respectively, show the gas-chromatograms for the extracts after the electrolyses corresponding to runs 3–6 in Table 1. The chromatograms were measured in the same conditions (column, G-450 (trifluoropropyl methyl silicone 1 μm/DC-QF-1; 1.2 mm inside diam.–40 m), FID, He 20 ml min^{-1}, column temperature; 50 °C (0 min) → 5°C min^{-1} → 180 °C (10 min)). The mass-spectra (70 eV) of the main products, (**1a**), (**2a**), (**2b**), (**3a**) and (**4a**), are also shown in Figs 8–11. In all cases, the retention times (r.t.) and the boiling point (b.p.) of fluoro-1,4-cyclohexadienes produced as main products were lower than those of the substrates. In contrast, r.t.'s and b.p.'s of fluoro-1,3-cyclohexadienes were higher than those of the substrates. *m*-Xylene (in the cases of (**1a**) and (**2a**)) and 3,4-dichlorotoluene ((**3a**) and (**4a**)) were chosen as extraction solvents, because of the effective isolation of FCHDs in pure states by fractional distillation. The solvents are fully stable under the distillation conditions, and their b.p.'s are moderately higher (30–60 °C) than those of FCHDs. Most of the FCHDs were recovered in the first fraction.

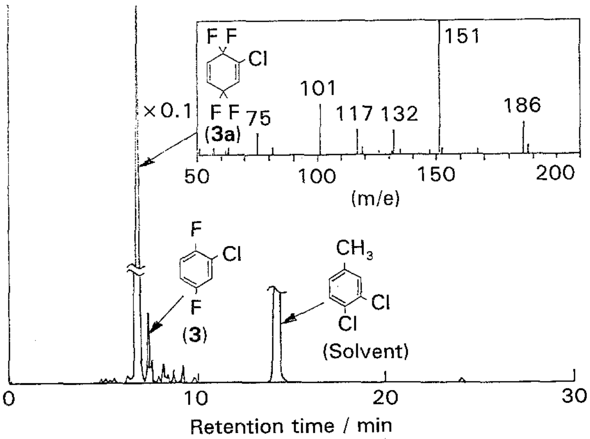


Fig. 10. Gas chromatogram of the extracted solution after electrolysis of (**3**) (run 5) and mass spectrum of (**3a**).

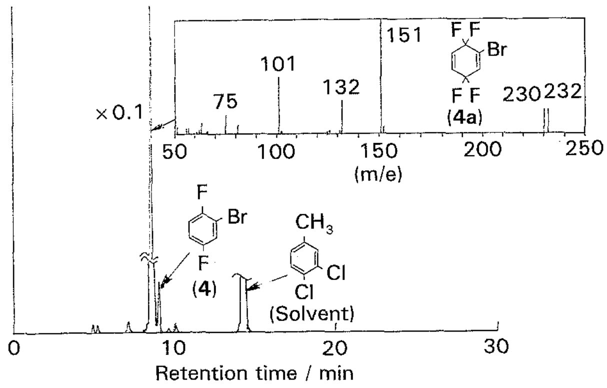


Fig. 11. Gas chromatogram of the extracted solution after electrolysis of (**4**) (run 6) and mass spectrum of (**4a**).

The results for the fractional distillation of the extracts containing (**1a**) (runs 1–3) are summarized in Table 2. A 99.8% assay of (**1a**) with 80–85% yield based on (**1**) as the first (< 87.5 °C) and the second (87.5–89.0 °C) fractions were isolated. Some (**1a**) was present in the third fraction (98.0–132 °C), where the main component was the solvent *m*-xylene. The content of (**1a**) in the residue was less than 0.2%.

Table 3 shows the results for the fractional distillation of the extract containing (**2a**) and (**2b**) (Fig. 9). Although a small amount of (**2a**) (38% yield based on (**2**)) was obtained in a pure state (97.2% of

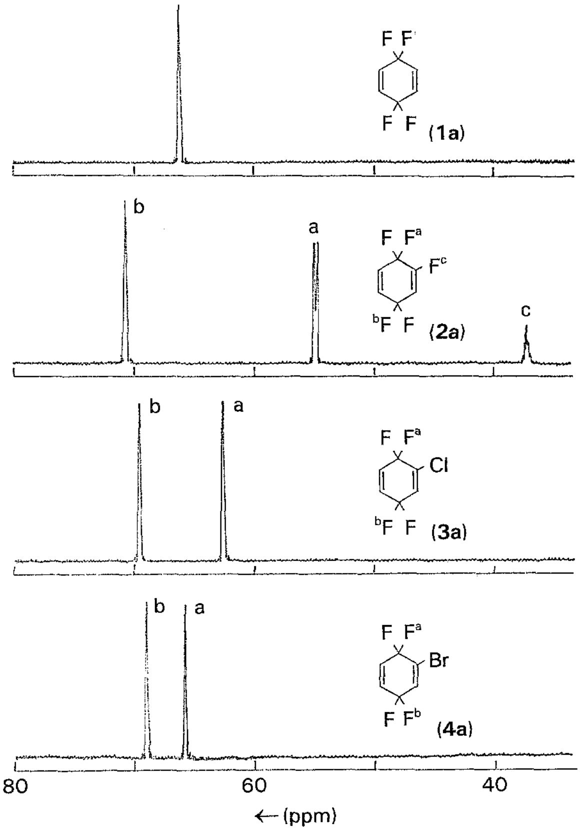


Fig. 12. ^{19}F NMR spectra of (**1a**), (**2a**), (**3a**) and (**4a**).

Table 2. Results for the fractional distillation of the extracts containing (**1a**)

Run	*First fraction* (<87.5 °C)	*Second fraction* (87.5–89.0 °C)	*Third fraction* (89.0–132.0 °C)	*Isolated yield**
1	2.6 g, 98.9%†	21.8 g, 99.8%	2.9 g, 21.9%	80.0%
2	3.1 g, 98.8%	22.5 g, 99.9%	3.8 g, 16.8%	84.2%
3	2.2 g, 98.7%	23.7 g, 99.9%	3.6 g, 14.6%	85.0%

* Isolated yields were calculated by the content of (**1a**) in the first and second fractions.
† Assay of (**1a**).

Table 3. Results for the fractional distillation of the extracts containing (**2a**) *and* (**2b**) (*run 4*)

Fraction	*Boiling range* /°C	*Weight* /g	*Component/%*			
			(**2a**)	(**2b**)	(**2**)	*m-xylene*
1	< 84.0	13.0	97.2	1.4	1.0	–
2	84.0–86.0	9.2	89.5	6.9	3.4	–
3	86.0–97.0	6.1	40.6	45.9	13.5	0.2
4	97.0–115.0	5.8	5.4	54.5	12.8	11.7

Table 5. Results for the fractional distillation of the extracts containing (**4a**)*

Run	*First fraction* (< 63.0 °C)	*Second fraction* (63.0–115.0 °C)	*Isolated yield*
6	37.2 g, 97.4%†	10.2 g, 10.5%	80.7%
7	38.1 g, 98.5%	8.5 g, 11.7%	83.4%
8	38.7 g, 99.3%	7.5 g, 12.7%	85.3%

* At reduced pressure (50 mm Hg).
† Assay of (**4a**).

assay), the total yields of (**2a**) and (**2b**) in the fractions were 69% and 20%, respectively.

The results for the fractional distillation of the extract containing (**3a**) (Fig. 10) are shown in Table 4. The isolated yield of (**3a**) in fractions 1 and 2 was 77%. It seems that the difference between the isolated yield (ca. 78%) and the GC yield (93.7%, run 5 in Table 1) is mainly due to the evaporation loss because the b.p. of (**3a**) was rather low (48.0 °C at 50 mm Hg) under the distillation conditions. Some products would be lost during the extraction process. The differences in the yields tended to increase with decreasing b.p.'s of the distillates.

Table 5 summarizes the results for the fractional distillation of the extracts containing (**4a**) (runs 6–8). In runs 7 and 8, the current was decreased step by step (500 → 300 → 100 mA) to keep the anode potential below 2.5 V. In this condition, as the product (**4a**) was not fluorinated electrochemically, both the improved yield of (**4a**) and the higher conversion of (**4**) were achieved in run 7 (compared with run 6). The quantities of electricity passed in runs 6 and 7 were 2.0 F mol^{-1}, and that in run 8 was 2.1 F mol^{-1}. About 0.4% of 3,4-dichlorotoluene was contained in the first fractions. The purity of (**4a**) in the first fraction of run 8 was higher than those in runs 6 and 7. The separation of the liquids (i.e. (**4a**) and (**4**)), whose boiling points lie close to each other, requires a column with a high number of theoretical plates. Therefore, the content of unreacted (**4**) in the electrolysed solution must be reduced as little as possible to isolate (**4a**) by fractional distillation. Generally, the substrate compounds, (**1**)–(**4**), were almost completely converted by passing an amount of electricity slightly in excess (2.1 F mol^{-1}, runs 1–3 and 8 in Table 1) to the theoretical value (2.0 F mol^{-1}).

Table 4. Results for the fractional distillation of the extract containing (**3a**) (*run 5*)

Fraction	*Boiling range* /°C, 50 mm Hg	*Weight* /g	*Component/%*		
			(**3a**)	(**3**)	*3,4-dichlorotoluene*
1	< 48.0	25.4	97.1	1.1	–
2	48.0–51.0	4.5	89.8	4.4	0.1
3	51.0–115.0	4.6	6.0	8.1	38.8

3.3. *Analyses*

The structural assignments for the FCHDs were made by ^{1}H and ^{19}F–NMR and MS. The ^{19}F NMR spectra for four kinds of 3,3,6,6-tetrafluoro-1,4-cyclohexadienes isolated in pure states are shown in Fig. 12.

NMR spectral data

(**1a**): ^{1}H NMR ($CDCl_3$/TMS) δ; 6.30 ppm (*m*, 4H), ^{19}F NMR ($CDCl_3$/C_6F_6); 66.2 (*s*, 4F). (**2a**): ^{1}H NMR; 5.90 (*m*, H, 2-CH), 6.26 (*m*, 2H, 4,5-CH), ^{19}F NMR; 37.3 (*m*, F, 1-CF), 54.8 (*d*, $J = 18.9$ Hz, 2F, 6-CF_2), 70.7 (*s*, 2F, 3-CF_2). (**3a**): ^{1}H NMR; 6.34 (*m*, 2H, 4,5-CH), 6.42 (*m*, H, 2-CH), ^{19}F NMR; 62.7 (*s*, 2F, 6-CF_2), 69.4 (*s*, 2F, 3-CF_2). (**4a**): ^{1}H NMR; 6.36 (*m*, 2H, 4,5-CH), 6.66 (*m*, H, 2-CH), ^{19}F NMR; 66.4 (*s*, 2F, 6-CF_2), 68.9 (*s*, 2F, 3-CF_2).

4. Conclusion

On a preparative scale, FCHDs (**1a**)–(**4a**), which have not previously been isolated, were isolated in pure states with high yields by electrochemical fluorination of (**1**)–(**4**), respectively in $Et_4NF \cdot mHF$ followed by fractional distillation. The substrate compounds were almost quantitatively fluorinated to the corresponding FCHDs by passing 2.0 F mol^{-1} of electricity and were completely fluorinated at 2.1 F mol^{-1}.

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