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Electrochemical fluorination of several esters derived from oxolane-2-yl-carboxylic acid, oxolane-2-yl-methanol and oxane-2-yl-methanol

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Abstract

Electrochemical fluorination (ECF) of the ester derivatives of oxolane-2-yl-carboxylic acid (**1**), oxolane-2-yl-methanol (**2**) and oxane-2-yl-methanol (**3**) were investigated. Perfluoro(oxolane-2-yl-carbonylfluoride) (**4**) was obtained from derivatives of **1** and **2**, and perfluoro(oxane-2-yl-carbonylfluoride) (**5**) was obtained from derivatives of **3** as the desired compounds, respectively. From the ECF of acetates of **2** and **3**, perfluorospiroethers having a dioxolane ring were also obtained as the cyclization product in low yield together with the desired perfluoroacid fluoride (**4** and **5**). The structure of these perfluorospiroethers was confirmed by analyzing the chlorinated products, which were obtained by the reaction with $AlCl_3$.

Keywords: Electrochemical fluorination; Organofluorine compound; Perfluorooxolane-2-yl-carbonyl fluoride; Perfluorooxane-2-yl-carbonylfluoride; Perfluorospiroether

1. Introduction

Perfluorooxolanes have been synthesized by various methods involving the fluorination of oxolane with metal fluorides (CoF_3, MnF_3, $KCoF_4$) [1,2]. Recently, a study was made for polyfluorooxolanes as the candidate for CFCs alternatives and several polyfluorooxolanes synthesized were evaluated as CFCs alternatives [2]. Though perfluoro-(oxolane-2-yl-carbonylfluoride) is an useful starting material for the synthesis of perfluorooxolene-3 as well as fluoro-compounds carrying a perfluorooxolane group, it has not been accessible easily because the special starting material was used [3].

We have investigated the preparation of perfluoro-(oxolane-2-yl-carbonylfluoride) (**4**) by the electrochemical fluorination (ECF) of the following samples: oxolane-2-yl-carbonyl chloride (**6**), methyl oxolane-2-yl-carboxylate (**7**), oxolane-2-yl-methyl oxolane-2-yl-carboxylate (**8**), oxolane-2-yl-methanol (**2**), oxolane-2-yl-methyl acetate (**9**) and oxolane-2-yl-methyl trifluoroacetate (**10**). Furthermore, ECF of acetates of oxane-2-yl-methanol [acetate (**11**), trifluoroacetate (**12**)] was investigated to obtain perfluoro-(oxane-2-yl-carbonylfluoride) (**5**).

2. Results and discussion

2.1. Preparation of perfluoro(oxolane-2-yl-carbonylfluoride) (4) and perfluoro(oxane-2-yl-carbonylfluoride) (5) by the electrochemical fluorination

It has been reported that perfluoro(oxolane-2yl-carbonxylic acid) (precursor for **4**) could be made using perfluoro(oxolane-2-yl-acetyl fluoride) as the starting material (Scheme 1) [1].

It consists of a multi-step synthesis involving following successive reactions: (1) preparation of potassium salt of

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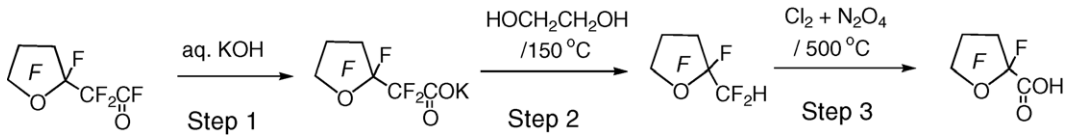


Scheme 1.

perfluoroacid having a perfluorooxolane ring; (2) thermal decomposition of the potassium salt in ethyleneglycol to form the CHF_2-group at the 2-position of the oxolane ring and (3) oxidation of the CHF_2-group to convert into the carboxyl group (precursor for **4**). It should be noted that the starting material [perfluoro(oxolane-2-yl-acetyl fluoride)] was obtained as a by-product from the electrochemical fluorination of adipic acid chloride [5] and moreover, it contained small quantities of isomeric perfluoro(oxane-2-yl-carbonyl fluoride). Therefore, we have investigated the direct preparation of perfluoro(oxolane-2-yl-carbonyl-fluoride) (**4**) by the ECF of derivatives of oxolane-2-yl-carboxylic acid (**6**, **7** and **8**) and those of oxolane-2-yl-methanol (**2**, **9** and **10**) [4].

The results of the fluorination are summarized in Table 1.

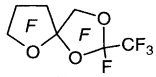
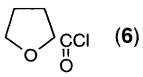
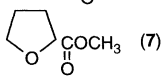
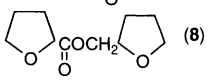
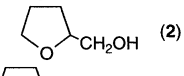
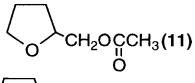
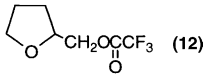
It is known that oxolane-2-yl-carbonylchloride (**6**) is not stable on shelf standing at room temperature [6,7]. Actually, the evolution of large quantities of gases was observed when dissolved in AHF. When compound **6** was subjected to ECF, the target perfluoro(oxolane-2-yl-carbonylfluoride) (**4**) was obtained in low yield (GC yield = 3%) affording perfluorooxolane (**13**) as the principal product, which was formed as a result of the C–C bond scission between the 2-position of the oxolane ring and carbonylchloride. However, the yield of **4** was improved considerably (12%) when methyl oxolane-2-yl-carboxylate (**7**) was fluorinated (Run 2). Though good yield of **4** was expected from ECF of oxolane-2-yl-methyl oxolane-2-yl-carboxylate (**8**) due to having the possibility to give 2 M precursor for **4** from 1 M of **8**, only 10% yield of **4** was obtained (Run 3). The reason for the low yield was ascribed partly for the formation of the tarry material during fluorination.

Next, the ECF of derivatives of oxolane-2-yl-methanol (**2**) was examined, as it is known that primary alcohol could serve as starting materials for perfluoroacid fluoride on ECF [8–11]. When **2** was subjected to ECF, the target **4** was obtained in 6% yield. The major cleaved product was **13** (23% yield).

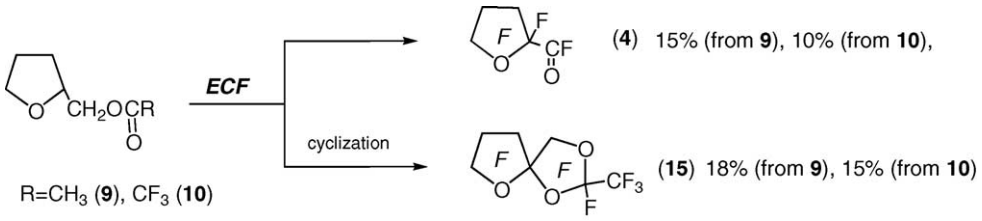
However, it was found that yield of **4** was improved (15 and 10%, respectively) when an acetate (**9**) and a trifluoroacetate (**10**) of **2** were fluorinated (Runs 5 and 6). Trifluoroacetyl fluoride (**14**) was formed as the major cleaved product. In addition, considerable amount of perfluoro(2-methyl-1,3,5-trioxa-spiro[4.4]octane) (**15**) was obtained both from **9** and **10** (Scheme 2). Identification of **15** is described later.

This new compound (**15**) was considered to be formed by the cyclization during fluorination, because, it was known

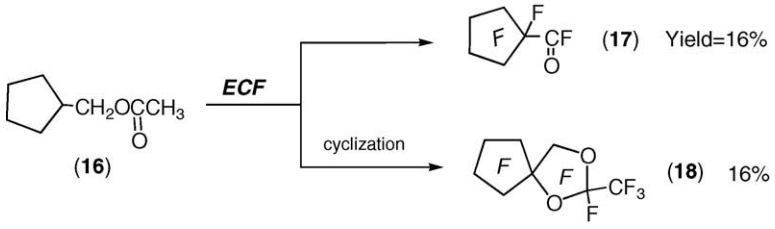
Table 1
Results of the electrochemical fluorination of oxolane derivatives

Run	Sample (compound no.)	Sample fed (g/mol)	Electricity[a] passed (Ahr)	Product (g)	Major fluorination products[b]/yield (%)			
							 (5)	 (15)
1	 (6)	22.7 (0.168)	70.5	20.9	45	1	3	–
2	 (7)	20.8 (0.160)	83.9	15.8	21	2	12	–
3	 (8)	22.1 (0.110)	98.4	18.1	20[c]	6	10[c]	–
4	 (2)	20.9 (0.205)	95.6	17.4	23	2	6	–
5	 (11)	20.6 (0.143)	101.5	14.0 [11.0][d]	16	4	15	18
6	 (12)	29.8 (0.151)	70.5	7.6 [4.5]	8	1	10	7

[a] Anodic current density: 1.98 A/dm^2.
[b] Arranged in order of GC retention time.
[c] Calculated assuming that 1 mol of eight yielded 2 mol of four.
[d] Cell drainings.



Scheme 2.



Scheme 3.

that perfluorodioxolanes were formed as by-products by the ECF of ethyl esters of morpholine-substituted carboxylic acids [12]. Furthermore, it has been reported that several perfluorospiroethers were formed by the fluorination of 3-(cycoalkyl)-substituted propionic acid methyl esters [13]. So, in order to investigate this side reaction (cyclization) of an acetate of cycloalkyl-substituted methanol, the fluorination of cyclopentymethyl acetate (**16**) as a model was conducted (Scheme 3).

As expected, perfluoro(cyclopentylcarbonylfluoride) (**17**) and perfluorospiro(2-methyl-1,3-dioxa-spiro[4.4]nonane) (**18**) were obtained as the major products together with cleaved products such as perfluorocyclopentane (**19**) and perfluoro(methylcyclopentane) (**20**).

It is assumed that the cyclization is completed by the attack of the radical species formed on the tertiary carbons of the cyclopentyl group toward carbonyl oxygen at the early stage of the fluorination (Scheme 4). In this cyclization, the formation of the intermediate radical (**21**), which is stabilized by two adjacent oxygen atoms will operate as the main driving force.

In the cases of **9** and **10**, it is considered that the presence of the oxygen of the oxolane ring facilitates the formation of the radical species on the tertiary carbon at the 2-position of the oxolane ring in their molecule, which leads to the easy formation of the skeleton of the 1,3,5-trioxa-2-methylspiro-[4.4]nonane successively.

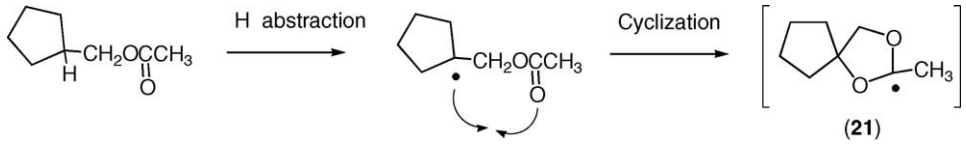
In order to obtain, perfluoro(oxane-2-yl-carbonyl fluoride) (**5**) as a cyclization product in a similar way to that from the ester derivatives of oxolane-2-yl-methanol (**4**), we have examined the ECF of the ester derivatives of oxane-2-yl-methanol (**3**) (Table 2).

When an acetate (**11**) and a trifluoroacetate (**12**) esters of **3** was fluorinated, an another set of products consisting of the target perfluoro(oxane-2-yl-carbonylfluoride) (**5**) and a perfluorospiro ether were formed along with other cleaved products. The latter was identified as perfluorospiro(2-methyl-1,3,5-trioxa-spiro[4.5]decane) (**22**) similarly (Scheme 5).

Formation of **22** would be explained clearly by the similar reaction path to the formation of **18** from **16**.

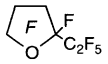
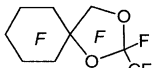
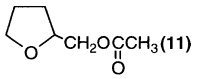
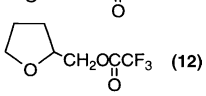
2.2. Determination of the structures of perfluorospiroethers (15, 18 and 22)

All perfluorospiroethers having a perfluorodioxolane ring were new compounds, which were characterized by the measurement of IR, MS and ^{19}F NMR and elemental analysis (carbon and fluorine). In the MS of **15**, **18** and **22**, characteristic ions like $[M–F]^+$ (the largest one) and $[M–CF_3]^+$ (the next largest one) were observed. Among three perfluorospiroethers, the structure of **18** were determined by its ^{19}F NMR analysis. Peaks due to CF_3- (δ −85.5), F- (δ −82.4) and five sets of AB quartet due to the geminal fluorines of the cyclic ring structure at the expected regions supported the proposed structure of **18** (Table 3). However, the structure of **15** and **22** could not be determined in a straight forward manner as these ^{19}F NMR spectra



Scheme 4.

Table 2
Results of the electrochemical fluorination of oxane derivatives

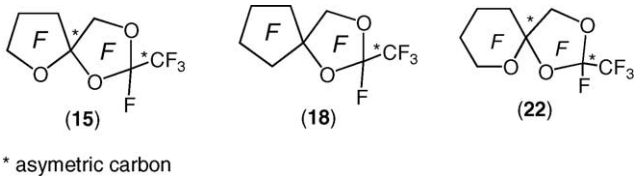
Run	Sample (compound no.)	Sample fed g (mol)	Electricity[a] passed (Ahr)	Product (g)	Major fluorination products[b]/yield (%)					
									 (5)	 (22)
1	 (11)	19.9 (0.127)	70.5	9.0 [14.1][c]	4	10	5	3	8	15
2	 (12)	27.8 (0.131)	88.2	7.0 [9.6]	3	7	4	3	8	7

[a] Anodic current density: 1.98 A/dm$^{2.}$
[b] Arranged in order of GC retention time.
[c] Cell drainings.

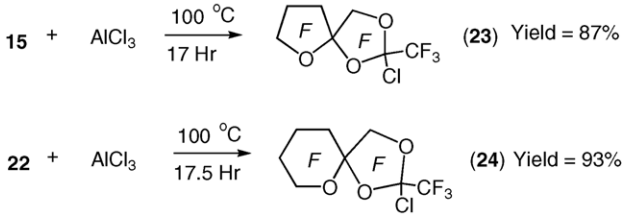
showed very complex ones due to having two asymetric carbons in the structure (Scheme 6).

Therefore, the structure of **15** and **22** was determined by studying the spectral data (MS and ^{19}F NMR) of the chlorinated compounds, which were obtained by the reactions with $AlCl_3$. It is known that fluorines at α-position of the oxygen of the perfluoro(2-alkyl-substituted oxolanes) react easily with Lewis acid such as $AlCl_3$ and BCl_3 giving perfluoro(2-alkyl-2,5,5-trichlorooxolanes) [14]. In this reaction, the methine fluorine (–CF_2–C**F**(OCF_3)–O–), which is located between two oxygens is more reactive than the fluorines (–CF_2–C**F**$_2$–O–) and/or the fluorine (–CF–C**F**(CF_3)–O–) on the carbon bonding with one oxygen [15]. We have used this reaction for the confirmation of the proposed structure, as both **15** and **22** contain the methine fluorine at the 2-position of the perfluoro(2-methyl-1,3-dioxolane) group which consist of the spiroether ring. Thus, by applying the controlled reaction conditions (temperature, 100 °C; reaction time, 17 h), mono-chlorine-substitution was achieved at the methine fluorine of the 2-position of the dioxolane ring to give perfluoro(2-chloro-2-methyl-1,3,6-trioxa[4,4,0]nonane) (**23**) and perfluoro(2-chloro-2-methyl-1,3,6-trioxa[4,5,0]decane) (**24**) successfully (Scheme 7).

^{19}F NMR spectra of **23** and **24** showed rather simplified ones as compared with those of **15** and **22**. However, they were still complicated due to the mixture of two diastereoisomers in each compounds. Characteristically, in the MS of **23** and **24**, ions as $[M–Cl]^+$ and $[M–CF_3]^+$ were observed similarly to those observed for **15** and **22**, which



Scheme 6.

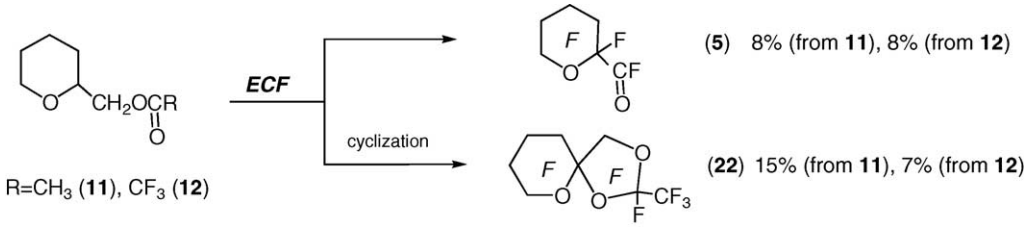


Scheme 7.

supported the presence of perfluoro(2-chloro-2-methyl-1,3-dioxolane) ring in the proposed structure.

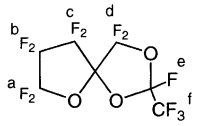
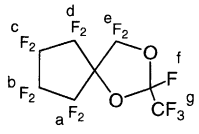
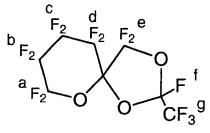
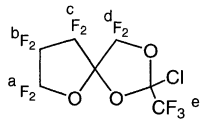
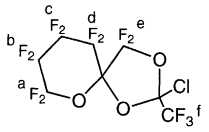
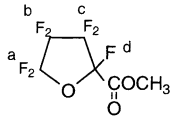
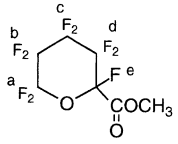
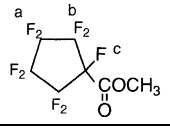
3. Experimental details

Boiling points were uncorrected. Oxolane-2-yl-methanol (**2**) (Wako Chemicals Co.) and methyl oxolane-2-yl-methyl acetate (**9**) (Research Chemicals Ltd.) were used as received. Oxolane-2-yl-carbonyl chloride (**6**) was prepared by the



Scheme 5.

Table 3
^{19}F NMR spectra of compounds **15**, **18**, **22**, **23**, **24**, **26**, **30** and **31**

Compound	Formula		Chemical shift[a,b]	J[b] (Hz)
15		a	−76.9 to −89.1	
		b	−131.2 (m), −131.5 (m)	
		c	−126.3, −137.7	J_{AB} = 244
		d, e	−76.9 to −89.1	
		f	−86.0 (m), −86.1 (m)	
18		a	−124.5, −132.4	J_{AB} = 266
		b	−124.7, −130.0	J_{AB} = 252
		c	−124.2, −130.0	J_{AB} = 252
		d	−124.0, −132.9	J_{AB} = 266
		e	−74.1 (m), −73.7 (m)	J_{AB} = 141
		f	−82.4 (m)	
		g	−85.5 (d)	J = 8.5
22		a	−74.7 to −91.7	
		b, c, d	−123.4 to −142.6	
		e, f	−74.7 to −91.7	
		g	−85.9 (m), −86.0 (m)	
23		a	−77.6 to −88.5	
		b	−131.1 (m), −131.5 (m)	
		c	−126.6,−138.1	J_{AB} = 249
		d	−77.6 to −88.5	
		e	−84.6 (m), −84.8 (m)	
24		a	−74.4 to −91.8	
		b, c, d	−123.3 to −142.6	
		e	−74.7 to −91.8	
		f	−84.4 (m), −84.8 (m)	
26		a	−82.9, −83.4	J_{AB} = 133
		b	−127.2, −130.8	J_{AB} = 259
		c	−126.0, −134.9	J_{AB} = 291
		d	−117.8 (multiplet)	
30		a	−78.7, −91.9	J_{AB} = 159
		b	−123.1, −133.0	J_{AB} = 282
		c	−127.5, −140.9	J_{AB} = 280
		d	−124.1, −138.9	J_{AB} = 268
		e	−124.1	
31		a	−126.7, −128.9	J_{AB} = 254
		b	−122.8, −130.2	J_{AB} = 267
		c	−182.5 (multiplet)	

[a] ^{19}F chemical shifts in ppm relative to internal $CC1_3F$ (negative shifts are upfield) and ^{1}H chemical shifts in ppm relative to TMS.
[b] Only obvious chemical shifts and coupling constants are given.

reaction of thionyl chloride and oxolane-2-yl-carboxylic acid (**1**) (Wako Chemicals Co.). Methyl oxolane-2-yl-carboxylate (**7**) and oxolane-2-yl-methyl oxolane-2-yl-carboxylate (**8**) was prepared by the reaction of **6** with methanol and **2**, respectively. Oxane-2-yl-methyl acetate (**11**) was prepared by the reaction of acetyl chloride (Wako Chemicals Co.) and oxane-2-yl-methanol (**3**) (Tokyo Kasei Co.). Oxolane-2-yl-methyl trifluoroacetate (**10**) and oxane-2-yl-methyl trifluoroacetate (**12**) were prepared by the reaction of **2** and **3** with trifluoroacetic acid (Wako Chemicals Co.), respectively.

The substrates synthesized for fluorination had the following boiling points: oxolane-2-yl-carbonyl chloride (**6**), bp 77–82 °C/30 mmHg (reported: bp 80–81 °C/30 mmHg [6]; bp 95–100 °C/33 mmHg [7]) methyl oxolane-2-yl-carboxylate (**7**), bp 87–92 °C/22 mmHg; oxolane-2-yl-methyl oxolane-2-yl-carboxylate (**8**), bp 130–132 °C/6 mmHg; oxolane-2-yl-methyl trifluoroacetate (**10**), bp

107–110 °C/105 mmHg; oxane-2-yl-methyl acetate (**11**), bp 104–105 °C/24 mmHg; oxane-2-yl-methyl trifluoroacetate (**12**), bp 111–112 °C/89 mmHg.

Purity of anhydrous hydrogen fluoride (AHF) (Daikin Industries Co.) was more than 99.9%. The electrolytic fluorination apparatus and operating procedures were similar to those described previously [12]. Analytical GLC work was carried out with a Shimadzu GC-14B gas chromatograph using stainless steel columns (3 mm diameter) packed with 25% Fomblin YR on Chromosorb PAW (6.4 m). New compounds were separated from the other products by use of semi-preparative GLC. For a semi-preparative work, a GASUKURO LL-75 modified gas chromatograph using an aluminum column (3/8 in. diameter) packed with 20% Fomblin YR on Chromosorb PAW (20 feet) was used. The carrier gas was helium in all cases. Infrared spectra were measured on a Shimadzu FTIR-8000PC spectrometer using a 6 cm gas cell with KBr windows. ^{19}F NMR spectra were measured on a JEOL ECA-300S spectrometer (282.75 MHz for ^{19}F and 300.53 MHz for ^{1}H, respectively). Chemical shifts for ^{19}F and ^{1}H NMR spectra were reported in relative to $CFCl_3$ and TMS, respectively. Positive shifts are downfield from the reference ($CFCl_3$ and TMS). Mass spectra were measured on a Shimadzu GC/MS-QP5000 instrument fitted with a capillary column (Neutra bond-1, 30 m long, 0.25 mm i.d., 1.5 μm thick) at 70 eV. Ion-exclusion chromatography was done on a Shimadsu Model LC-10 with a conductivity detector CDD-6A. Elemental analyses were performed by Mikroanalytisches Labor Beller/Metthies in Göttingen, Germany.

3.1. Fluorination of oxolane-2-yl-methanol (*2*)

Sample **2** (20.9 g, 0.205 mol) was charged into a cell containing 450 ml electrolytically purified AHF and the solution was subjected to fluorination with an anodic current density of 1.98 A/dm^2, a cell voltage of 5.3–5.9 V and a cell temperature of 7–8 °C over a period of 415 min (96 Ah).

The effluent gases from the cell were passed over NaF pellets and then condensed in a trap cooled to −78 °C. The gaseous products, which did not condense in the −78 °C trap were then bubbled through a fluoropolymer bottle containing water (for the trap of perfluoroacid fluorides) and a gas washing bottle containing an aqueous solution of a mixture of K_2CO_3, KOH and KI. All products except new ones were identified by comparison of their infrared spectra and GLC retention times with those of authenticated samples. Ion-exclusion chromatography was used for the analysis of perfluoroacid fluoride in the gas-washing bottle. However, no significant amount of perfluoro(oxolane-2-yl-carboxylic acid) derived from **4** was found in it [16].

The products (17.4 g) condensed in the −78 °C trap consisted of perfluorooxolane (**13**) (10.1 g), perfluoro(2-methyloxolane) (**25**) (1.0 g), perfluoro(oxolane-2yl-carbonylfluoride) (**4**) (3.2 g) and unidentified products (3.1 g). The GC yield of **4** was 6%. Spectral data of **4** are shown below. IR (gas): 1888 (ms) [ν(C=O)], 1391 (w), 1346 (ms), 1270 (ms, sh), 1227 (s), 1181 (ms), 1161 (ms), 1109 (vs), 1080 (s, sh), 1007 (ms), 910 (ms), 698 (w), 571 (w).

Further characterization of **4** was conducted in a form of the methyl ester. Methyl perfluoro(oxolane-2-yl-carboxylate) (**26**) was prepared by mixing about 2 g cell drainings with 1 ml of methanol. The reaction was completed within a few minutes. The lower layer was separated by means of semi-preparative GC to give **26**. Physicochemical properties and spectral data (IR and MS) of **26** are shown below. ^{19}F NMR data of **26** are shown in Table 3.

Methyl perfluoro(oxolane-2-yl-carboxylate) (**26**) had bp 103.5–104.5 °C (reported; bp 106 °C [3]), d_4^{20} 1.5654 and n_D^{20} 1.3158. IR (capillary film): 2972 (w) ν(CH), 1790 (s) [ν(C=O)], 1445 (m), 1873 (m), 1352 (ms), 1302 (ms), 1217–161 (vs–s), 1126 (s), 1082 (vs), 1007 (s), 962 (ms), 904 (m), 777 (m). MS: 197 $[M–C(O)OMe]^+$ (1.8), 169 $C_4F_8^+$ (13.5), 109 $CF_2C(O)OMe^+$ (5.7), 100 $C_2F_4^+$ (13.8), 69 CF_3^+ (46.0), 59 $C(O)OMe^+$ (100).

3.2. Fluorination of oxolane-2-yl-carbonyl chloride (*6*)

Sample **6** (22.7 g, 0.168 mol) was fluorinated similarly under the following conditions: 1.98 A/dm^2, 5.4–6.3 V, 7–8 °C, 281 min (71 Ah). The work-up gave the following products in the −78 °C trap (20.9 g): perfluorooxolane (**13**) (16.3 g), perfluoro(2-methyloxolane) (**25**) (0.6 g), perfluoro(oxolane-2-yl-carbonyl fluoride) (**4**) (1.0 g) and unidentified products (3.0 g). The GC yield of **4** was 3%.

3.3. Fluorination of methyl oxolane-2-yl-carboxylate (*7*)

Sample **7** (20.8 g, 0.160 mol) was fluorinated similarly under the following conditions: 1.98 A/dm^2, 5.7–6.5 V, 7–8 °C, 408 min (84 Ah). The work-up gave the following products in the −78 °C trap (15.8 g): **13** (15.8 g), **25** (7.5 g), **4** (4.6 g) and unidentified products (3.0 g). The GC yield of **4** was 12%.

3.4. Fluorination of oxolane-2-yl-methyl oxolane-2-yl-carboxylate (*8*)

Sample **8** (22.1 g, 0.110 mol) was fluorinated similarly under the following conditions: 1.98 A/dm^2, 5.5–6.8 V, 7–8 °C, 426 min (98 Ah). The work-up gave the following products in the −78 °C trap (18.1 g): **13** (9.6 g), **25** (1.8 g), **4** (5.3 g) and unidentified products (1.4 g). The GC yield of **4** was 20%.

3.5. Fluorination of oxolane-2-yl-methyl acetate (*9*)

Sample **9** (20.6 g, 0.143 mol) was fluorinated similarly under the following conditions: 1.98 A/dm^2, 5.3–6.1 V, 7–8 °C, 405 min (102 Ah). In this case, a high boiling products

(cell drainings) were drained from the cell after completion of the electrolysis. The work-up gave the following products in the −78 °C trap (14.0g): **13** (5.0 g), **25** (1.4 g), **4** (4.9 g) and unidentified products (1.5 g). Cell drainings (11.0 g) consisted of **4** (0.2 g), perfluoro(2-methyl-1,3,5-trioxa-spiro[4.4]nonane) (**15**) (8.2 g) and unidentified product (2.6 g). The GC yields of **4** and **15** were 15 and 18%, respectively.

Perfluoro(2-methyl-1,3,5-trioxa-spiro[4.4]nonane) (**15**) was separated from other products by use of semi-preparative GLC. Physicochemical properties and spectral data (IR and MS) of **15** are shown below. ^{19}F NMR data of **15** are shown in Table 3.

Perfluoro(2-methyl-1,3,5-trioxa-spiro[4.4]nonane) (**15**) (nc): bp 70.5–72.5 °C, d_4^{20} 1.7075, $n_D^{20} < 1.28$. IR (gas): 1331 (m), 1300 (m), 1244 (vs), 1225 (s, sh), 1194 (ms), 1182 (ms), 1155 (ms), 1130 (m), 1088 (s), 1034 (s), 1007 (m). MS: 375 $[M–F]^+$ (4.2), 325 $[M–CF_3]^+$ (17.9), 259 $C_6F_9O^+$ (12.9), 209 $C_5F_7O^+$ (23.7), 181 $C_4F_7^+$ (32.0), 131 $C_3F_5^+$ (100), 119 $C_2F_5^+$ (28.0), 109 $C_3F_3O^+$ (34.9), 100 $C_2F_4^+$ (40.1), 69 CF_3^+ (65.7). Analysis: Calc. for $C_7F_{12}O_3$: C, 23.33%; F, 63.33%. Found: C, 23.3%; F, 63.5%.

3.6. Fluorination of oxolane-2-yl-methyl trifluoroacetate (*10*)

Sample (29.8 g, 0.151 mol) was fluorinated similarly under the following conditions: 1.98 A/dm^2, 5.2–6.0 V, 7 ∼ 8 °C, 282 min (71 Ah). The work-up gave the following products in the −78 °C trap (7.6 g): **13** (2.6 g), **25** (0.5 g), **4** (3.3 g) and unidentified products (0.7 g). Cell drainings (4.5 g) consisted of **4** (0.5 g), **15** (3.2 g) and unidentified product (0.8 g). The GC yields of **4** and **15** were 10 and 7%, respectively.

3.7. Fluorination of oxane-2-yl-methyl acetate (*11*)

Sample **11** (19.9 g, 0.127 mol) was fluorinated similarly under the following conditions: 1.98 A/dm^2, 5.4–5.5 V, 7–8 °C, 357 min (89.9 Ah). In this case, a high boiling products (cell drainings) were drained from the cell after the completion of the electrolysis similarly. The work-up gave the following products in the −78 °C trap (9.0 g): **25** (1.5 g), perfluorooxane (**27**) (3.1 g), perfluoro(2-ethyloxolane) (**28**) (1.2 g), perfluoro(2-methyloane) (**29**) (0.7 g), perfluoro(oxane-2-yl-carbonylfluoride) (**5**) (1.1 g) and unidentified products (1.3 g). Cell drainings (14.1 g) consisted of **27** (0.3 g), **28** (0.8 g), **29** (0.7 g), **5** (1.8 g), **22** (7.8 g) and unidentified products (2.7 g). The GC yields of **5** and **22** were 8 and 7%, respectively.

Perfluoro(oxane-2-yl-carbonylfluoride) (**5**) showed following IR spectra (gas): 1886 (m) [ν(C=O)], 1355 (w), 1340 (w), 1286 (ms), 1254 (ms, sh), 1286 (s, sh), 1207 (s), 1140 (vs), 1055 (ms), 986 (ms), 899 (ms), 802 (w). Methyl ester of **5** (**30**) was prepared for further characterization in a similar manner as explained for **4**.

Physicochemical properties and spectral data (IR and MS) of **30** and **19** are shown below. ^{19}F NMR of **30** and **19** are shown in Table 3.

Methyl perfluoro(oxane-2-yl-carboxylate) (**30**) (nc): bp 93.5–94.5 °C, d_4^{20} 1.6579, n_D^{20} 1.3211. IR (capillary film): 2972 (w) ν(CH), 1790 (s) [ν(C=O)], 1443 (m), 1342–1135 (vs–s), 1057 (ms), 988 (s), 957 (ms), 894 (m), 779 (ms), 642 (m), 613 (m). MS: 247 $[M–C(O)OMe]^+$ (1.4), 131 $C_3F_5^+$ (17.7), 100 $C_2F_4^+$ (18.5), 69 CF_3^+ (41.3), 59 $C(O)OMe^+$ (100). Analysis: Calc. for $C_7F_9O_3H_3$: C, 27.45%; F, 55.88%. Found: C, 27.3%; F, 56.2%.

Perfluoro(2-methyl-1,3,5-trioxa-spiro[4.5]decane) (**22**) (nc): bp 93.5–94.5 °C, d_4^{20} 1.774, n_D^{20} 1.2856. IR (gas): 1301 (m), 1246 (vs), 1223 (s), 1204 (s), 1161 (s), 1122 (ms), 1107 (vs), 1182 (s), 989 (ms). MS: 391 $[M–F]^+$ (1.3), 341 $[M–CF_3]^+$ (5.7), 131 $C_3F_5^+$ (49.7), 100 $C_2F_4^+$ (100), 97 $C_2F_3O^+$ (5.6), 78 $C_2F_2O^+$ (31.1), 69 CF_3^+ (83.4), 47 $C(O)F^+$ (38.4). Analysis: Calc. for $C_8F_{14}O_3$: C, 23.41%; F, 64.88%. Found: C, 23.3%; F, 65.3%.

3.8. Fluorination of oxane-2-yl-methyl trifluoroacetate (*12*)

Sample **12** (27.9 g, 0.131 mol) was fluorinated similarly under the following conditions; 1.98 A/dm^2, 5.1–5.6 V, 7–8 °C, 349 min (88 Ah). The work-up gave the following products in the −78 °C trap (7.0 g): **25** (1.0 g), **27** (2.2 g), **28** (0.9 g), **29** (0.6 g), **5** (1.1 g) and unidentified products (1.2 g). Cell drainings (9.6 g) consisted of **27** (0.3 g), **28** (0.7 g), **29** (0.6 g), **5** (2.0 g), **22** (3.8 g) and unidentified products (2.2 g). The GC yields of **5** and 2**2** were 8 and 7%, respectively.

3.9. Fluorination of cyclopentylmethyl acetate (*16*)

Sample **16** (20.0 g, 0.141 mol) was fluorinated similarly under the following conditions: 1.98 A/dm^2, 5.4–7.3 V, 7–8 °C, 369 min (90 Ah). The work-up gave the following products in the −78 °C trap (6.8 g): perfluorocyclopentane (**19**) (1.4 g), perfluoro(2-methylcyclopentane) (**20**) (1.5 g), perfluoro(cyclopentylcarbonyl fluoride) (**17**) (3.2 g) and unidentified products (0.4 g). Cell drainings (4.3 g) consisted of **17** (0.5 g), perfluoro(1,3-dioxa-2-methyl[4.4.0]nonane) (**18**) (2.7 g) and unidentified products (1.1 g). The GC yields of **17** and **18** were 9 and 5%, respectively.

Perfluoro(cyclopentyl carbonylfluoride) (**17**) showed following IR spectra (gas): 1881 (m) [ν(C=O)], 1312 (ms), 1258 (s), 1227 (vs), 1207 (s, sh), 1138 (ms), 980 (s). Methyl ester of **17** (**31**) was prepared for further characterization in a similar manner as explained for **4**. Physicochemical properties and spectral data (IR and MS) of **18** and **31** are shown below. ^{19}F NMR data of **18** and **31** are shown in Table 3.

Perfluoro(2-methyl-1,3-dioxa-spiro[4.4]nonane) (**18**) (nc): bp 88.0–89.0 °C, d_4^{20} 1.7823, n_D^{20} 1.2876. IR (gas): 1319 (ms), 1271 (m), 1244 (vs), 1225 (s), 1138 (m), 978

(m). MS: 375 $[M–F]^+$ (4.2), 325 $[M–CF_3]^+$ (17.9), 259 $C_6F_9O^+$ (12.9), 209 $C_5F_7O^+$ (23.7), 181 $C_4F_7^+$ (32.0), 131 $C_3F_5^+$ (100), 119 $C_2F_5^+$ (28.0), 109 $C_3F_3O^+$ (34.9), 100 $C_2F_4^+$ (40.0), 69 CF_3^+ (65.7). Analysis: Calc. for $C_8F_{14}O_2$: C, 24.37%; F, 67.51%. Found: C, 24.0%; F, 67.5%.

Methyl perfluoro(cyclopentylcarboxylate)(**31**) (nc): bp 109–110 °C, d_4^{20} 1.6520, n_D^{20} 1.3207. IR (capillary film): 2972 (w) ν(CH), 1774 (s) [ν(C=O)], 1443 (m), 1207–1319 (vs–s), 1132 (ms), 1030 (ms), 976 (s), 900 (m), 777 (s). MS: 259 $[M–OCH_3]^+$ (11.9), 231 $[M–C(O)OMe]^+$ (6.9), 181 $C_4F_7^+$ (12.1), 162 $C_4F_6^+$ (8.3), 131 $C_3F_5^+$ (25.3), 69 CF_3^+ (9.8), 59 $C(O)OMe^+$ (100). Analysis: Calc. for $C_7F_9O_2H_3$: C, 28.97%; F, 58.97%. Found: C, 29.2%; F, 58.2%.

*3.10. Reaction of perfluoro(2-methyl-1,3,5-trioxa[4.4.0]nonane) (**15**) with $AlCl_3$*

In a 30 ml Hoke bomb, a mixture of **15** (1.69 g, 4.7 mmol) and $AlCl_3$ (0.6 g, 4.7 mmol) was kept at 100 °C for 17 h. While the bomb was kept at −78 °C, volatile products were removed by passing through a trap at −196 °C to a vacuum system. The compound, which remained in the bomb was transferred to a trap at −78 °C to a vacuum system, which was analyzed and purified by GC. Thus, **23** (1.59 g, 87% yield) was obtained. Physicochemical properties and spectral data (IR and MS) of **23** are shown below. ^{19}F NMR data of **23** are shown in Table 3.

Perfluoro(2-chloro-2-methyl-1,3-dioxa-spiro[4.4]nonane) (**23**) (nc) had bp 99.5–100.0 °C, d_4^{20} 1.7297, n_D^{20} 1.3053. MS: 341 $[M–Cl^{35}]^+$ (50.5), 307 $[M–CF_3]^+$ (11.4), 100 $C_2F_4^+$ (28.6), 97 $C_2F_3O^+$ (33.9), 78 $C_2F_2O^+$ (25.0), 69 CF_3^+ (100). Analysis: Calc. for $C_7F_{11}O_3Cl$: C, 22.31%; F, 55.51%; Cl, 9.43. Found: C, 22.24%; F, 55.3%; Cl, 9.36%.

*3.11. Reaction of perfluoro(2-methyl-1,3,5-trioxa[4.5.0]decane)(**22**) with $AlCl_3$*

Similarly, a reaction mixture of **22** (1.24 g, 3.03 mmol) and $AlCl_3$ in a 30 ml Hoke bomb was kept at 100 °C for 17.5 h. The work-up of the products was the same as that explained for the reaction of **15**. Thus, **24** (1.07 g, 93% yield) was obtained. Physicochemical properties and spectral data (IR and MS) of **24** are shown below. ^{19}F NMR data of **24** are shown in Table 3.

Perfluoro(2-chloro-2-methyl-1,3-dioxa-spiro[4.5]decane) (**24**) (nc) had bp 119–120 °C, d_4^{20} 1.7868, n_4^{20} 1.3120. MS: 391 $[M–Cl^{35}]^+$ (31.1), 357 $[M–CF_3]^+$ (7.9), 131 $C_3F_5^+$ (20.6), 100 $C_2F_4^+$ (36.6), 97 $C_2F_3O^+$ (38.0), 78 $C_2F_2O^+$ (11.4), 69 CF_3^+ (100). Analysis: Calc. for $C_8F_{13}O_3Cl$: C, 22.51%; F, 57.91%; Cl, 8.32%. Found: C, 22.55%; F, 57.6%; Cl, 8.44%.

(1) The prefix of "*F*-" in this paper designates "Perfluoro" (all C–H bonds are replaced by C–F bonds).

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[16] After the completion of the electrolysis, ion-exclusion chromatography (IEC) was done for the analysis of perfluoro(oxolane-2-yl-carboxylic acid) (hydrolysis product from 4) through the Runs of 1–6 in Table 1 in the absorption trap containing a water. However, only small amount of perfluoro(oxolane-2-yl-carboxylic acid) was found in it. While, a large quantity of $CF_3C(O)OH$ (hydrolysis product from 14) was found in the Runs of 5 and 6 (fluorination of 9 and 10), which amounted to about 23–25% of theory. Analytical data {retention volumes [V_R(ml)] and distribution coefficients (K_d) of perfluorocarboxylic acids and fluoride ion} are as follows. $CF_3C(O)OH$: V_R = 6.7, K_d = 0.13, perfluoro(oxolane-2-yl-carboxylic acid): V_R = 7.7, K_d = 0.30 and F^-: V_R = 10.0, K_d = 0.67 {analytical conditions, eluent: 6 mM benzoic acid, column: TSK Gel OApak-A (Tosoh Co.) (30 cm × 7.8 mm i.d.), column temperature: 40 °C, flow-rate: 0.6 ml/min}. For further information about the analysis of perfluorocarboxylic acid by IEC, see the following literature. T. Abe, H. Baba, I. Soloshonok, K. Tanaka, J. Chromatogr. A, 884 (2000) 91–103.