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Journal of Fluorine Chemistry 120 (2003) 105–110
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

Development of direct fluorination technology for application to materials for lithium battery

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Received 1 August 2002; received in revised form 7 October 2002; accepted 11 October 2002

Abstract

Direct fluorination of 1,3-dioxolan-2-one with elemental fluorine was successfully carried out to provide 4-fluoro-1,3-dioxolan-2-one, which was expected as an additive for lithium ion secondary battery. 4-Fluoro-1,3-dioxolan-2-one was also further fluorinated with elemental fluorine to give three isomers of difluoro derivatives by the same methodology. Another topic is the preparation of trifluoromethanesulfonyl fluoride, an intermediate of lithium battery electrolyte, by the reaction of methanesulfonyl fluoride with elemental fluorine. The use of perfluoro-2-methylpentane as a solvent gave satisfactory selectivity of trifluoromethanesulfonyl fluoride.

Keywords: Direct fluorination; Elemental fluorine; Lithium battery; 4-Fluoro-1,3-dioxolan-2-one; 4,5-Difluoro-13-dioxolan-2-one; 4,4-Difluoro-1,3-dioxolan-2-one; Trifluoromethanesulfonyl fluoride; Difluoromethanesulfonyl fluoride; Fluoromethanesulfonyl fluoride

1. Introduction

4-Fluoro-1,3-dioxolan-2-one (fluoroethylene carbonate) has been expected as an attractive additive or solvent for lithium ion secondary battery because of reducing the electrolyte decomposition and substantially increasing the cell efficiency [1]. Usually 4-fluoro-1,3-dioxolan-2-one is prepared by the reaction of 4-chloro-1,3-dioxolan-2-one with potassium fluoride, but this reaction requires severe reaction conditions [2]. In recent years, electrochemical fluorination of 1,3-dioxolan-2-one (ethylene carbonate) without solvent has been reported to give 4-fluoro-1,3-dioxolan-2-one in a reasonable yield [3]. The use of elemental fluorine as a fluorine source is profitable because the most fundamental method for the introduction of fluorine atom into an organic molecule is the direct substitution of hydrogen for fluorine. Recently, direct fluorination of γ-butyrolactone with elemental fluorine was reported to provide a mixture of fluorinated γ-butyrolactones [4]. We have new developed an efficient method for preparing 4-fluoro-1,3-dioxolan-2-one by direct fluorination of 1,3-dioxolan-2-one with elemental fluorine [5]. 4-Fluoro-1,3-dioxolan-2-one has also been found to be transformed to three isomers of difluorinated 1,3-dioxolan-2-ones by the same methodology [6].

Another topic is the preparation of trifluoromethanesulfonyl fluoride by the reaction of methanesulfonyl fluoride with elemental fluorine. Trifluoromethanesulfonyl fluoride is one of the important intermediates of lithium salts used as an electrolyte in lithium ion secondary battery. For producing trifluoromethanesulfonyl fluoride is widely employed the electrochemical fluorination of methanesulfonyl fluoride [7]. Gas phase direct fluorination of dimethylsulfone gives bis(trifluoromethyl)sulfone as well as trifluoromethanesulfonyl fluoride [8]. We have also developed a new method for the preparation of trifluoromethanesulfonyl fluoride by the reaction of methanesulfonyl fluoride with elemental fluorine [9].

2. Results and discussion

2.1. Direct fluorination of 1,3-dioxolan-2-one (1)

First, fluorination of 1,3-dioxolan-2-one (**1**) with elemental fluorine was carried out in various solvents and the results are summarized in Table 1. The conversion of **1** (as well as the selectivity of 4-fluoro-1,3-dioxolan-2-one (**2**) were

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PII: S0022-1139(02)00317-2

Table 1
Direct fluorination of 1,3-dioxolan-2-one (**1**)

Solvent	Ratio (wt/wt) **1**:solvent	Reaction temperature (°C)	F_2[a] (eq)	Passing time (ml/min)	Conversion (%)	Selectivity[b] of **2** (%)
$CHCl_3$	5:95	0	0.6	50	0	0
$(CF_3)_2CFCF_2CF_2CF_3$	2:98	0	0.4	50	12	95
$(CF_3)_2CFCF_2CF_2CF_3$	2:98	50	1.0	50	33	79
$CClF_2CCl_2F$	10:90	50	1.0	50	52	68
HF	17:83	10	1.0	50	71	93
No solvent	100:0	50	1.7	350	85	86 (70)[c]

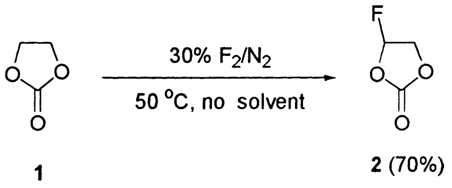
[a] Fluorine, 30% mixture in nitrogen, was passed through the reaction mixture (50–350 ml/min).

[b] GC analysis.

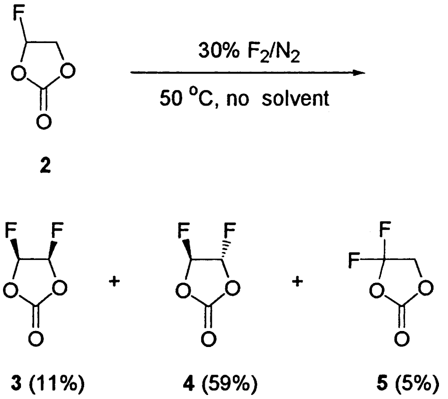
[c] Isolated yield (in parentheses) based on **1**.

strongly dependent on a choice of solvents. Fluorination of **1** in chloroform did not give **2** at all. This is presumably due to preferential fluorination of chloroform. Peffluoro-2-methylpentane and 1,1,2-trichloro-1,2,2-trifluoroethane are known as effective solvents for the liquid phase direct fluorination of organic compounds with elemental fluorine [10] because of their inactive nature toward elemental fluorine at ambient temperature. The use of perfluoro-2-methylpentane as the solvent resulted in the formation of a significant amount of **2**. At 0 °C, the conversion of **1** was low and the reaction rate was slow. It is considered that **1** would be less reactive toward elemental fluorine at such low temperature as 0 °C. On raising the reaction temperature, the reaction proceeded faster but the selectivity of **2** did not increase. Polyfluorinated byproducts were formed together with **2**. Fluorination of **1** in 1,1,2-trichloro-1,2,2-trifluoroethane also gave similar result. Hydrogen fluoride is known as effective solvent, and the fluorination of **1** in hydrogen fluoride at 0 °C led to the formation of **2** with good selectivity. However, the reaction was very slow at this temperature. It is difficult to carry out the fluorination in hydrogen fluoride at high temperature such as 50 °C, because of the low boiling point of hydrogen fluoride. Although the flow rate of fluorine at 0 °C was increased, the reaction was not accelerated and a large amount of unreacted fluorine remained. Finally we found that the reaction of **1** with elemental fluorine proceeded efficiently at 50 °C without solvent, giving **2** with good selectivity (86%) and good isolated yield (70%).

Compound **2** was also fluorinated without solvent to give three difluorinated compounds, *cis*-4,5-difluoro-1,3-dioxolan-2-one (**3**), *trans*-4,5-difluoro-1,3-dioxolan-2-one (**4**) and 4,4-difluoro-1,3-dioxolan-2-one (**5**) (Schemes 1–3). The ratio of **3**:**4**:**5** was about 2.5:6.5:1. Each compound **3**, **4** and **5** was separated by distillation followed by recrystallization to obtain in 11, 59, and 5% yield, respectively.



Scheme 1.



Scheme 2.

^1H NMR of **3** showed a doublet–doublet like signal around $\delta = 6.23$ ppm. But the splitting pattern was complicated. ^{19}F NMR of **3** also showed a doublet–doublet like signal around $\delta = -148.1$ ppm, whose splitting pattern was complicated. Similarly, ^1H and ^{19}F NMR spectra of **4** showed doublet–doublet like signals around $\delta = 6.14$ ppm (^1H NMR) and -134.8 ppm (^{19}F NMR), respectively. Here again both of the splitting patterns were complicated. The shape of the ^1H NMR signal of **3** was closed to that of **4**. Similarly, the shape of the ^{19}F NMR signal of **3** was also closed to that of **4**. These NMR data strongly suggested that **3** and **4** were regarded as two vicinal difluoro compounds.

In order to determine the absolute structures of **3** and **4**, X-ray analysis was examined. Fortunately, **3** could be

$$\underset{\textbf{6}}{CH_3SO_2F} \xrightarrow[(CF_3)_2CFCF_2CF_2CF_3]{30\%\ F_2/N_2,\ 40\ ^{\circ}C}$$

$$\underset{\textbf{7}\ (64\%)}{CF_3SO_2F} + \underset{\textbf{8}\ (2\%)}{CHF_2SO_2F} + \underset{\textbf{9}\ (7\%)}{CH_2FSO_2F}$$

$$+\ CF_4 + CO_2 + C_2F_6 + SO_2F_2$$

Scheme 3.

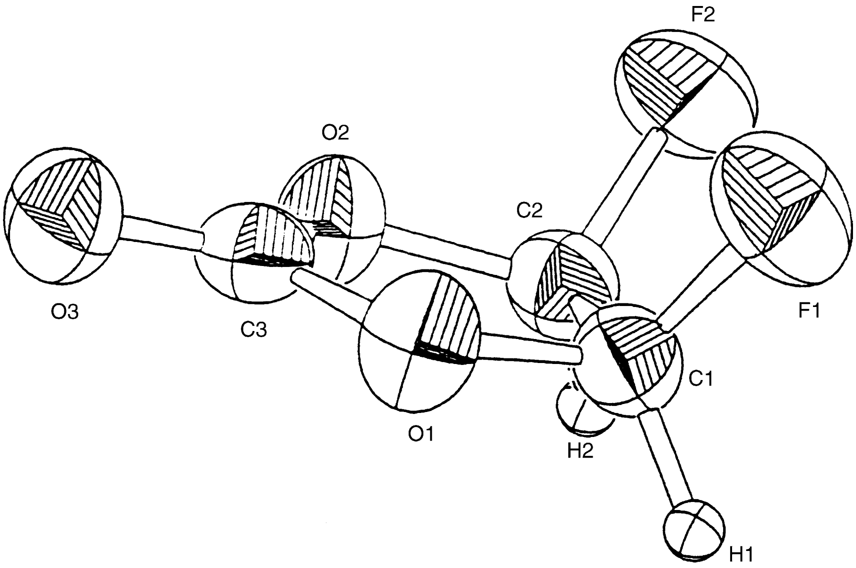


Fig. 1. X-Ray ORTEP of *cis*-4,5-difluoro-1,3-dioxolan-2-one (**3**). Crystal system: orthorhombic, lattice parameters: $a = 0.7240$ (nm), $b = 1.0807$ (nm), $c = 0.5513$ (nm), space group: $P212121$, Z value: 4, residuals: R; $R_w = 0.029$; 0.024.

crystalized readily and the X-ray analysis of **3** was successfully performed. The ORTEP structure of **3** obtained by X-ray analysis is shown in Fig. 1. It was found that each fluorine atom was attached to each carbon atom in *cis* position. So the compound **3** has *cis* structure. Another isomer **4** was determined as the *trans* isomer.

^{1}H NMR spectrum of **5** showed a triplet signal due to methylene protons around $\delta = 4.68$ ppm with a coupling constant of 11.6 Hz. Similarly, ^{19}F NMR spectrum of **5** showed a triplet signal due to difluoromelylene fluorine atoms around $\delta = -72.8$ ppm with a coupling constant of 11.6 Hz.

Table 2 summarizes some physical properties of the fluorinated 1,3-dioxolan-2-ones, together with those of common carbonates. An introduction of fluorine atom(s) to 1,3-dioxolan-2-one decreased the boiling point and melting point, except *cis*-4,5-difluoro-1,3-dioxolan-2-one. Viscosities of fluorinated 1,3-dioxolan-2-ones were increased while dielectric constants and electric conductivities were decreased.

2.2. Direct fluorination of methanesulfonyl fluoride (6)

Fluorination of methanesulfonyl fluoride (**6**) with elemental fluorine in liquid phase was examined in several solvents and the results are summarized in Table 3. Fluorination of methanesulfonyl fluoride without solvent at 80 °C did not give desired trifluoromethanesulfonyl fluoride (**7**) but gave CF_4, CO_2, C_2F_6 and SO_2F_2, which would be formed by a decomposition of **6**. In contrast, fluorination of **6** without solvent at 20 °C gave an appreciable amount of **7** but the selectivity was poor. In this reaction, a trace of difluoromethanesulfonyl fluoride (**8**) and 12% of fluoromethanesulfonyl fluoride (**9**) were also obtained together with recovered **6** (80%). It would be considered that solvent-free fluorination gave partially fluorinated compounds in preference of perfluorinated compound. Presumably, a large excess of the substrate against elemental fluorine in the reaction media prevented perfluorination, so that the substrate should be diluted with a solvent. The use of hydrogen fluoride as the solvent resulted in a recovery of **6**. A large amount of unreacted fluorine gas was observed. Fluorination in formic acid [13] afforded only carbon dioxide which would be formed by a reaction of formic acid with elemental fluorine followed by hydrolysis. The reaction in perfluoro-2-methylpentane proceeded successfully to give **7** with good selectivity (87.7%) and moderate isolated yield (64%) together with **8** (2%), **9** (7%), and recovered **6** (22%).

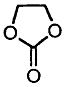
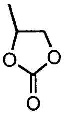
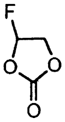
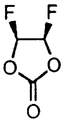
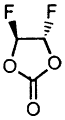
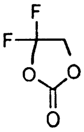
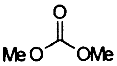
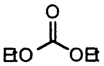
The partially fluorinated byproducts **8** and **9** could be regarded as intermediates of **7**, so that the compounds **8** and **9** would be recycled and used as starting materials for the preparation of **7**. In fact, the fluorination of **9** gave **7** with good selectivity (88.8% selectivity of **7**). Similarly the fluorination of **8** proceeded smoothly, affording **7** with excellent selectivity (97.1% selectivity of **7**).

3. Experimental

3.1. General experimental procedures

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 NMR spectrometer. Chemical shifts were reported in ppm relative to internal tetramethylsilane, and $CDCl_3$, was used as the solvent. ^{19}F NMR spectra were recorded on a Varian Gemini 200 NMR spectrometer. Chemical shifts were reported in ppm relative to internal $CFCl_3$, and $CDCl_3$ was used as the solvent. Low-resolution mass

Table 2
Physical properties of non-fluorinated and fluorinated carbonates

Compounds	bp (°C)	mp (°C)	Density d (kg m^{-3})	Viscosity η ($\times 10^{-3}$ Pa s)	Dielectric constant ε (−)	Electric conductivity κ (S m^{-1})[a]	Ref[b]
	238	37	1321	1.9[c]	90[c]	1.31[c]	[11]
	242	−49	1209	2.5[d]	65[d]	1.06[d]	[11]
	210	17.3	1497	4.1[e]	78.4[e]	1.04[e]	Our data
	187	56.6	1592	2.3[f]	No data	1.53[f]	Our data
	129	7.8	1508	2.5[e]	37.1[e]	0.95[e]	Our data
	134	3.2	1567	2.1[e]	34[e]	1.16[e]	Our data
	91	3	1069	0.6[g]	0.6[g]	0.11[g]	[12]
	126	−43	975	0.7[g]	2.8[g]	0.06[g]	[12]

[a] The electric conductivity was measured by a conductivity meter equipped with an H-type conductivity cell charged with organic liquid electrolyte containing 1 M Et_4NBF_4.

[b] Physical properties are cited from ref. [11,12] except our data.

[c] At 40 °C.

[d] At 20 °C.

[e] At 23 °C.

[f] At 60 °C.

[g] At 25 °C.

Table 3
Direct fluorination of methanesulfonyl fluoride (**6**)[a]

Solvent	Temperature (°C)	Conversion (%)	GC selectivity[b]					
			7	**8**	CF_4	CO_2	C_2F_6	SO_2F_2
No solvent	80	5	nd	nd	36.7	14.2	3.1	46.0
No solvent[c]	20	20	30.5	Trace	20.1	22.9	0.7	25.8
HF[d]	10	<1	nd	nd	Trace	Trace	nd	Trace
HCOOH	30	<1	nd	nd	Trace	99.8	nd	0.2
$(CF_3)_2CFCF_2CF_2CF_3$	40	76	87.7 (64)[e]	0.6	2.2	4.1	0.1	4.2

[a] Fluorine, 30% mixture in nitrogen, was passed through the reaction mixture (50–200 ml/min).

[b] GC analysis of the gaseous products.

[c] **8** (Trace), **9** (12% GC yield), **6** (80% GC yield).

[d] Large amount of F_2 was recovered.

[e] Isolated yield (in parentheses) based on **6**.

spectra were obtained on a Shimazu GC–MS-QP5050A in an electron impact mode. FT-IR spectra were recorded on a JEOL JIR MICRO6000 reported in cm^{-1}. Boiling points were determined during fractional distillation using a thermometer, and are uncorrected. Melting points were recorded on a Rigaku DSC8230L. All chemicals and solvents were used without further purification.

*3.2. Synthesis of 4-fluoro-1,3-dioxolan-2-one (**2**)*

The carbonate **1** (528 g, 6 mol) was charged into a 1 l PFA vessel and stirred vigorously at 50 °C by passing N_2 (200 ml/min, 30 min). Fluorine gas, 30% mixture in nitrogen, was passed at a constant flow rate (350 ml/min) through the substrate. When 10.8 mol of fluorine was passed to the reaction mixture, the gas line and the reactor were parged with N_2 (200 ml/min, 30 min). The reaction mixture was washed with ice water (100 ml) and extracted with dichloromethane (200 ml × 3). The combined organic layers were dried over anhyd. $MgSO_4$, followed by filtration and removal of the solvents by a rotary evaporator. The organic residue was purified by distillation to give 440 g (4.2 mol, 70%) of **2** as a colorless liquid. mp 17.3 °C. bp 210 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.29 (ddd, $J_{HH} = 1.2, 4.1$ Hz, $J_{HF} = 64.0$ Hz, 1H, CHF) 4.60 (ddd, $J_{HH} = 4.1, 11.0$ Hz, $J_{HF} = 32.9$ Hz, 1H) 4.49 (ddd, $J_{HH} = 1.2, 11.0$ Hz, $J_{HF} = 21.9$ Hz, 1H). ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 152.7 (s, 1C, C=O) 105.0 (d, 1C, CHF) 70.7 (d, 1C, CH_2). ^{19}F NMR (188 MHz, $CDCl_3$) δ −121.7 (ddd, $J = 22.0, 32.7, 63.9$ Hz, 1F). IR (neat): 3046, 1834, 1362, 1157, 1082, 909. EIMS (probe) 70 eV, *m/z* (rel. int.) 106 $[M]^+$ (20) 73 (10), 62 (100) 58 (40) 43 (70).

3.3. Synthesis of difluorinated 1-3-dioxolan-2-ones

The carbonate **2** (160 g, 1.5 mol) was charged into a 250 ml PFA vessel and stirred vigorously at 50 °C by passing N_2 (200 ml/min, 30 min). Fluorine gas, 30% mixture in nitrogen, was passed at a constant flow rate (250 ml/min) through the substrate. When 2.25 mol of fluorine (1.5 equivalent of **2**) was passed to the reaction mixture, the gas line and the reactor were parged with N_2 (200 ml/min, 30 min). The reaction mixture was washed with ice water (100 ml) and extracted with dichloromethane (250 ml × 6). The combined organic layers were dried over anhyd. $MgSO_4$, followed by filtration and removal of the solvents by a rotary evaporator. The crude products were purified by distillation affording colorless crystals of **3** (21 g, 0.17 mol, 11%) colorless liquid of **4** (109 g, 0.88 mol, 59%) and colorless liquid of **5** (10 g, 0.08 mol, 5%).

*3.3.1. cis-4,5-Difluoro-1,3-dioxolan-2-one (**3**)*

Melting point DCl_3) δ 6.23 (*m*, 2H). ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 148.2 (*m*, 1C, C=O) 102.7 (dddd, 2C). ^{19}F NMR (188 MHz, $CDCl_3$) δ −148.1 (*m*, 2F). IR (neat): 3047, 1874, 1386, 13 18, 1095, 995. EIMS (probe) 70 eV, *m/z* (rel. int.) 124 $[M]^+$ (2) 76 (45) 61 (15) 48 (40) 32 (95) 29 (100). Anal Calcd. for $C_3H_2F_2O_3$: C, 29.05; H, 1.63. Found: C, 29.03; H, 1.61.

*3.3.2. trans-4,5-Difluoro-1,3-dioxolan-2-one (**4**)*

Melting point 7.8 °C. bp 128.7 °C. ^{1}HNMR (200 MHz, $CDCl_3$) δ 6.14 (*m*, 2H). ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 150.2 (tt, C=O) 105.9 (dddd, 2C). ^{19}F NMR (188 MHz, $CDCl_3$) δ −134.8 (*m*, 2F). IR (neat): 3040, 1861, 1392, 1365, 1172, 1094. EIMS (probe) 70 eV, *m/z* (rel. int.) 124 $[M]^+$ (5) 76 (80) 61 (20) 48 (48) 32 (95) 29 (100). Anal Calcd. for $C_3H_2F_2O_3$: C, 29.05; H, 1.63. Found: C, 29.00; H, 1.55.

*3.3.3. 4,4-Difluoro-1, 3-dioxolan-2-one (**5**)*

Melting point 3.2 °C. bp 134 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.68 (t, $J = 11.6$ Hz, 2H). ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 147.8 (t, C=O) 124.6 (tt, CF,) 70.6 (tt, CH_2). ^{19}F NMR (188 MHz, $CDCl_3$) δ −72.8 (t, $J = 11.6$ Hz, 2F). IR (neat): 3054, 3003, 1866, 1467, 1403, 1313, 1264, 1204, 1167, 1084, 958. EIMS (probe) 70 eV, *m/z* (rel. int.) 124 $[M]^+$ (3) 80 (95), 61 (15) 5 1 (30) 32 (95) 29 (100). Anal Calcd. for $C_3H_2F_2O_3$: C, 29.05; H, 1.63. Found: C, 29.01; H, 1.50.

*3.4. Synthesis of trifluoromethanesulfonyl fluoride (**7**)*

The compound **6** (50 g, 0.61 mol) and perfluoro-2-methylpenthane (500 g, 1.48 mol) were charged into a 1 l PFA vessel and stirred vigorously at 40 °C by passing N_2 (200 ml/min, 30 min). Fluorine gas, 30% mixture in nitrogen, was passed at a constant flow rate (200 ml/min, total 328 g (8.62 mol)) through a mixture of the substrate and the solvent. The substrate **6** was continuously added with a pump to the reaction mixture (total 250 g, 2.56 mol). The gaseous product, which came out of the vessel, was washed with water and trapped to a 500 ml SUS cylinder cooled by liquid nitrogen. The gaseous product was purified to give 303 g (1.99 mol, 64%) of **7**. GCMS analysis of **7** showed peaks corresponding to the parent minus CF_3, and other prominent peaks corresponding to CF_3^+, and SOF^+. The ^{19}F NMR spectra and the observed mass fragment pattern were superimposed to those in the literature [8]. Boiling point (bp) −25 °C. ^{19}F NMR δ −113.8 (t, 1F, SO_2F) 2.71 (d, $J = 17.9$ Hz, 3F, CF_3). EIMS (probe) 70 eV, *m/z* (rel. int.) 83 $[M\text{-}CF_3]^+$ (3) 69 $[CF_3]^+$ (100) 67 $[SOF]^+$ (13), 50 (3), 48 (4), 31 (3).

The upper layer (a mixture of **6**, **8**, and **9**) of reaction mixture was separated from perfluoro-2-methylpentane (lower layer) and washed with water (50 ml). The organic layer was dried over anhyd. $MgSO_4$. The crude products were purified by distillation affording colorless liquid of **8** (7 g, 0.05 mol, 2%), colorless liquid of **9** (24 g, 0.21 mol, 7%) and recovered **6** (65 g, 0.67 mol, 22%).

*3.4.1. Difluoromethanesulfonyl fluoride (**8**)*

Boiling point 52 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.53 (dt, $J = 3.5, 52.0$ Hz, 1H). ^{13}C NMR (50.28 MHz, $CDCl_3$) 112.1 (ddt). ^{19}F NMR (188 MHz, $CDCl_3$) δ 37.9 (dt,

$J_{HF} = 3.5$ Hz, $J_{FF} = 3.3$ Hz, 1F, SO_2F) −119.3 (dd, $J_{HF} = 52.0$ Hz, $J_{FF} = 3.3$ Hz, 2F, CHF_2). IR (neat): 3050, 1560, 1229, 1126. EIMS (probe) 70 eV, *m/z* (rel. int.) 83 [M-CHF_2]$^+$ (1) 67 [SOF]$^+$ (10), 64 (5) 51 [CMF_2]$^+$ (100). Anal Calcd. for CHF_3O_2S: C, 8.96; H, 0.75. Found: C, 8.78; H, 0.79.

3.4.2. Fluoromethanesulfonyl fluoride (9)

Boiling point 102 °C. ^{1}H NMR (200 MHz, $CDCl_3$) 6 5.49 (dd, $J = 7.0$, 46.0 Hz, 2H). ^{13}C NMR (50.28 MHz, $CDCl_3$) 87.8 (ddt). ^{19}F NMR (188 MHz, $CDCl_3$) δ 48.34 (td, $J_{HF} = 7.0$ Hz, $J_{FF} = 8.9$ Hz, 1F, SO_2F) −213.5 (td, $J_{HF} = 46.0$ Hz, $J_{FF} = 8.9$ Hz, 1F, CH_2F). IR (neat): 3032, 3031, 2968, 1456, 1211, 1090, 829. EIMS (probe) 70 eV *m/z* (rel. int.) 83 [M-CH_2F]$^+$ (1) 67 [SOF]$^+$ (26) 64 (10), 48 (10), 33 [CH_2F]$^+$ (100). Anal Calcd. for $CH_2F_2O_2S$: C, 10.35; H, 1.74. Found: C, 10.08; H, 1.99.

4. Conclusions

Fluoroethylene carbonate could be produced by a solvent-free direct fluorination of ethylene carbonate with elemental fluorine. Further fluorination of fluoroethylene carbonate gave difluoroethylene carbonates. The physical properties of these compounds were measured, and they would be expected for effective additives of lithium battery electrolyte.

Perfluorination of methanesulfonyl fluoride was carried out in perfluoro-2-methylpentane. The desired trifluoromethanesulfonyl fluoride was formed in reasonable yield. The partially fluorinated byproducts (fluoromethanesulfonyl fluoride and difluoromethanesulfonyl fluoride) could be recycled and used as the starting materials for the preparation of methanesulfonyl fluoride.

Acknowledgements

The authors thank to professor Jun Nishimura and Dr. Yosuke Nakamura in Gunma University for X-ray analysis. The authors also acknowledge to Dr. Tomoya Kitazume in Tokyo institute of Technology for elemental analysis.

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