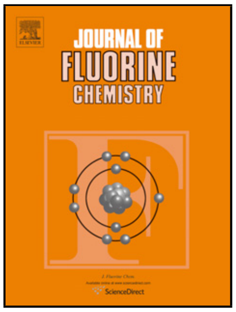

Title: Synthesis of $FSO_2CF_2CF_2OCF_2I$ from difluoro(fluorosulfonyl)acetyl fluoride and its relevant salt $FSO_2CF_2CF_2O^-K^+$ in the presence of I_2 or CF_2I_2

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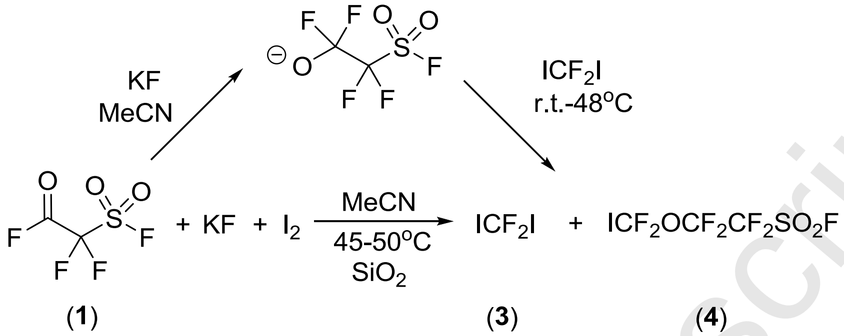
Graphical Abstract



Highlights

- The reaction of diiododifluoromethane with fluorinated alkoxide.
- The reaction of difluorocarbene with fluorinated alkoxide.
- The synthesis of fluorinated telomers.

Synthesis of $FSO_2CF_2CF_2OCF_2I$ from difluoro(fluorosulfonyl)acetyl fluoride and its relevant salt $FSO_2CF_2CF_2O^-K^+$ in the presence of I_2 or CF_2I_2.

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Abstract

The synthesis of $FSO_2CF_2CF_2OCF_2I$ via two routes was studied: the direct reaction between ICF_2I and $FSO_2CF_2CF_2O^-K^+$ and the reaction between $FSO_2CF_2CF_2O^-K^+$ and difluorocarbene generated from difluoro(fluorosulfonyl)acetyl fluoride in the presence of iodine.

Keywords: DFSAF, difluorodiiodomethane, perfluoroalkyl sulfonyl fluoride

1. Introduction

Difluoro(fluorosulfonyl)acetyl fluoride (FSO_2CF_2COF (**1**), DFSAF) under treatment of KF gives fluorosulfonyltetrafluoro potassium ethanolate $FSO_2CF_2CF_2O^-K^+$ (**5**) which reacts further with tetrafluoroethylene and iodine to give 2-(2-iodo-1,1,2,2-tetrafluoroethoxy)-1,1,2,2-tetrafluoroethanesulfonyl fluoride $FSO_2CF_2CF_2OCF_2CF_2I$ (**2**). This compound can be converted into higher telomers possessing iodo and fluorosulfonyl as terminal groups by radical addition of **2** to TFE or C_3F_6 [1].

DFSAF can serve also as a source of difluorocarbene. In the presence of catalytic amounts of SiO_2, (**1**) reacts with potassium iodide and iodine to give difluorodiiodomethane (**3**) in 60-70% yield [2]. The modification of that procedure by us resulted in a mixture of

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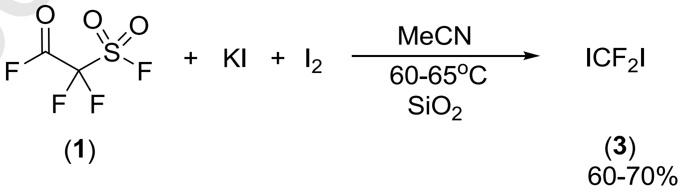
ICF_2I (**3**) and $FSO_2CF_2CF_2OCF_2I$ (**4**) in a ratio 2.6:1. The formation of **4** in a reaction conditions can be explained by reaction of $FSO_2CF_2CF_2O^-K^+$ (**5**) with $:CF_2$ generated from **1** followed by the reaction with iodine. 2-(Difluoro-iodo-methoxy)-1,1,2,2-tetrafluoro-ethane sulfonyl fluoride (**4**) is an interesting monomer which formation in low yields was previously revealed during the reaction of tetrafluoroethane-β-sultone with TFE and ICl in the presence of KF [3].

Considering other possibilities of $FSO_2CF_2CF_2OCF_2I$ (**4**) formation we decided also to study the direct reaction of difluorodiiodomethane (**3**) with $FSO_2CF_2CF_2O^-K^+$ (**5**). Similar reactions of ICF_2I with ethoxide, phenoxide and thiophenoxide ions were reported. However only with phenoxide and thiophenoxide ions corresponding aryldifluoroiodoethers and thioeters were obtained in low yields [4]. In the case of ethoxide ion as main products carbonate (EtOCOOEt) and fluoride ion were obtained. Such reactions occur via anionic chain mechanism (with evolution of difluorocarbene) or via single electron transfer [4].

Here we report the results of our studies on the reaction between $FSO_2CF_2CF_2O^-K^+$ (**5**) and $:CF_2$ generated from **1** in the presence of iodine and on the direct reaction of difluorodiiodomethane (**3**) with $FSO_2CF_2CF_2O^-K^+$ (**5**).

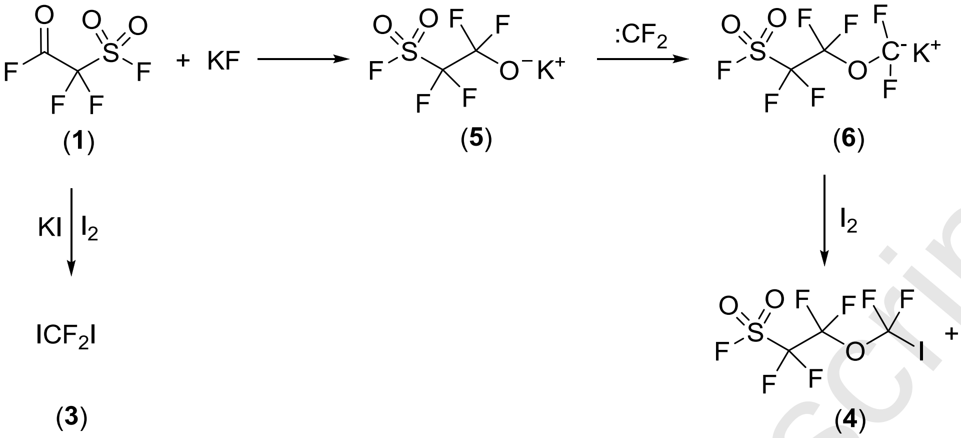
2. Results and discussion

It was reported by Xiao that formation of ICF_2I requires the following conditions: ratio $KI:I_2$ equal 1:1, the presence of SiO_2 used in amounts of 5-10 mol% and the concentration of I_3^- in a range 1.3-1.5 mol/l. The authors claimed also that formation of ICF_2I is inhibited in the absence of KI or if less than 1 eq. of KI was used (Scheme 1).



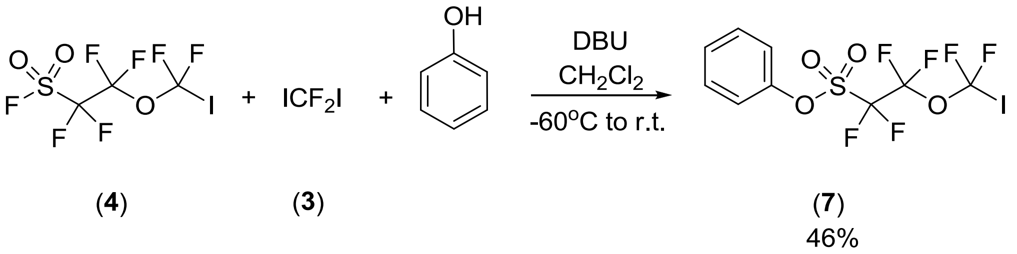
Scheme 1

Reproducing of that procedure we discovered that decreasing temperature to 40-50°C and adding DFSAF (**1**) relatively fast under reduced pressure led to a mixture of ICF_2I (**3**) and $FSO_2CF_2CF_2OCF_2I$ (**4**) in a 2.6:1 ratio. We suppose that **4** was formed via the following pathway: first in a reaction between fluoride ion and DFSAF, the $FSO_2CF_2CF_2O^-K^+$ (**5**) is generated, which further reacts with :CF_2 and then with iodine to give compound **4** (Scheme 2).



Scheme 2

Initial attempts to separate the mixture of **3** and **4** by distillation were not successful implying similar physical properties and structures of both compounds. Compound $FSO_2CF_2CF_2OCF_2CF_2I$ (**2**), with a boiling point 127°C [1] let us presume that **4** ought to have a boiling point between 127 and 95°C, whereas CF_2I_2 boils at 101°C. ICF_2I can be isolated with minor losses by washing the mixture of both compounds with 5% solution of NaOH in methanol at 0-10°C. The structure of compound **4** was confirmed not only by ^{19}F NMR, but also by GC-MS. No molecular ion was found, but peaks corresponding to $FSO_2CF_2CF_2OCF_2$, ICF_2O, ICF_2, FSO_2, FSO_2CF_2, OCF_2 fragments were observed. In the ^{13}C NMR spectrum of the sample of both compounds (**4** : **3** in a 5:1 ratio), beside a signal of ICF_2I at 1.6 ppm (t, *J* = 377 Hz) [lit. 2.29 ppm, t, *J* = 378 Hz], we observed a triplet at 74.95 ppm (*J* = 343 Hz), which we assigned to the OCF_2I group and two signals: at 114.06 ppm (ttd, *J* = 293 Hz, *J* = 30 Hz, *J* = 2Hz) due to $FSO_2CF_2\underline{C}F_2O$ and at 112.47 ppm (tq, *J* = 303 Hz, *J* = 39 Hz) due to the $FSO_2\underline{C}F_2CF_2$ group. Additionally, the sample of compounds (**4** : **3** in a 5:1 ratio) was treated with phenol in the presence of DBU and the product $PhOSO_2CF_2CF_2OCF_2I$ (**7**) was isolated after column chromatography in 46% yield (Scheme 3).



Scheme 3

In a further investigation we decided to prove if compound **4** can be obtained exclusively if the external source of fluoride ion, namely KF will be applied. The reactions were conducted only in the presence of iodine without KI aiming to inhibit the formation of ICF_2I, however it should be taken into account that KI is generated *in situ* during reaction between iodine and $FSO_2CF_2CF_2OCF_2^-K^+$ (**6**) and probably the formation of ICF_2I can be only limited but not excluded. The results are summarized in Table 1. The yields of **4** were estimated by NMR spectroscopy. In all cases the mixture of ICF_2I (**3**) and $FSO_2CF_2CF_2OCF_2I$ (**4**) was obtained. The yields of compound **4** were rather low and did not exceed 40%, what can be explained by competition between two reactions: reaction of $:CF_2$ with KI_3 leading to ICF_2I (**3**) and the reaction of $:CF_2$ with $FSO_2CF_2CF_2O^-K^+$ (**5**) leading to **4**.

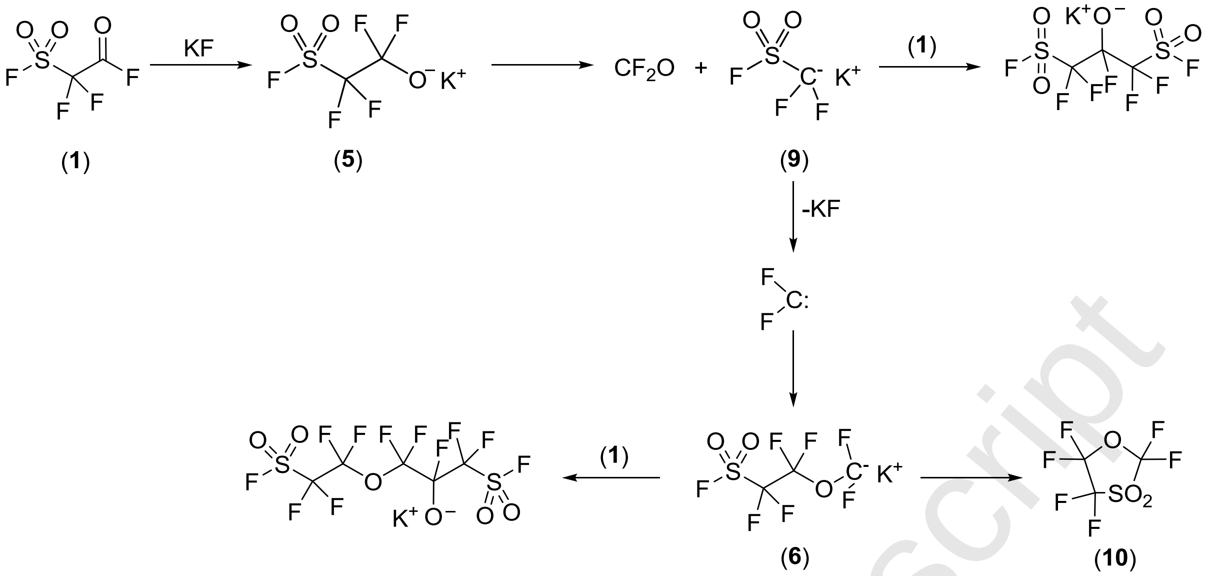
Table 1

Synthesis of **4** from DFSAF in a presence of KF and I_2

No	**DFSAF**[a]	**KF**	**I_2**	**SiO_2**[d] **(mol%)**	**Ratio of products**[b]			**Yield**[c] **[%]**
					ICF_2I (3)	**ICF_2SO_2F (8)**	**$ICF_2OCF_2CF_2SO_2F$ (4)**	
1	1.95	1	1.0	4	12	1	4	12
2	4	1	1.0	2	9	1	7	35
3	2	1	0.66	1.8	23	1	32	**42(28)**[f]
4	2	1	1	2.2	24	1	15	25[e]

[a] all reactions were carried out in ampoule in MeCN at 45-50^{0}C during 21-23h; [b] after work up procedure (the mixture was poured into water and the bottom phase was collected); [c] NMR yield of **4** based on amount of I_2 used; [d] counted on amount of DFSAF; [e] two days of stirring at 45^{0}C; [f] NMR yield of **4** based on amount of KF used.

It is known that $FSO_2CF_2CF_2O^-K^+$ (**5**) is not stable [5] and in 50-60^{0}C in diglyme undergoes fragmentation to give $FSO_2CF_2^-K^+$ (**9**) which decomposes further to difluorocarbene (Scheme 4). Decomposition of **5** during prolonged heating was the reason why an excess of **1** was required and lower temperature (45-50^{0}C) was applied. Acetonitrile was used as a reaction medium because the increased stability of **5** in that solvent was reported [6].



Scheme 4

Our attempts to obtain compound **4** via decomposition of **5** in a presence of iodine were not successful.

The reaction between ICF_2I (**3**) and $FSO_2CF_2CF_2O^-K^+$ (**5**) was also investigated. An initial experiment conducted with a reagent **3** : **5** ratio of 1:1 at 48^{0}C gave a mixture of ICF_2I (**3**) and $FSO_2CF_2CF_2OCF_2I$ (**4**) in a ratio 1.1:1. The NMR yield of **4** was estimated for 42%. When the progress of the reaction of **5** : **3** in a 1.2:1 ratio was followed by ^{19}F NMR, it was found that reactions start immediately at room temperature, resulting in a mixture of products **3** : **4** (1:1.8) after 1 day at 45°C. Further progress of the reaction was not observed, what let us to conclusion that **5** decomposes slowly and an excess of this reagent is required to reach higher conversion.

It was proven that the application of an excess of **5** resulted not only in an advantageous ratio of products **4** : **3** (6:1) but also increased amount of by-products from decomposition of **5**, however most of them were easily washed off with water. The main signals can be assigned to sulfone **10** (5% in a reaction mixture after work-up). It seems interesting that the intermediary carbanion $FSO_2CF_2CF_2OCF_2^-$ (**6**) (see Scheme 4) formed during decomposition of $FSO_2CF_2CF_2O^-K^+$ (**5**) did not react with ICF_2I. Similar reactions of carbanions with CF_2Br_2 were reported [7].

Application of excess of **5** resulted also in a product of double substitution $CF_2(OCF_2CF_2SO_2F)_2$ (**11**). Compound **11** was previously synthesized by electrochemical fluorination of the corresponding disulfonyl fluoride [8]. In the ^{19}F NMR spectrum of the reaction mixture (see entry 5, Table 2) a signal at -46.58 ppm was observed which was assigned to the OCF_2O group of compound **11** (2.4% in reaction mixture after work-up).

The results of the reaction between $FSO_2CF_2CF_2O^-K^+$ (**5**) and ICF_2I (**3**) are summarized in Table 2. The yields of **4** were estimated by NMR spectroscopy. In all cases complete conversion was not reached and ICF_2I was always present in the reaction mixtures.

Table 2

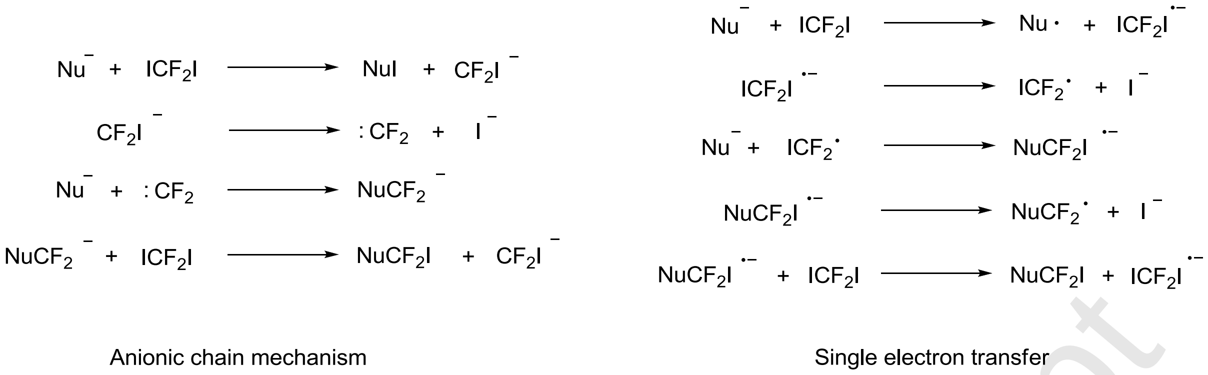
Results of reaction between $FSO_2CF_2CF_2O^-K^+$ (pre-generated) and ICF_2I

No	DFSAF[a]	KF	ICF_2I	Temp.[C]	Time [h]	Ratio of products[b]		Yield (4) [%][b,c]
						$ICF_2OCF_2CF_2SO_2F$ (4)	ICF_2I (3)	
1	1	1	1	48	23.5	1.1	1	42
2	1.6	1.5	1	45	48	5.5	1	55
3	1.4	1.18	1	r.t	26	1.2	1	48
4	3.4	3.2	1	35-37	23	3.2	1	51
5	4.6	4.1	1	35-37, 45[d]	48	6	1	**67**[b,c]

[a] all reactions were carried out in MeCN in ampoule; [b] after work up procedure (the mixture was poured into water and the bottom phase was collected) ; [c] NMR yield based on amount of ICF_2I used.; [d] 1 day at 35-37^{0}C, 1 day at 45^{0}C;

It was found that, application of a longer reaction time or four-fold excess of $FSO_2CF_2CF_2O^-K^+$ (**5**) lead to an optimal yield and ratio of ICF_2I (**3**) : $ICF_2OCF_2CF_2SO_2F$ (**4**) (entry 5, Table 2). However similar result can be obtained using 1.4 fold excess of **5** and conducting the reaction at room temperature (entry 3, Table 2), what can be explained by slower decomposition of **5** in that temperature. Once the reaction is completed the product can be isolated by phase separation after addition of water. Having in mind that **4** cannot be separated from **3** by distillation, the crude mixture of both compounds (entry 5, Table 2) was treated with PhOH in a presence of DBU and gave after column chromatography $PhOSO_2CF_2CF_2OCF_2I$ (**7**) in 30% yield.

The yields of **4** (42-67%) obtained in the direct reaction between ICF_2I (**3**) and $FSO_2CF_2CF_2O^-K^+$ (**5**) were higher than yields of **4** (12-35%) obtained in the reaction between $FSO_2CF_2CF_2O^-K^+$ (**5**) and $:CF_2$ generated from **1**. In the case of ICF_2I (**3**) and $FSO_2CF_2CF_2O^-K^+$ (**5**), two pathways can occur via anionic chain mechanism (with evolution of difluorocarbene) or via single electron transfer (Scheme 5).



Scheme 5

It was never proven which mechanism is more favoured during the reaction between ICF_2I (**3**) and nucleophiles like phenoxide or thiopenoxide ions [4]. According to our knowledge the reaction of such nucleophile like $FSO_2CF_2CF_2O^-K^+$ (**5**) with compounds type CF_2X_2 (X = Cl, Br, I) was not reported previously.

3. Experimental

Boiling points were measured during distillation; both are uncorrected. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded with JEOL ECX 400 spectrometer, in $CDCl_3$ or CD_3CN solutions. Chemical shifts are quoted in ppm from internal TMS for ^{1}H and from internal $CFCl_3$ for ^{19}F nuclei. GC-MS analyzes were performed with a Varian Saturn 2100T apparatus (30 m, capillary column, VF-5ms). Difluoro(fluorosulfonyl)acetyl fluoride was donated us by DUPONT. ICF_2I was prepared according known procedures [2, 9].

*3.1. General procedure for the reaction between ICF_2I (**3**) and $FSO_2CF_2CF_2O^-K^+$ (**5**)*

In a glass ampoule 5.01 g (0.086 mol) of dry KF and 1.8 ml of dry MeCN were placed, than 17.7 g (0.098 mol) of FSO_2CF_2COF was condensed into it. The content of ampoule was stirred 2 h at room temperature, than the ampoule was cooled down to -30^{0}C, opened under nitrogen, than 6.64 g (0.021 mol) of ICF_2I and 60 ml of dry acetonitrile was added into it. The reaction mixture was stirred 24 h in 35-37^{0}C and 24 h in 45^{0}C. After that time the ampoule was opened and analyzed by NMR spectroscopy, than the content of ampoule was poured into water. The bottom organic phase (7.58 g) was collected, dried over sodium sulfate and analyzed by NMR with BTF as standard, proving the presence of ICF_2I (**3**) and $ICF_2OCF_2CF_2SO_2F$ (**4**) in a ratio 1:6. The NMR yield of **4** was 67%. In the collected organic phase beside signals of compound **3** and **4**, three minor signals from compound **10** were observed (5%) and signals of compound **11** (2.4 %).

Difluorodiiodomethane (**3**):

^{19}F NMR (CD_3CN) δ: 17.76 (s, 2F), ^{13}C NMR ($CDCl_3$) δ: 1.6 (t, *J* = 377 Hz); GC-MS: m/z: 304 $(M)^+$; 177 $(ICF_2)^+$;

2-(Difluoro-iodo-methoxy)-1,1,2,2-tetrafluoro-ethane sulfonyl fluoride (**4**):

^{19}F NMR (CD_3CN) δ: 44.7 (m, 1F, SO_2F), -10.3 (m, 2F, $OC\underline{F}_2I$), -83.1 (m, 2F, $OC\underline{F}_2CF_2$), -113.1 (m, 2F, $CF_2C\underline{F}_2SO_2F$); ^{13}C NMR ($CDCl_3$) δ: 74.95 (*J* = 343 Hz, $O\underline{C}F_2I$); 114.06 (ttd, *J* = 293 Hz, *J* = 30 Hz, *J* = 2Hz, $FSO_2CF_2\underline{C}F_2$); 112.47 (tq, *J* = 303 Hz, *J* = 39 Hz, $FSO_2\underline{C}F_2CF_2$); GC-MS: m/z: 249 $(M-I)^+$; 193 $(ICF_2O)^+$; 183 $(FSO_2CF_2CF_2)^+$; 177 $(ICF_2)^+$; 133 $(FSO_2CF_2)^+$, 119 $(C_2F_5)^+$; 100 $(C_2F_4)^+$; 83 $(FSO_2)^+$; 67 $(CF_2O)^+$;

2,2,4,4,5,5-Hexafluoro-[1,3]-oxathiolane-3,3-dioxide (**10**):

^{19}F NMR (CD_3CN) δ: -75.41 (m, 2F), -82.92 (m, 2F), -119.22 (m, 2F);

2-[Difluoro-(1,1,2,2-tetrafluoro-2-fluorosulfonyl-ethoxy)-methoxy]-1,1,2,2-tetrafluoro-ethane sulfonyl fluoride (**11**):

^{19}F NMR (CD_3CN) δ: 44.7 (m, 2F, SO_2F); -46.58 (m, 2F, $OC\underline{F}_2O$); -83.1 (m, 4F, $OC\underline{F}_2CF_2$); -113.1 (m, 4F, $CF_2C\underline{F}_2SO_2F$);

3.2. Synthesis of 2-(Difluoro-iodo-methoxy)-1,1,2,2-tetrafluoro-ethane-sulfonic acid phenyl ester $PhOSO_2CF_2CF_2OCF_2I$ (7):

In a glass ampoule 4.86 g (0.083 mol) of dry KF and 1.8 ml of dry MeCN were placed, than 17.9 g (0.099 mol) of FSO_2CF_2COF was condensed into it. The content of ampoule was stirred 2 h at room temperature, than the ampoule was cooled down to -30^{0}C, opened under nitrogen, than 6.66 g (0.021 mol) of ICF_2I and 60 ml of dry acetonitrile was added into it. The reaction mixture was stirred 48 h in 45^{0}C. After that time the ampoule was opened and analyzed by NMR spectroscopy, than the content of ampoule was poured into water. The bottom organic phase (8.41 g) was collected, dried over sodium sulfate and analyzed by NMR with BTF as standard, proving the presence of ICF_2I (**3**) and $ICF_2OCF_2CF_2SO_2F$ (**4**) in a ratio 1:5. In the collected organic phase beside signals of compound **3** and **4**, three minor signals from compound **10** were observed (9.5%) and signals of compound **11** (3.5 %).

In a flask under nitrogen 2.19 g (0.023 mol) of phenol, 6.07 g (0.039 mol) of DBU and 25 ml of dry CH_2Cl_2 were placed. The flask was cooled down to -60^{0}C and the mixture (8.41 g) of compounds **3** : **4** in a ratio 1:5 was added into it. The flask was slowly warm up to the room temperature and the content of it was stirred 2 h at that temperature. After that time, reaction mixture was poured into water. The organic phase was washed twice by water and dried over sodium sulfate. The solvent was removed at rotary evaporator and the residue (4.93 g) was purified by column chromatography to give compound **7** in 30% (3.02 g) yield.

2-(Difluoro-iodo-methoxy)-1,1,2,2-tetrafluoro-ethane-sulfonic acid phenyl ester (**7**):

Yellowish liquid. ^{19}F NMR ($CDCl_3$) δ: -8.32 (t, J = 11.56 Hz, 2F); -81.74 (t, J = 11.56 Hz, 2F); -112.7 (m, 2F); ^{13}C NMR ($CDCl_3$) δ: 75.26 (t, J = 341.9 Hz, $O\underline{C}F_2I$); 112.87 (tt, J = 300.55 Hz, J = 37.6 Hz, $O\underline{C}F_2CF_2$); 114.65 (tt, J = 290.92 Hz, J = 29.9 Hz, $OCF_2\underline{C}F_2SO_2$); 121.51 (C-2, Ph); 128.38 (C-4, Ph); 130.31 (C-3, Ph); 149.95 (C-1, Ph); ^{1}H NMR ($CDCl_3$) δ: 7.28-7.32 (m, 2H), 7.38-7.49 (m, 3H);

*3.3. General procedure for the reaction between $FSO_2CF_2CF_2O^-K^+$ (**5**) and :CF_2 generated from FSO_2CF_2COF (**1**):*

In a glass ampoule 4.05 g (0.069 mol) of dry KF and 11.7 g (0.046 mol) of I_2, 0.15 g (0.0025 mol) of SiO_2, 40 ml of dry MeCN were placed, than 25.5 g (0.141 mol) of FSO_2CF_2COF was condensed into it. The content of ampoule was stirred 21-23 h in 45-50°C. After that time the reaction mixture was poured into water. The bottom organic phase (13.87 g) was collected, dried over sodium sulfate and analyzed by NMR with BTF as standard, proving the presence of ICF_2I (**3**) and $ICF_2OCF_2CF_2SO_2F$ (**4**) and ICF_2SO_2F (**8**) in a ratio: 23: 32: 1. The NMR yield of **4** was 28.3% (based on the amount of KF used).

Difluorodiiodomethane (**3**): ^{19}F NMR ($CDCl_3$) δ: 19.2 (s, 2F);

2-(Difluoro-iodo-methoxy)-1,1,2,2-tetrafluoro-ethane sulfonyl fluoride (**4**): ^{19}F NMR ($CDCl_3$) δ: 46.00 (s, 1F); -8.85 (m, 2F); -82.04 (m, 2F); -111.91 (m, 2F);

Difluoro-iodo-methane-sulfonyl fluoride (**8**): ^{19}F NMR ($CDCl_3$) δ: 26.0 (m, 1F); -50.4 (m, 2F); GC-MS: m/z: 260 $(M)^+$; 177 $(ICF_2)^+$; 67 $(CF_2O)^+$; 48 $(SO)^+$;

4. Acknowledgment

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