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Reactions of 1,3,5-tris(fluorosulfonyl)benzene with some nucleophilic reagents

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ABSTRACT

The reactions of 1,3,5-tris(fluorosulfonyl)benzene 1 with nucleophilic agents were investigated. It was found that morpholine, β,β,β-trifluoroethanol in the presence of triethylamine and sodium azide formed corresponding 1,3,5-trisulfonyl derivatives. In contrast, nucleophiles such as aniline, thiourea, and potassium thiocyanate do not react with compound **1** even in excess and under moderate heating. The conditions for the selective fluorine atom substitution in one SO_2F group with morpholine, DMAP and aniline in the presence of triethylamine as well as in two SO_2F groups with DMAP were found. Anionic σ-complex of compound **1** with nitromethane was isolated as individual compound.

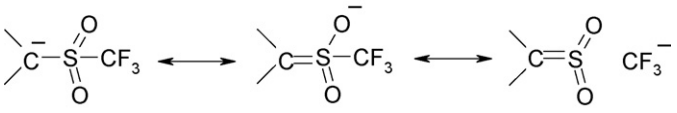
1. Introduction

The subject of our investigation is 1,3,5-tris(fluorosulfonyl)-benzene **1**. Recently [1] we have shown that compound **1** is able to undergo nucleophilic addition at free position on the aromatic ring with the formation of anionic σ-complexes. However, these reactions often proceed ambiguously and products of fluorine substitution in SO_2F groups appear. Thus, taking into account that compound **1** has at least two different reaction centers for a nucleophilic attack—the fluorosulfonyl group and a free position of the aromatic ring—we performed a detailed investigation of compound's **1** reactivity with various nucleophilic agents.

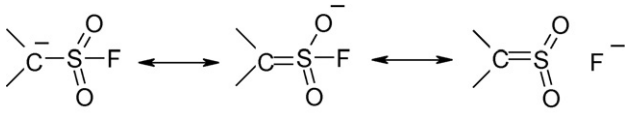
It should be noted that the reaction ability of aromatic sulfonic acid fluorides towards nucleophilic agents is quite weak. These compounds are essentially resistant to heating in weak alkaline aqueous and organo-aqueous mediums [2] and can be distilled with a steam. For example, during the fluorination of *p*-acetylaminobenzene sulfonyl chloride by aqueous KF (135–140 °C), apart from the formation of the corresponding fluorosulfonyl derivative, hydrolysis of the acetyl group was observed. The formed fluorosulfonyl group was stable under these conditions [3]. Hydrolysis of benzene sulfonic acid fluoride proceeded ~5000 times slower than that of benzene sulfonic acid chloride [4]. The reactions of *p*-substituted phenyl sulfonyl fluorides with benzyl amines were significantly slower than those of analogous aryl sulfonyl chlorides [5].

Moreover, the SO_2F group is known to be a strong electron-withdrawing substituent. Its σ_p values (0.91–1.54 defined by various methods [6]) are almost identical to that of the SO_2CF_3 group (0.91–1.63 [6]). According to this fact, compound **1** can be considered as an analog of 1,3,5-tris(trifluoromethylsulfonyl)benzene (sulfone **2**) [7].

Such a comparison may be quite appropriate in the context of the recognition of electron-withdrawing nature of sulfonyl groups. This question is intensively discussed until present time [8]. For example, delocalization of the negative charge in molecules containing SO_2CF_3 groups is represented as follows:



In molecules containing SO_2F groups, similar resonance structures can be drawn:



Taking into account the resonance structures presented above, it may be expected that the ^{19}F NMR chemical shift of the fluorine

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atom, directly connected with a sulfonyl electrophilic center, must be sensitive to the electronic environment and structure differences of the molecule's core.

There were only two reports on the synthesis of 1,3,5-tris(fluorosulfonyl)benzene **1** [2a,9]. Both of them were based on the substitution of the chlorine atom in a deficient 1,3,5-tris(chlorosulfonyl)benzene. Additionally, the yields of **1** were rather low (46–50%). That is why chemical properties of sulfonyl fluoride **1** were almost uninvestigated before our work. It was only known that in the reaction with KF at 200–210 °C one or two SO_2F groups can be substituted by the fluorine atom [9].

Recently a new method of synthesis of compound **1** was proposed based on the reduction of 2,4,6-tris(fluorosulfonyl)-chlorobenzene with Zn [10].

2. Results and discussion

It was found that sulfonyl fluoride **1** exhibits a versatile reactivity in reactions with nucleophilic agents. With morpholine, triethylammonium-, and 4-dimethylaminopyridinium β,β,β-trifluoroethoxide, or even with such moderate nucleophile as sodium azide, exclusive fluoride substitution in all SO_2F groups occurs yielding the corresponding trisulfonyl derivatives **3**–**5**. Other reagents such as aniline, thiourea, and potassium thiocyanate do not react with compound **1** at all even in excess and under moderate heating (Scheme 1).

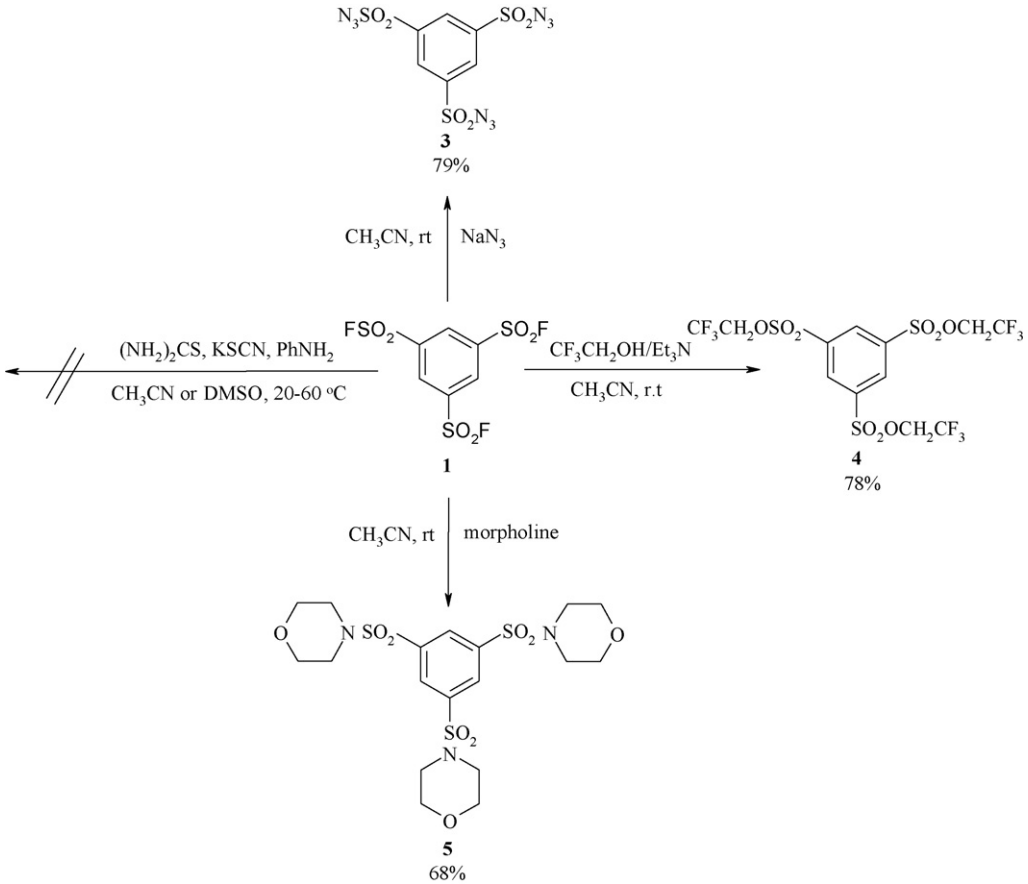
To realize selective fluorine substitution in one or two fluorosulfonyl groups seems to be rather difficult. The reaction of compound **1** with morpholine and sodium azide in acetonitrile even at low temperature (−60 °C) and equimolar amount of the reagent affords a mixture of mono-, di-, and tri-substituted sulfonyl derivatives. The same result is obtained in the reactions with $CF_3CH_2O^-$, despite changes in reaction conditions such as variation of solvent (diethyl ether, benzene, acetonitrile, benzene/acetonitrile), temperature (from −10 to 35 °C) and methods of $CF_3CH_2O^-$ generation (CF_3CH_2OH/Et_3N, CF_3CH_2ONa, CF_3CH_2O-$SiMe_3/CsF$ or $CF_3CH_2OSiMe_3/Me_4NF$). It is found that the reaction begins at 8–10 °C but even slow addition of any source of $CF_3CH_2O^-$ at this temperature does not improve the selectivity. The reaction of compound **1** with two equivalents of CF_3CH_2O results in the formation of 1,3,5-tris(trifluoroethoxysulfonyl)benzene **4** as the major product.

Nevertheless, we found reaction conditions for the selective fluorine substitution for some nucleophiles. For example, the reaction of compound **1** proceeds rather selectively with morpholine in THF or DME at 30–35 °C. The gradual addition of this nucleophile (2 eq.) to the sulfonyl fluoride **1** leads to the formation of mono-sulfonyl morpholide **6** with a minor quantity of disubstituted product **7** (Scheme 2).

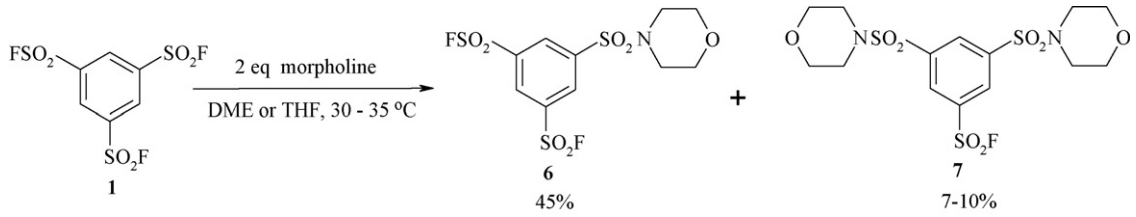
As mentioned above, aniline does not react with compound **1** even in excess and under moderate heating. But we found that this reaction is possible when triethylamine is used as a base. Dropwise addition of an equimolar mixture of aniline and triethylamine into the diluted solution of sulfonyl fluoride **1** in acetonitrile provides the sulfonic acid anilide **8** (Scheme 3).

A base was also required in the reaction of aniline with 1,3,5-trinitrobenzene [11]. But as far as compound **1** is activated by electron-withdrawing groups, which are stronger then NO_2 and possess several reaction centers, we expected reactions with aniline even in the absence of a base as it occurs in the case of 4,6-dinitrobenzofuroxan [12].

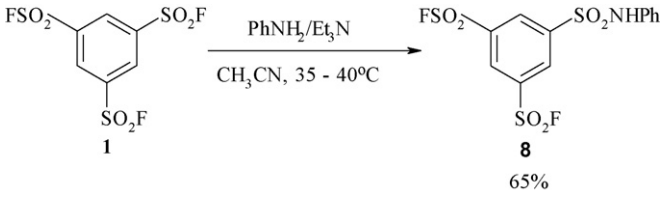
Interestingly, the sulfonyl pyridinium derivative **9** is formed when compound **1** is reacted with aniline in the presence of DMAP instead of Et_3N. Application of two or more equivalents of DMAP



Scheme 1.



Scheme 2.



Scheme 3.

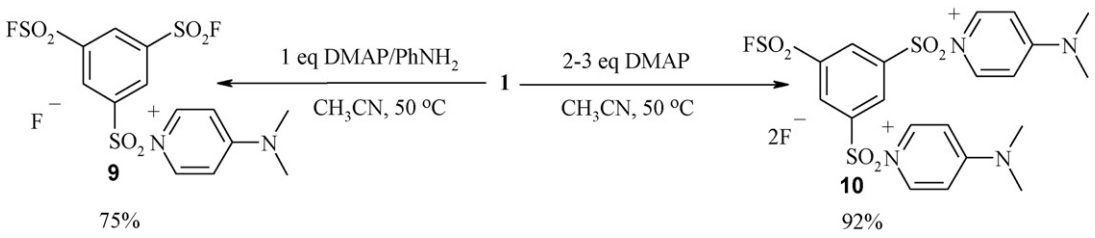
leads to the formation of the disulfonyl pyridinium derivative **10** (Scheme 4).

Thus, depending on the reaction conditions and type of nucleophilic agent it is possible to prepare products of mono-, di- or tri-substitution of fluorine in compound **1**.

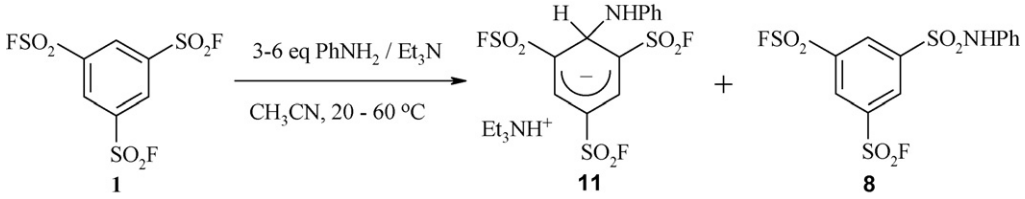
An unexpected result is observed when an excess of $PhNH_2$ and Et_3N (3–6 eq.) is used. Instead of the estimated tri-substituted product an anionic σ-complex **11** is formed in addition to compound **8** either at 20–25 °C or under moderate heating (Scheme 5). The molar ratio of compounds **11**, **8** and **1** in the reaction mixture is 4.5:1:1.5. The adduct **11** is stable up to 60 °C.

As it was mentioned above, trisulfonic acid trifluoride **1** can add nucleophilic reagents to an unsubstituted position in the aromatic ring forming the anionic σ-complexes **12**–**17** (Scheme 6) [1].

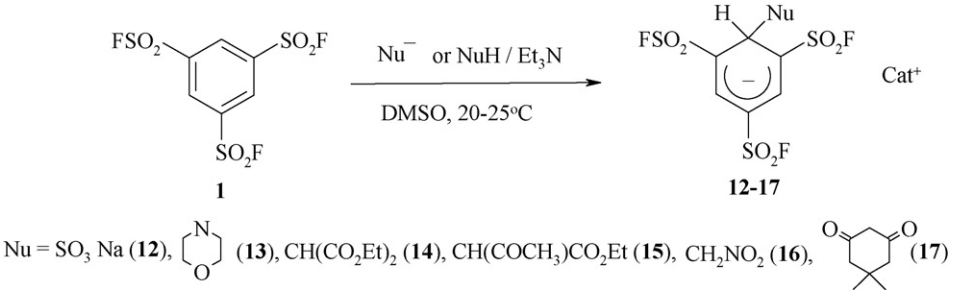
These adducts exhibit different stabilities. The ^{19}F NMR signals of the anionic σ-complex **15** can be detected only within the first 15 min, besides of signals of the fluorine substitution products. In contrast, the corresponding adducts with sodium sulfite **12**, malonic ester **14** and dimedone **17** are stable in DMSO solution for 7–8 days. Despite the stability of these σ-complexes in solution we were not able to isolate them. Therefore, we tried to obtain them in other polar solvents like DMF, acetonitrile, dioxane, and acetone. It was possible to prepare these adducts in DMF but isolation was also quite difficult. In other solvents the ^{19}F NMR signals of the variety of substitution products are seen immediately after mixing of the reagents. Later we found out that it is possible to obtain anionic σ-complex with nitromethane in DME and THF (Scheme 7).



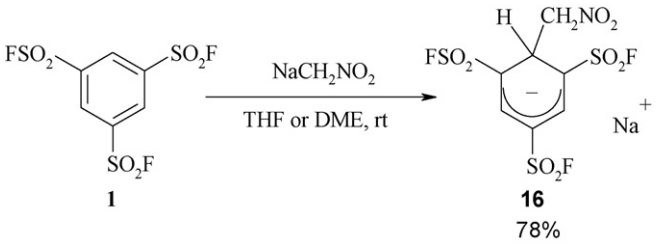
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

Triethylamine has been used as a base in the synthesis of all adducts mentioned above except **12** and **13**. However, using a sodium salt of nitromethane for the preparation of σ-complex **16** provides this adduct more selectively making its isolation possible as an individual compound. Compound **16** is a yellow solid soluble in polar organic solvents. Under anhydrous conditions it can be stored for a long time. In the presence of mineral acids **16** transforms into the initial compound **1**.

During the investigation of anionic σ-complexes **12–17** we observed an interesting phenomenon. As it was shown earlier [13], the negative charge of the associated nucleophilic agent is displaced into the aromatic rings of the initial compounds. That is why in the NMR spectra both the signals of the aromatic protons in all anionic σ-complexes and of the fluorine atoms of the adducts of sulfones **2** [7a–c] are shifted to higher field as compared to their positions in the NMR spectra of the initial compounds. Similar high field shifts are also observed for the proton resonances of the σ-complexes **12–17** [1]. In contrast, their ^{19}F NMR signals appear downfield (Fig. 1). However, there is no clear regularity.

For example, the signals of all SO_2F groups of adducts **12–15** are shifted downfield. At that, in complexes **14** and **15** the signals of these groups in the *ortho*- and *para*-positions coincide. In case of compounds **16** and **17** the signals of *p*-SO_2F groups are shifted downfield while the signals of *o*-SO_2F groups are shifted high field. Furthermore, in the spectra of complex with dimedone **17** *o*-SO_2F groups exhibit two different resonances. Probably this can be referred to the presence of the bulky dimedone moiety in the geminal position of σ-complex **17**, which makes the *o*-SO_2F groups nonequivalent.

Thus, the position of the resonance signals in ^{19}F NMR spectra found for of **12–17** can not be simply correlated with changes of the atomic charges and have a more complex nature. Consequently,

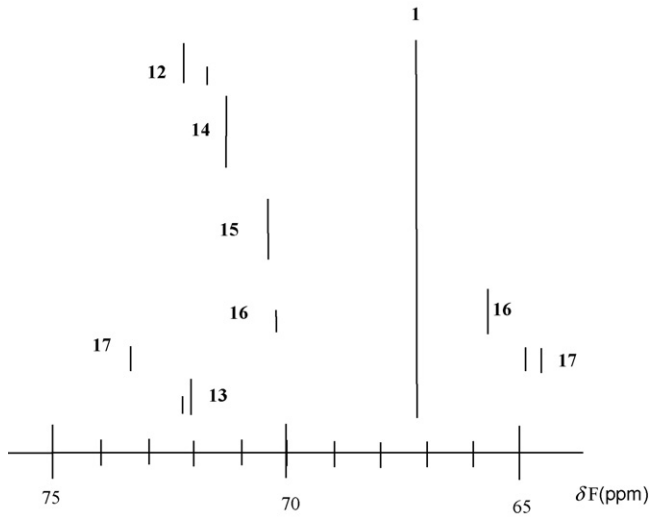


Fig. 1. The position of the ^{19}F NMR signals of adducts **12–17** relative to compound **1**.

the molecular and electronic structure of the corresponding anionic σ-complexes are of great interest and deserve to be investigated in detail by computational methods.

3. Conclusions

Depending on the reaction conditions and the type of the nucleophile the reactions of 1,3,5-tris(fluorosulfonyl)benzene **1** with various nucleophilic agents can proceed both at the sulfonyl centre yielding products of complete or partial substitution of fluorine atoms and/or anionic σ-complexes as a result of the nucleophilic addition at a free position of the aromatic ring.

4. Experimental

All reactions were carried out in a dry argon atmosphere by using Schlenk techniques. 2,2,2-Trifluoroethoxytrimethylsilane was synthesized according to literature procedure [14]. Sodium salt of nitromethane was obtained by the reaction of nitromethane with sodium hydride. All solvents were purified according to literature procedures [15]. ^{1}H, ^{19}F, ^{13}C NMR spectra were recorded in DMSO-d_6 as a solvent using Varian VXR-300 (299.95 MHz), Varian Gemini-200 (188.14 MHz), and Bruker Avance DRX-500 (125.77 MHz) spectrometers, respectively. Chemical shifts are given in ppm. Tetramethylsilane (^{1}H NMR: δ = 0.00 ppm; ^{13}C NMR: δ = 0.00 ppm) and CCl_3F (^{19}F NMR: δ = 0.00 ppm) were used as internal standards for ^{1}H, ^{13}C, and ^{19}F NMR spectra. Melting points were determined on the electro-thermal apparatus and are uncorrected. Elemental analysis was carried out in the Analytical Laboratory of the Institute of Organic Chemistry, NAS of Ukraine, Kyiv.

4.1. General procedure for the preparation of tris-sulfonyl derivatives (3–5)

To a stirred solution of 1,3,5-tris(fluorosulfonyl)benzene **1** (0.1 g, 0.31 mmol) in acetonitrile (5 ml) the excess of corresponding nucleophile was added. The mixture was stirred at 20–25 °C for 6 h. The product formation was monitored by ^{19}F NMR spectra. All products were crystallized from benzene.

4.1.1. 1,3,5-Tris(azidosulfonyl)benzene (3)

The best results were obtained when sodium azide (0.06 g, 0.92 mmol) is used.

White solid: 79% yield; mp., 134–135 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 8.9 (H, s, Ar). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 131.69 (s, Ar), 140.97 (s, Ar). Anal. Calcd. for $C_6H_3N_9O_6S_3$: C 17.5; H 1.2; N 30.6. Found: C 17.22; H 1.5; N 31.3.

4.1.2. 1,3,5-Tris(β,β,β-trifluoroethoxysulfonyl)benzene (4)

The best results are obtained when CF_3CH_2OH (1 mmol) and DMAP (0.9 mmol) are used.

White solid: 78% yield; mp., 164–165 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 5.03 (6H, q, $J_{H,F}$ = 8.3 Hz, OCH_2CF_3), 8.87 (3H, s, Ar). ^{19}F NMR (188.1 MHz, CCl_3F): δ −73.5 (t, 9F, $J_{F,H}$ = 8.2 Hz, CF_3). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 66.02 (q, $J_{C,F}$ = 34.47 Hz, CH_2), 122.26 (q, $J_{C,F}$ = 277.92 Hz, CF_3), 133.0 (s, Ar), 137.88 (s, Ar). Anal. Calcd. for $C_{12}H_9F_9O_9S_3$: C 25.54; H 1.6; F 29.57; S 17.04. Found: C 25.61; H 2.1; F 29.81; S 17.23.

4.1.3. 1,3,5-Tris(morpholinosulfonyl)benzene (5)

The best results are obtained when morpholine (0.16 g, 1.8 mmol) is used.

White solid: 68% yield; mp., >250 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 3.17 (12H, t, $J_{H,H}$ = 4.6 Hz, CH_2), 3.75 (12H, t, $J_{H,H}$ = 4.6 Hz, CH_2), 8.3 (3H, s, Ar). ^{13}C NMR (125.77 MHz,

DMSO-d_6): δ 45.37 (s, CH_2), 65.39 (s, CH_2), 129.97 (s, Ar), 138.02 (s, Ar). Anal. Calcd. for $C_{18}H_{27}N_3O_9S_3$: C 40.67; H 2.94; N 8.18. Found: C 40.56; H 3.11; N 8.33.

4.2. Preparation of 3,5-bis(fluorosulfonyl)benzene sulfonyl morpholide (6)

A solution of morpholine (0.14 g, 1.65 mmol) in THF (1 ml) was added dropwise under stirring at 30–35 °C to the solution of compound **1** (0.25 g, 0.77 mmol) in THF (2 ml). Then reaction mixture was stirred at the same temperature for 4 h. The formed precipitate (morpholine hydrochloride) was filtered and the solvent was evaporated in vacuum. The crude product was washed with cold aqueous HCl (5%, 3 ml), dried and crystallized from methylene chloride to afford a desired product **6** (0.14 g), as a white solid: 45% yield; mp. 207–209 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 3.13 (4H, t, $J_{H,H}$ = 4.6 Hz, CH_2), 3.65 (4H, t, $J_{H,H}$ = 4.6 Hz, CH_2), 8.71 (2H, d, $J_{H,H}$ = 1.4 Hz, Ar), 9.12 (1H, t, $J_{H,H}$ = 1.4 Hz, Ar). ^{19}F NMR (188.1 MHz, CCl_3F): δ 67.15 (s, F, SO_2F). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 45.49 (s, CH_2), 65.27 (s, CH_2), 132.6 (s, Ar), 133.62 (s, Ar), 135.26 (d, $J_{C,F}$ = 28.92 Hz, Ar), 139.43 (s, Ar). Anal. Calcd. for $C_{10}H_{11}F_2NO_7S_3$: C 42.99; H 3.97; F 13.6; N 5.01; S 34.43. Found: C 43.09; H 4.02; F 13.83; N 5.09; S 34.51.

4.3. Preparation of 3,5-bis(fluorosulfonyl)benzene sulfonyl anilide (8)

A solution of triethylamine (0.16 g, 1.63 mmol) in acetonitrile (5 ml) was added dropwise under stirring at 40–45 °C to the mixture of compound **1** (0.2 g, 0.62 mmol) and aniline (0.088 g, 0.95 mmol) in acetonitrile (5 ml). Then the reaction mixture was stirred at the same temperature for 6 h, acidified with concentrated HCl to the pH 5–6 and the solvent was evaporated in vacuum. The crude product was washed quickly with cold water (10 ml), dried and crystallized from dioxane to afford a desired product **8** (0.16 g) as a white solid: 65% yield; mp. >200 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 7.81 (5H, m, C_6H_5), 8.96 (2H, d, $J_{H,H}$ = 1.4 Hz, Ar), 9.13 (1H, t, $J_{H,H}$ = 1.4 Hz, Ar), 10.02 (1H, s, NH). ^{19}F NMR (188.1 MHz, CCl_3F): δ 67.15 (s, F, SO_2F). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 127.91 (s, C_6H_5NH), 128.64 (s Ar), 129.79 (s, C_6H_5NH), 131.61 (s, Ar), 132.05 (s, Ar), 133.82 (d, $J_{C,F}$ = 26.4 Hz, Ar), 152.02 (s, C_6H_5NH). Anal. Calcd. for $C_{12}H_9F_2O_6S_3$: C 36.27; H 2.28; F 9.56; N 3.5. Found: C 36.33; H 2.4; F 9.67; N 3.45.

4.4. General procedure for the preparation of 3,5-bis(fluorosulfonyl)benzenesulfonyl-4′-dimethylaminopyridinium fluoride (9) and fluorosulfonylbenzene-3,5-bis(sylfonyl-4′-dimethylaminopyridinium) difluoride (10)

A solution of compound **1** (0.1 g, 0.31 mmol) and 4-dimethylaminopyridine (0.037 g, 0.303 mmol for **9** and 0.075 g, 0.61 mmol for **10**) in acetonitrile (2 ml) was well stirred at 50–55 °C for 7 h and then at r.t. overnight. The product formation was monitored by ^{19}F NMR spectra. The solvent was evaporated in vacuum. The crude product was washed with benzene (2 × 2 ml) to remove the excess of the initial compound **1** and crystallized from dioxane to afford a desired products **9** (0.1 g) or **10** (0.163 g).

4.4.1. 3,5-Bis(fluorosulfonyl)benzenesulfonyl-4′-dimethylaminopyridinium fluoride (9)

White solid: 75% yield; mp, 186–187 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 3.11 (6H, s, CH_3), 6.98 (2H, d, $J_{H,H}$ = 6.4 Hz, CH), 8.22 (2H, d, $J_{H,H}$ = 6.4 Hz, CH), 8.55 (2H, d, $J_{H,H}$ = 1.5 Hz, Ar), 8.73 (1H, t, $J_{H,H}$ = 1.5 Hz, Ar). ^{19}F NMR (188.1 MHz, CCl_3F): δ −155.63 (s, 1F, F^-), 66.82 (s, 1F SO_2F). ^{13}C NMR (DMSO-d6, 125.77 MHz): δ 39.09 (s, CH_3), 106.88 (s, DMAP), 124.65 (s, Ar), 128.58 (s, Ar), 130.0 (s, Ar), 133.71 (d, $J_{C,F}$ = 28.92 Hz, Ar), 152.05 (s, DMAP), 156.85 (s, DMAP). Anal. Calcd. for $C_{13}H_{13}F_3N_2O_6S_3$: C 34.98; H 2.94; F 12.77; N 6.27; S 21.55. Found: C 35.11; H 3.01; F 12.93; N 6.35; S 21.76.

4.4.2. Fluorosulfonylbenzene-3,5-bis(sylfonyl-4′-dimethylaminopyridinium) difluoride (10)

White solid: 92% yield; mp., 191–193 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 3.11 (12H, s, CH_3), 6.86 (4H, d, $J_{H,H}$ = 6.4 Hz, CH), 8.17 (4H, d, $J_{H,H}$ = 6.4 Hz, CH), 8.55 (2H, d, $J_{H,H}$ = 1.5 Hz, Ar), 8.73 (1H, t, $J_{H,H}$ = 1.5 Hz, Ar). ^{19}F NMR (188.1 MHz, CCl_3F): δ −155.63 (s, 2F, F^-), 64.96 (s, 1F SO_2F). ^{13}C NMR (DMSO-d6, 125.77 MHz): δ 39.09 (s, CH_3), 106.82 (s, DMAP), 124.64 (s, Ar), 128.53 (s, Ar), 130.2 (s, Ar) 133.72 (d, $J_{C,F}$ = 28.92 Hz, Ar), 151.96 (s, DMAP), 156.85 (s, DMAP). Anal. Calcd. for $C_{20}H_{23}F_3N_4O_6S_3$: C 42.24; H 4.08; N 9.85; S 16.92. Found: C 42.31; H 4.21; F 10.18; N 9.87; S 17.03.

4.5. Preparation of sodium 1-nitromethyl-2,4,6-tris(fluorosulfonyl)cyclohexadienate (16)

To a cooled (−15 °C), stirred solution of compound **1** (0.1 g, 0.34 mmol) in THF (2 ml) a sodium salt of nitromethane (0.04 g, 0.3 mmol) was added. During the first 5 min the reaction mixture was colored in bright yellow. Interaction was successfully completed in 30 min. After the solvent evaporation a crude product was washed with benzene (2 ml) and dried in vacuum to afford compound **16** (0.55 g) as a yellow solid: 78% yield; mp. >250 °C; ^{1}H NMR spectral data (299.9 MHz, DMSO-d_6): δ 4.5 (2H, d, $J_{H,H}$ = 5 Hz, CH_2), 4.71 (1H, t, $J_{H,H}$ = 5 Hz, CH_{gem}), 7.53 (2H, s, CH). ^{19}F NMR (188.1 MHz, CCl_3F): δ 63.67 (s, 2F, *o*-SO_2F), 67.89 (s, 1F, *n*-SO_2F). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 25.09 (s, CH_2NO_2), 66.98 (s, CH_{gem}), 93.7 (d, $J_{C,F}$ = 28.92 Hz, C-SO_2F), 98.9 (d, $J_{C,F}$ = 25.15 Hz, C-SO_2F), 139.63 (s, 3,5-CH). Anal. Calcd. for $C_7H_5F_3NNaO_8S_3$: C 20.64; H 1.24; F 13.99; S 23.62. Found: C 20.77; H 1.37; F 14.07; S 23.98.

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