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Anionic σ-complexes of 1,3,5-tris(fluorosulfonyl)benzene

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Abstract

We have found that symmetrical benzene trisulfonic-acid trifluoride **1** is able to undergo nucleophilic addition at free positions on the aromatic ring. Its reactions with sodium sulfite, morpholine and carbanions of malonic and acetoacetic esters, dimedone and nitromethane lead to the formation of comparatively stable anionic σ-complexes **3**–**8**.
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The reactions of benzene derivatives which contain strong electron-withdrawing groups at the 1,3,5-positions with different nucleophilic agents are of great interest because of the formation of products of both nucleophilic aromatic substitution and intermediate Meisenheimer-type anionic σ-complexes. There are numerous investigations devoted to such complexes of sym-trinitrobenzene.[1]

1,3,5-Tris(trifluoromethylsulfonyl)benzene (**2**) is known to form more stable σ-complexes[2] because the SO_2CF_3 group is a stronger electron-withdrawing group (σ_p 1.04)[3] than a nitro group (σ_p 0.78).[4] At the same time the SO_2F (σ_p 1.01)[5] and SO_2CF_3 groups are very similar in their electronic nature.

1   **2**
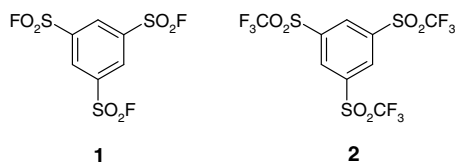
Although 1,3,5-tris(fluorosulfonyl)benzene **1** is a known compound,[6] its reactions with nucleophilic agents have not been investigated previously. The exception is heating with potassium fluoride when the SO_2F group is substituted by a fluorine atom.[6b] However, it is known that aromatic sulfonic-acid fluorides, in contrast to aryl trifluoromethyl sulfones, prefer to interact with nucleophilic agents on the sulfonyl centre. For example, in reactions with anilines, the corresponding sulfonyl anilides are formed[7] and when $ArSO_2F$ is activated by strong electron-withdrawing groups, hydrolysis can occur even in neutral aqueous dioxane.[8]

Nevertheless, we have found that compound **1** on reaction with nucleophilic agents such as sodium sulfite, morpholine, the carbanions of malonic and acetoacetic esters, dimedone and nitromethane in DMSO forms the Meisenheimer-type anionic σ-complexes **3**–**8** (Scheme 1).

Equimolar mixtures of sulfonyl fluoride **1** and the previously mentioned reagents (for morpholine 2 equiv) at 10 °C to room temperature form bright yellow, fluorescent-coloured solutions. Both the ^{19}F and ^1H NMR spectra exhibit two signals (intensity 2:1) instead of the one singlet typical for compound **1** (Table 1). Acidification of the complexes (e.g., **7** and **8**) causes discolouration of the solutions and the disappearance of the two signals in the NMR spectra. Instead the singlet of the starting sulfonyl fluoride **1** reappears.

The ^{13}C NMR spectra of adducts **3**–**8** also demonstrate typical signal shifts similar to those of 1,3,5-trinitrobenzene[9] or 2,4,6-trinitroanisole.[10] The signals of the C2, C4 and C6 atoms are shifted high field, whereas those of the C3 and C5 atoms moved downfield (Table 2).

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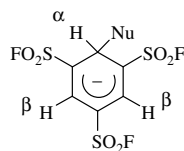 *E-mail address:* boikovolodymyr@yandex.ru (V. N. Boiko).
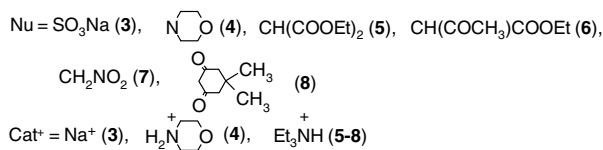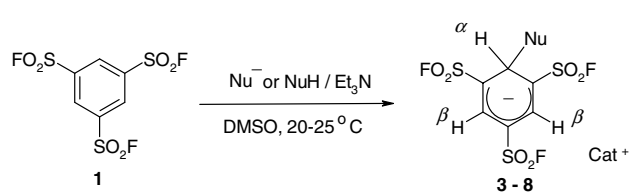
Scheme 1.

There are some unexpected features in the ^{19}F NMR spectra of the reported σ-complexes. In adducts **5** and **6** the signals of the SO_2F groups at the *ortho-* and *para*-positions are merged together, while in their ^1H NMR spectra, the signals of the H^α and H^β protons are typical of those for anionic σ-complexes. The analogous situation was observed in σ-complexes of sulfone **2** with nucleophiles such as PhSNa and C_4H_9SNa.[2b] In contrast, σ-complex **8** exhibits two different signals for the two *ortho*-SO_2F groups. This is probably a result of the presence of the bulky dimedone in the σ-complex. This may result in the asymmetry of the two *ortho*-SO_2F groups in the plane of the cyclohexadiene ring and impede their rotation.

Of interest is the fact that in contrast to the corresponding σ-complexes of sulfone **2**[2] most of the investigated adducts **3**–**8** demonstrate ^{19}F NMR signals shifted downfield compared to compound **1** (Fig. 1). At the same time their ^1H NMR spectra are typical for anionic σ-complexes. They show the corresponding signals of the H^α and H^β protons in the high field region.

The exceptions are the σ-complexes of nitromethane **7** and dimedone **8**. The fluorine signals of the *ortho*-SO_2F groups are shifted high field in comparison to the initial

Table 1
^{19}F and ^1H NMR spectra, δ, ppm (integral intensity) of adducts **3**–**8**[a] in DMSO-d_6

Compound	Nu	^{19}F (200 MHz, CCl_3F)		^1H (300 MHz, $J_{H,H}$, Hz)		
		o-SO_2F (2)	p-SO_2F (1)	H^α (1)	H^β (2)	Others
3	SO_3Na	72.2	71.7	4.7	7.4	
4	N◯O	72.06	72.12	4.93	7.61	2.47 (t, $J = 4.9$, 4H, CH_2), 3.11 (t, $J = 4.9$, 4H, CH_2)
5	$CH(COOEt)_2$	71.29		4.93 (d, $J = 3.5$)	7.49	3.15 (t, $J = 6.5$, 6H, CH_3), 3.47 (d, $J = 3.5$, 1H, CH), 4.12 (q, $J = 4.1$, 4H, CH_2)
6	CH⟨COCH_3 / COOEt	70.33		4.92 (d, $J = 3.0$)	7.41	2.08 (s, 3H, $COCH_3$), 3.38 (d, $J = 3.0$, 1H, CH)[b]
7	CH_2NO_2	65.86	70.05	4.68 (t, $J = 5.1$)	7.50	4.47 (d, $J = 5.1$, 2H, CH_2)
8	(dimedone)	64.86(1), 64.88(1)	73.32	5.42 (d, $J = 3.0$)	7.21	3.40 (d, $J = 3.0$, 1H, CH), 2.16 (s, 4H, CH_2), 0.95 (s, 6H, CH_3)

[a] NMR spectra of compound **1** in DMSO-d_6: δF 67.1 s, δH 9.2 s.
[b] The signals for the C_2H_5 and $(C_2H_5)_3NH^+$ groups are superimposed.

Table 2
^{13}C NMR spectra of compound **1** and adducts **3** and **8** (125 MHz, DMSO-d_6, δ, ppm, J, Hz)

Atom	**1**[a]	**3**	Δδ: (**3**–**1**)	**8**	Δδ: (**8**–**1**)
C1	136.05 s	54.23 s	−81.82	102.90 s	−33.15
C2 (C6)	135.66 d, $J_{C,F} = 28.9$	100.87 d, $J_{C,F} = 23.9$	−34.79	105.11 d, $J_{C,F} = 13.6$	−30.55
C3 (C5)	136.05 s	137.98 s	+1.93	138.80 s	+2.75
C4	135.66 d, $J_{C,F} = 28.9$	94.03 d, $J_{C,F} = 25.15$	−41.63	104.96 d, $J_{C,F} = 13.6$	−30.70

[a] The numbering of the C-atoms in compound **1** is the same as in adducts **3**–**8**:
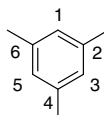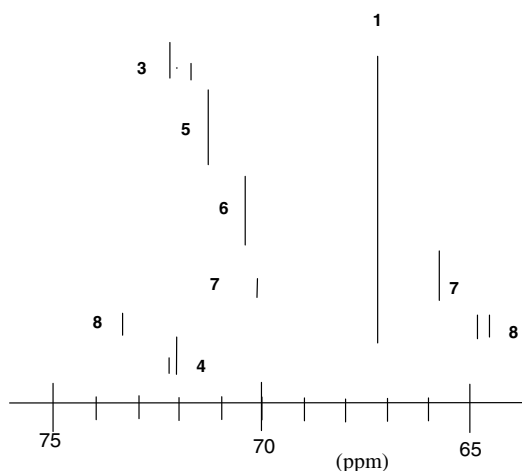
Fig. 1. The position of the ^{19}F NMR signals of adducts **3–8** relative to compound **1**.

compound **1**. Evidently, the location of the fluorine atom signals in the ^{19}F NMR spectra of σ-complexes **3–8** depends upon several factors. With analogy to anionic σ-complexes of sulfone **2**[11] it can be proposed that in adducts **3–8**[12] the positive charge on the sulfur atoms is also enlarged. Moreover, the position of the fluorine atom adjacent to the S=O double bond results in its π-donating properties.

It should be noted that anionic σ-complexes **3**, **7** and **8** occurred as comparatively stable structures. Unfortunately, they still have not been isolated as individual compounds. However, in DMSO solution they were stable for 7–8 days at room temperature after which their solutions became discoloured and the ^{19}F NMR spectra demonstrated signals of rearranged products. For example, in the case of adduct **8,** both the ^{19}F and ^{1}H NMR spectra indicated the formation of the sulfone **9** (^{1}H NMR (300 MHz): δ 1.07 (s, 6H, CH$_3$), 2.21 (s, 4H, CH$_2$), 5.32 (s, 1H, CH), 8.72 (t, $J = 1.6$ Hz, 1H, H$_{aryl}$), 8.76 (d, $J = 1.6$ Hz, 2H, H$_{aryl}$); ^{19}F NMR (200 MHz): δ 66.3 (s, SO$_2$F).

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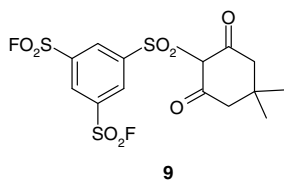
Therefore, despite compound **1** being a strong aromatic sulfonic-acid halide in reactions with various nucleophilic agents it can undergo aromatic addition. However, the anionic σ-complexes formed are not as stable as those of 1,3,5-tris(trifluoromethylsulfonyl)benzene **2** and undergo further transformations.

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12. *Typical experimental procedure*: To a solution of 1,3,5-tris(fluorosulfonyl)benzene **1** (50 mg, 0.15 mmol) in DMSO-d_6 (2 mL) cooled to 10–15 °C, the corresponding nucleophilic agent (0.15 mmol) (for **4**—0.30 mmol), H$_2$O (0.4 mL; for **3** only) and Et$_3$N (0.15 mmol; for **5–8**) were added. The reaction solutions were stirred for 30 min at this temperature then allowed to warm to 20 °C and after 15–20 h the ^{19}F, ^{1}H and ^{13}C NMR spectra were recorded.