Journal of Fluorine Chemistry 132 (2011) 1219–1226

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

A convenient synthetic route to 2,4,6-tris(chlorosulfonyl)- and 2,4,6-tris(fluorosulfonyl)phenol, aniline and chlorobenzene

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ARTICLE INFO

Article history:
Received 18 May 2011
Received in revised form 25 June 2011
Accepted 29 June 2011
Available online 6 July 2011

Keywords:
Arenes
Sulfonylchlorides
Sulfonylfluorides
Nucleophilic substitution
Synthetic methods
Molecular structures

ABSTRACT

Convenient and preparative synthetic procedures of 2,4,6-tris(chlorosulfonyl)- and 2,4,6-tris(fluorosulfonyl)phenol, -chlorobenzene and -aniline have been elaborated. Chlorine exchange for fluorine by KF interaction on 2,4,6-tris(chlorosulfonyl)aniline and especially 2,4,6-tris(chlorosulfonyl)phenol proceeds easily and selectively under anhydrous conditions in dioxane. Unlike, 2,4,6-tris(chlorosulfonyl)chlorobenzene transformation requires the presence of water. On the basis of 2,4,6-tris(fluorosulfonyl)phenol and some of its salts, XRD measurements demonstrated the structural similarity to picric acid and its derivatives in the solid state.

1. Introduction

Phenols bearing three strong electron withdrawing groups in 2,4,6 ring positions – with picric acid being the most historically famous representative – are involved in a variety of fundamental processes of organic and applied chemistry. Unfailing interest in the picric acid as well as polynitro benzene derivatives lie in their unique chemical nature essence of its high reactivity towards nucleophilic agents [1], formation of stable σ- [2] and π-complexes [3] and a number of other useful properties; utilization of these compounds is limited due to their high explosive potential.

The replacement of nitro groups by more electronegative SO_2CF_3 groups allows to minimize these negative properties and at the same time to increase the activity of those compounds [4]. For example, 2,4,6-tris(trifluoromethylsulfonyl)phenol (pK_a −1 [5]; −2.5 [6]) is rather more acidic than 2,4,6-trinitrophenol (pK_a 0.38 [7]), and in three exponent parts more effective as a metal extractive reagent [6]. The conductivity of lithium 2,4,6-tris(trifluoromethylsulfonyl)phenolate solutions essentially exceeds these parameters for $LiOSO_2CF_3$, $LiClO_4$ and $LiN(SO_2CF_3)_2$ [8].

The synthesis of 2,4,6-tris(trifluoromethylsulfonyl) derivatives of phenol, chlorobenzene and aniline is possible via trifluoromethylation of the corresponding trimercapto compounds obtained from 2,4,6-trisulfonylbenzene chlorides followed by oxidation [9]. An alternative route to prepare 2,4,6-tris(trifluoromethylsulfonyl)phenol comprises a two step process reacting phenol with CF_3SCl followed by subsequent oxidation [8]. However, taking into account the high costs of CF_3I and CF_3SCl, practical application of the above mentioned methods is difficult to realize to prepare bigger quantities of the desired phenols.

In terms of electronic properties, the group SO_2F (σ_p 1.01) compares absolutely to the moiety SO_2CF_3 (σ_p 1.04–1.06) [10,11]. The electron withdrawing ability of the SO_2F group is nearly the same as that determined for the trifluoromethylsulfonyl one, but substantially higher than that of the nitro group (σ_p 0.78 [7]). Moreover, the aryl sulfonyl fluoride synthesis is convenient and well developed. It is noteworthy to outline the high hydrolytic stability of fluorosulfonyl arenes dramatically differing from other haloanhydrides; i.e. a typical purification procedure for aryl sulfonyl fluorides is steam distillation (!). Thus, it should be admitted that, in our opinion, aromatic sulfonyl fluorides may compete with expensive or rare aryl trifluoromethyl sulfones as key compounds for various practical applications.

Up to present investigation, methods to obtain 2,4,6-tris(fluorosulfonyl)arenes were limited to the corresponding aniline, the latter was prepared in low yield [12]. To the best of our knowledge, the similar phenol and chlorobenzene derivatives were not described apart from hypothetical record of the last in Beilstein

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doi:10.1016/j.jfluchem.2011.06.045

[13], while in the cited source [14a] the 2,3,6-isomer was described.

The intention of this work was to develop simple and effective synthetic methods for 2,4,6-tris(fluorosulfonyl) derivatives of phenol, chlorobenzene and aniline that would make these compounds available for thorough investigations and potential utilizations [15]. To reach this aim, it was necessary to revise known methods to obtain the corresponding chlorosulfonyl substituted benzenes as the most perspective precursors to be finally converted into fluorosulfonyl derivatives by simple chlorine-fluorine exchange.

2. Results and discussion

2.1. Preparation of 2,4,6-tris(chlorosulfonyl)phenol, -aniline and -chlorobenzene

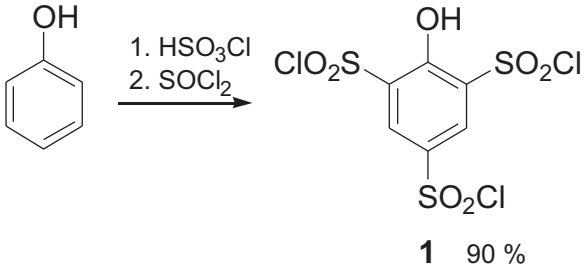
The at present known synthetic methods to obtain 2,4,6-tris(chlorosulfonyl)phenol (**1**) [16a,b] and 2,4,6-tris(chlorosulfonyl)aniline (**2**) [12a–d] did not exceed 9–10% yields (phenol **1**), and 7–29% (aniline **2**) that required considerable revision.

We found out that one pot two steps reaction of starting compounds – phenol, acyl sulfanilic acid or acetanilide – with chlorosulfonic acid (8–13 equiv.) followed by thionyl chloride addition (4–5 equiv.) allowed to synthesize the corresponding trisulfonyl chlorides **1** and **2** in 90 and 60% yields respectively. This method does not only allow the use of HSO_3Cl avoiding large excess (10 equiv. for each group in typical procedure), but substantially facilitates the isolation of the raw materials **1** and **2** as well (Schemes 1 and 2).

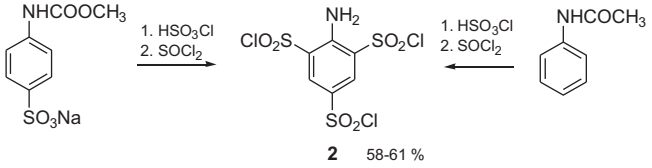
It was previously documented that conversion of 2,4,6-tris(chlorosulfonyl)phenol (**1**) into 2,4,6-tris(chlorosulfonyl)chlorobenzene (**3**) by heating with a $PCl_5/POCl_3$ mixture [17] or with PCl_5 [16b] gave unpurified sulfonylchloride **3** in about 10% yield [16b]. We revealed that desired sulfonyl chloride **3** can be obtained in 90–94% yield by heating phenol **1** with PCl_5 in toluene or with $POCl_3$/catalytic quantity of pyridine (Scheme 3).

2.2. Preparation of 2,4,6-tris(fluorosulfonyl)phenol, -aniline and -chlorobenzene

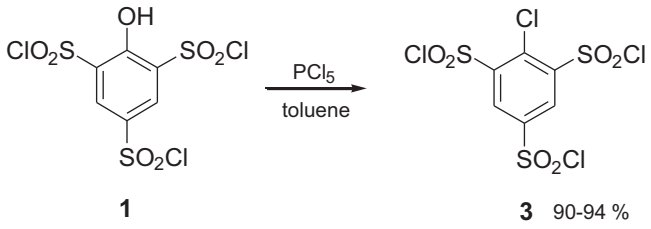
The most common and inexpensive technique for aromatic sulfonyl fluorides preparation is replacement of the chlorine atom



Scheme 1.



Scheme 2.



Scheme 3.

in SO_2Cl groups for fluorine by KF action in water or water–organic solvent mixture [14a–c]. As it was documented previously, application of these conditions for 2,4,6-tris(chlorosulfonyl)phenol (**1**) failed probably due to the hydrolysis of sulfonyl chloride groups [14a]. For the similar halogen exchange in 1,3,5-tris(chlorosulfonyl)benzene and 2,3,6-tris(chlorosulfonyl)chlorobenzene the same authors recommended a water-xylene mixture to obtain the tris(fluorosulfonyl) derivatives in moderate yields (46% and 40%, respectively). Thus, a principal improvement of the Halex procedure with respect to substituents attached to the benzene ring was necessary.

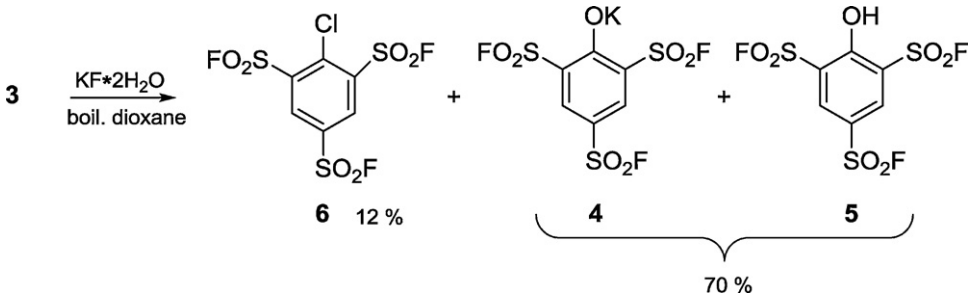
It has been found that short-term (30 min) boiling of 2,4,6-tris(chlorosulfonyl)chlorobenzene (**3**) with $KF{\cdot}2H_2O$ in dioxane caused chlorine substitution in SO_2Cl groups with nearly exhaustive conversion. But as it turned out, in these conditions not only sulfonic acid halides are affected, but chlorine atom linked to benzene ring was changed to a hydroxy function. The main products of this reaction were 2,4,6-tris(fluorosulfonyl)phenole **5** and the corresponding potassium phenolate **4**, while a minor product was chlorobenzene **6**, with a total conversion of 82% (Scheme 4). Separation of the products was achieved by aqueous work-up based on the experimental finding that the chlorobenzene **6** was insoluble in hot water in contrast to compounds **4** and **5**.

The disadvantage of this procedure is a reaction mixture constituted of a dioxane solution and water–salt paste adhering to walls making effective stirring difficult. In order to overcome this complication, the quantity of water was decreased by using anhydrous KF and addition of 1–1.5 equiv. of H_2O giving a well-stirred suspension.

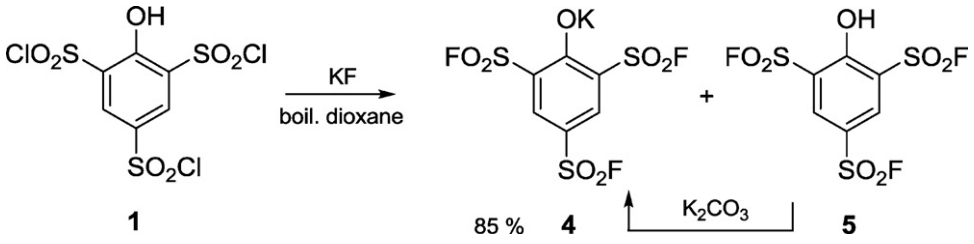
Attempts to carry out reactions in anhydrous dioxane with dried KF with the expectation of 2,4,6-tris(fluorosulfonyl)fluorobenzene formation, did not give any evidence for an exchange at all and the sulfonyl chloride **3** was recovered quantitatively. Under anhydrous conditions, a reaction with KF was only observed in the presence of a catalyst (such as crown-ethers [18a] or PEG-400 [18b]) or at elevated temperature [18c]. On the other hand, the effectiveness of ZnF_2 in pyridine [18c,19] in related transformations may be due to electrophilic catalysis by pyridine solvated zinc cations.

Anhydrous conditions were applied successfully for chlorine substitution in 2,4,6-tris(chlorosulfonyl)phenol (**1**). Heating of the phenol **1** in dioxane solution with calcinated KF caused the formation of the desired phenolate **4** and phenol **5** within 30 min. The water insoluble potassium salt **4** was isolated as the only product in 85% yield by treatment of the reaction mixture with an aqueous K_2CO_3 solution (Scheme 5). In case of $KF{\cdot}2H_2O$, the key compounds were obtained only in 20–30% yield. Thus, the presence of a hydroxy group in this molecule, unlike 2,4,6-tris(chlorosulfonyl)chlorobenzene (**3**), promotes the interaction in the absence of water.

The phenol **5** is difficult to isolate from the reaction mixture due to its high acidity and excellent solubility in water. Extraction with CH_2Cl_2 after treatment of the potassium salt **4** with concentrated



Scheme 4.



Scheme 5.

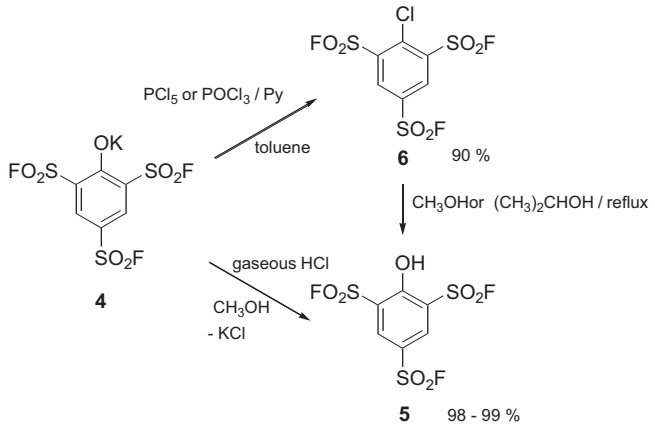
H_2SO_4 was less effective and required large quantities of dichloromethane. Bubbling gaseous HCl into a methanolic solution of potassium phenolate **4** afforded the conversion into the phenol **5** in quantitative yield. The phenol **5** was also obtained in high yield upon refluxing 2,4,6-tris(fluorosulfonyl)chlorobenzene (**6**) in methanol or propan-2-ol in the same manner as described for the alcoholysis of 2,4,6-tris(trifluoromethylsulfonyl)chlorobenzene [20]. In turn, 2,4,6-tris(fluorosulfonyl)chlorobenzene (**6**) can be easily obtained from the phenolate **4** by reacting it with PCl_5 or $POCl_3$/Py, respectively (Scheme 6).

Anhydrous conditions turned out to be suitable for the fluorination of 2,4,6-tris(chlorosulfonyl)aniline (**2**). While in a water–dioxane mixture 2,4,6-tris(fluorosulfonyl)aniline (**7**) formation was achieved in only 26% [12c], heating to reflux for 5 h in anhydrous dioxane with calcinated KF allowed halogen exchange up to 60–70%. The reaction proceeded faster upon addition of water (1–2 equiv.) (Scheme 7).

2.3. Preparation of metal, pyridinium and ammonium based 2,4,6-tris(fluorosulfonyl)phenolates

Due to its high acidity, 2,4,6-tris(fluorosulfonyl)phenol (**5**) (pK_a 5.66 in CH_3CN [21]), which may be compared with the acidity of 2,4,6-tris(trifluoromethylsulfonyl)phenol (pK_a 4.93 in CH_3CN [21]), is able to form salts by interaction not only with bases (Li_2CO_3, various pyridines, Bu_4NOH) but also with metals (Mg, Zn), metal salts of mineral acids (Cs_2SO_4, $BaCl_2$) and tetraalkylammonium halides ($(CH_3)_4NI$, $(C_2H_5)_4NI$) (Scheme 8).

Phenolates **8** (Li) and **4** (K) may be obtained by metathesis one from the other.



Scheme 6.

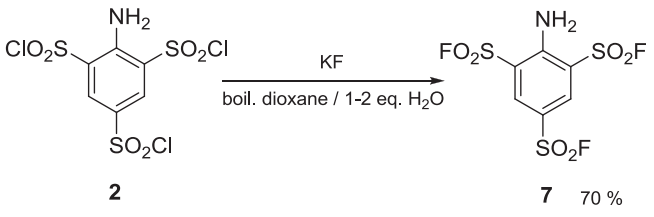
2.4. X-ray diffraction investigation

2.4.1. The molecular structure of 2,4,6-tris(fluorosulfonyl)phenol (5)

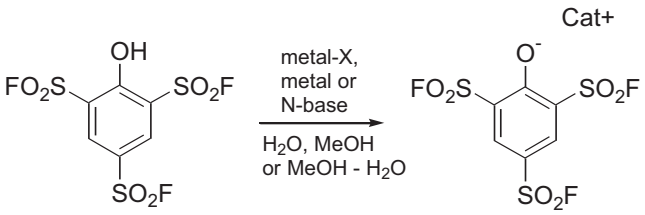
The molecular structure of the phenol **5** is monomeric with only one intramolecular H···O contact of the hydroxyl proton directed onto an oxygen atom of one adjacent SO_2F-group and resembles the structure of picric acid [22] (Fig. 1). The contact falls into the characteristic range of O–H···O bridges with the hydrogen bonding mode D–H 0.74(5) Å; H···*A* 2.15(5) Å; D···*A* 2.80(5) Å; D–H···*A* 146(5) Å. This contact generates a six-membered ring thus characterized by the graph-set motif *S*(6) [23].

2.4.2. The molecular structure of lithium 2,4,6-tris(fluorosulfonyl)phenolate hydrate dimer (8), [Li(OC_6H_2(2,4,6-SO_2F)$_3$·H_2O)]$_2$

The molecular structure of [Li(OC_6H_2(2,4,6-SO_2F)$_3$·H_2O)]$_2$ constitutes a centrosymmetric dimer wherein a pair of anions are bound together by a pair of cations in the manner as depicted in Fig. 2. To a first approximation, the dimer appears to be planar in as much as the lithium atoms are displaced out of the plane to the centre of a square pyramid with a water molecule at its apex. This motif resembles strongly that of the corresponding picrate [24]. Due to the increased sterical demand of the SO_2F groups in comparison with the NO_2 groups of the picrate, Li–O contacts to the oxygen atoms of the 2,6-substituents appear to be elongated by up



Scheme 7.



Cat: Li (**8**), Cs (**9**), 1/2 Ba (**10**), 1/2 Mg (**11**), 1/2 Zn (**12**), PyH (**13**), 2,4,6-$(CH_3)_3$PyH (**14**), 4-(*N*,*N*-$(CH_3)_2$)PyH (**15**), $N(CH_3)_4$ (**16**), $N(C_2H_5)_4$ (**17**), $N(C_4H_9)_4$ (**18**)

Scheme 8.

to 0.14 Å, while the Li–OH_2 contact of approximately 1.92 Å is nearly identical in both cases.

*2.4.3. The crystal structure of hexaaquazinc bis(2,4,6-tris(fluorosulfonyl)phenolate) pentasesqui hydrate (**12**), $[Zn(H_2O)_6][OC_6H_2(2,4,6\text{-}SO_2F)_3]_2{\cdot}5.5H_2O$*

Two formula units make up the asymmetric unit consisting of two independent $[Zn(H_2O)_6]$ dications without crystallographically imposed symmetry, four independent phenolate anions and eleven intercalated water molecules. Cations and anions form separate stacks extending along the c axis without any ligation of the anions to the metal cation (Fig. 3). To our knowledge, such a motif has been reported only twice for the related picrates $[Mg(H_2O)_6][OC_6H_2(2,4,6\text{-}NO_2)_3]_2{\cdot}3H_2O$ [25] and $[Fe(H_2O)_6][OC_6H_2(2,4,6\text{-}NO_2)_3]_2{\cdot}2H_2O$ [26] and seems to be an exception in the solid state structures of metal picrates in general [27].

*2.4.4. The molecular structures of 2,4,6-trimethylpyridinium 2,4,6-tris(fluorosulfonyl)phenolate (**14**), $[2,4,6\text{-}Me_3C_5H_2NH][OC_6H_2(2,4,6\text{-}SO_2F)_3]$ and 4-(N,N-dimethylamino)pyridinium 2,4,6-tris(fluorosulfonyl)phenolate (**15**), $[4\text{-}Me_2NC_5H_4NH][OC_6H_2(2,4,6\text{-}SO_2F)_3]$*

In the molecular structures of $[2,4,6\text{-}Me_3C_5H_2NH][OC_6H_2(2,4,6\text{-}SO_2F)_3]$ and $[4\text{-}Me_2NC_5H_4NH][OC_6H_2(2,4,6\text{-}SO_2F)_3]$, motifs which are well-documented for picrates of *N*-containing heterocycles are retrieved [28]. Although cations and anions are arranged in different manner, the graph-set motif $R_1^2(6)$ [23] found in both compounds is the same as in related picrates such as pyridinium picrate [29] or 4-dimethylaminopyridinium picrate [30] (Figs. 4 and 5).

The hydrogen bonding mode is for the 2,4,6-trimethylpyridinum derivative *D*–H 0.89(4) Å; H···*A* 1.83(3) Å; *D*···*A* 2.72(2) Å; *D*–H···*A* 176(3) Å for N–H···O and *D*–H 0.89(4) Å; H···*A* 2.81(3) Å; *D*···*A* 3.14(2) Å; *D*–H···*A* 103(3) Å for N–H···OSOF and for the 4-dimethylaminopyridinum derivative *D*–H 0.85(3) Å; H···*A*

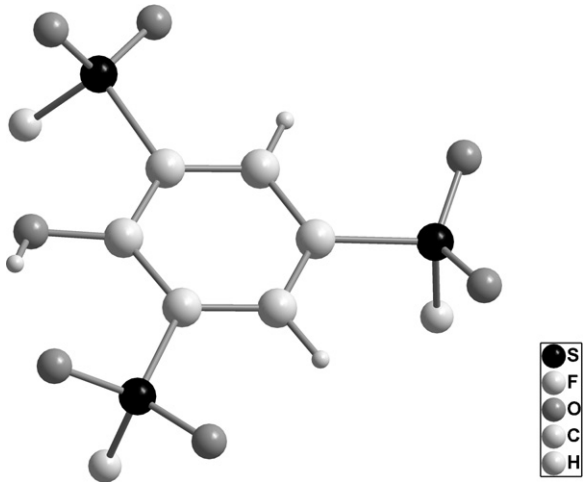


Fig. 1. Molecular structure of 2,4,6-tris(fluorosulfonyl)phenol (**5**).

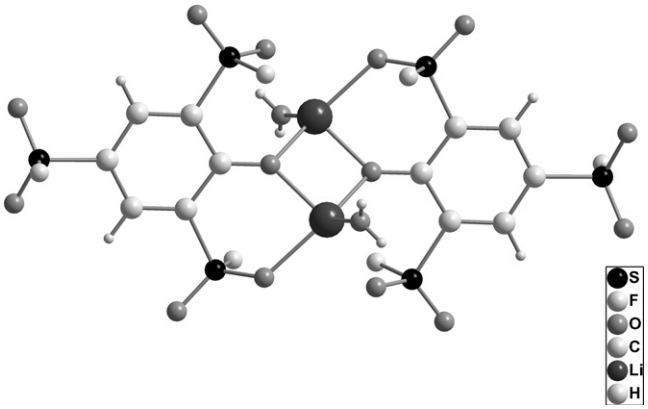


Fig. 2. Molecular structure of lithium 2,4,6-tris(fluorosulfonyl)phenolate hydrate (**8**).

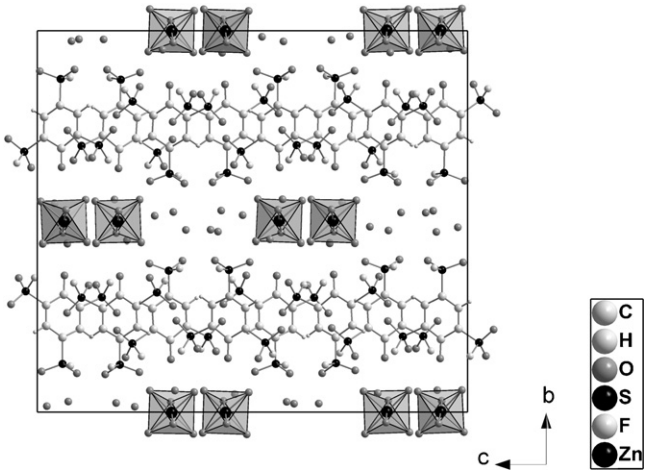


Fig. 3. View onto the unit cell of hexaaquazinc bis(2,4,6-tris(fluorosulfonyl)phenolate) pentasesqui hydrate (**12**) along the crystallographic *a*-axis.

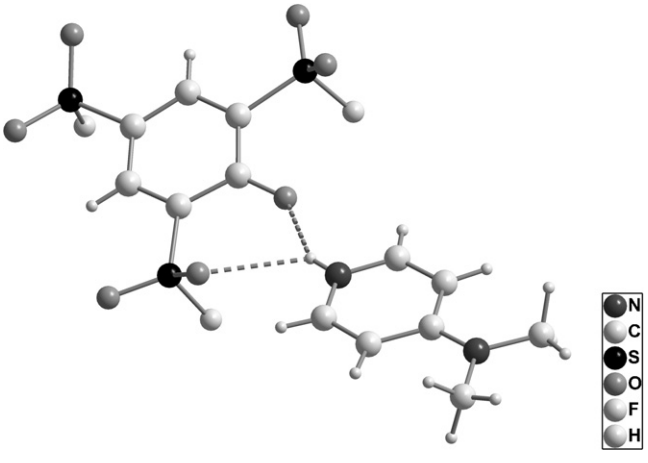


Fig. 4. Molecular structure 4-(*N*,*N*-dimethylamino)pyridinium 2,4,6-tris(fluorosulfonyl)phenolate (**15**).

Table 1
Crystallographic data for compounds **5**, **8**, **12**, **14** and **15**.

	5	**8**	**12**	**14**	**15**
Empirical formula	$C_6H_3F_3O_7S_3$	$C_{12}H_8F_6Li_2O_{16}S_6$	$C_{24}H_{54}F_{12}O_{51}S_{12}Zn_2$	$C_{14}H_{14}F_3NO_7S_3$	$C_{13}H_{13}F_3N_2O_7S_3$
Formula mass	340.26	728.42	1902.13	461.44	462.43
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a [Å]	12.681(2)	12.419(1)	9.621(1)	9.095(1)	28.613(2)
b [Å]	9.356(1)	11.615(2)	24.955(2)	9.562(1)	8.104(1)
c [Å]	9.764(1)	9.553(1)	28.180(2)	10.806(2)	17.284(1)
α [°]				97.74(1)	
β [°]	91.79(1)	111.98(1)		94.74(1)	115.88(1)
γ [°]				98.45(1)	
V [Å^3]	1157.9(2)	1277.8(3)	6765.7(9)	916.0(2)	3605.9(6)
Z	4	2	4	2	8
$D_{calcd.}$ [g cm^{-3}]	1.952	1.893	1.223	1.673	1.704
Independent reflections	2785	2952	15064	5115	4023
R (R_w)	0.0466 (0.1154)	0.0340 (0.0888)	0.0494 (0.1220)	0.0379 (0.1002)	0.0311 (0.0847)
CCDC	675317	675318	675321	675320	675319

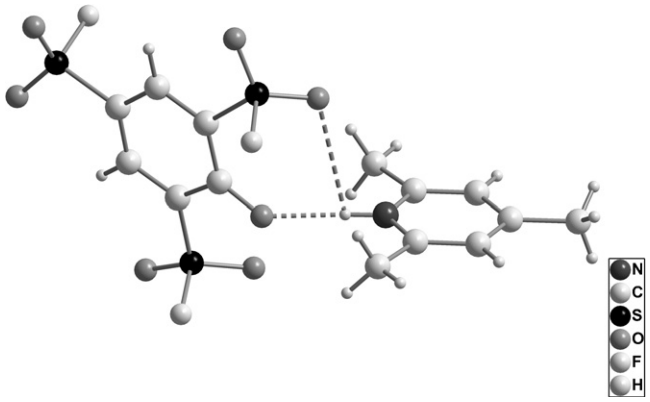


Fig. 5. Molecular structure of 2,4,6-trimethylpyridinium 2,4,6-tris(fluorosulfonyl) phenolate (**14**).

1.95(3) Å; $D\cdots A$ 2.73(2) Å; D–H$\cdots A$ 151(3) Å for N–H$\cdots$O and D–H 0.85(3) Å; H$\cdots A$ 2.45(3) Å; $D\cdots A$ 3.04(2) Å; D–H$\cdots A$ 126(3) Å for N–H$\cdots$OSOF. The contacts found in the 4-dimethylaminopyridinium 2,4,6-tris(fluorosulfonyl)phenolate are marginally longer than in the 4-dimethylaminopyridinium picrate [30]; a fact that must be attributed to the bulkier SO_2F substituents.

In solid state structures, the picrate anions adopt a keto form in most cases [26]. The same has to be applied for the 2,4,6-tris(fluorosulfonyl)phenolate anion with C–O bond lengths of 1.257(2) Å (**14**) [1.252(2) Å(**15**)] and C–C bond lengths (C1–C2; C1–C6) of 1.442(2); 1.445(2) Å (**14**) and 1.443(2); 1.447(2) Å (**15**), respectively. These values differ considerably from those found in the "free" 2,4,6-tris(fluorosulfonyl)phenol (C–O: 1.335(4) Å; C–C: 1.401(4); 1.405(4) Å) which crystallizes apparently in the enol form.

These structural features demonstrate the similarity of both picric acid and 2,4,6-tris(fluorosulfonyl)phenol and their derivatives in the solid state (Table 1).

3. Conclusions

In this work, we demonstrated that 2,4,6-tris(chlorosulfonyl)-phenol (**1**) and 2,4,6-tris(chlorosulfonyl)aniline (**2**) can be synthesized on a preparative scale in high yields. The simple Halex-process for the preparation of corresponding 2,4,6-tris(fluorosulfonyl) derivatives **5** and **6** is better to be realized with KF in dry or almost dry dioxane, while anhydrous conditions are not suitable for the fluorination of 2,4,6-tris(chlorosulfonyl)chlorobenzene (**3**). 2,4,6-Tris(fluorosulfonyl)phenol (**5**) due to its high acidity is able to produce corresponding salts by reactions not only with bases, but as well with metals or metal salts. Crystallographic measurements of 2,4,6-tris(fluorosulfonyl)phenol (**5**) and some of its salts have been carried out elucidating impressively the similarity of their structural motifs to picric acid and its derivatives.

4. Experimental

4.1. General

All starting materials were obtained commercially. All solvents were dried using literature procedure.

^{1}H NMR spectra were recorded with a Varian-Gemini VXR 300 spectrometer at 299.9 MHz, ^{19}F NMR spectra – with a Bruker 200 spectrometer at 188.1 MHz and ^{13}C NMR spectra – with an Avance DRX 500 spectrometer in the solvents indicated.

Residual signals of the solvent protons with the chemical shifts δ = 7.25 ppm ($CDCl_3$), δ = 2.07 ppm ([D_6]acetone), δ = 2.50 ppm ([D_6]DMSO) were used as an internal reference. For ^{19}F NMR spectra CCl_3F was used as an internal standard. Whenever possible the reactions were monitored by thin-layer chromatography (TLC). TLCs were run on Merck Kieselgel 60 F_{254} plates. Melting points are uncorrected and were measured with an electro thermal apparatus.

4.2. X-ray crystallographic data

CCDC-675317–675321 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2.1. 2,4,6-Tris(chlorosulfonyl)phenol (1)

Chlorosulfonic acid (700 mL, 10.75 mol) was slowly added to phenol (126 g, 1.34 mol) under stirring by a mechanical stirrer. Temperature was kept at 60–70 °C and evolved HCl was absorbed with H_2O. The reaction mixture was heated to 140–145 °C for 3 h, then cooled to 30–40 °C and $SOCl_2$ (490 mL, 6.84 mol) was added dropwise avoiding excessive foaming. The reaction mixture was stirred at 70–90 °C until the gas evolution was finished (about 3 h), cooled to room temperature, and the precipitate was filtered off, mixed in portions with ice-water, filtered off, washed with cold concentrated HCl and dried in a vacuum desiccator over NaOH and H_2SO_4 to afford sulfonyl chloride **1** (473 g, 90.6%). M.p. 187–188 °C;

after crystallization from *p*-xylene: m.p. 189–190 °C (lit. m.p. 193 °C [16a]).

4.2.2. 2,4,6-Tris(chlorosulfonyl)aniline (2)

4.2.2.1. From sodium p-methoxycarbonylaminobenzene sulfonate. Sodium *p*-methoxycarbonylaminobenzene sulfonate (40 g, 0.16 mol) was slowly added to chlorosulfonic acid (135 mL, 2.07 mol) under stirring and evolved HCl was absorbed with H_2O. Temperature of reaction mixture was slowly raised to 140–145 °C and kept at this level for 4.5 h. After cooling to 35–40 °C $SOCl_2$ (46 mL, 0.64 mol) was added dropwise and mixture was heated at 70–85 °C for 5 h. The reaction mass was mixed by portions with crushed ice, the precipitate was filtered off, washed with cold water up to pH 7 and dried under reduced pressure. The crude product obtained (50.0 g) was dissolved in hot $CHCl_3$ (~500 mL) and quickly filtered through Al_2O_3 (15–20 mm layer). The solvent was removed under reduced pressure to afford aniline **2** (37.5 g, 61%). M.p. 170–172 °C (lit. m.p. 168–170 °C [12c]; 175–177 °C [12d]).

4.2.2.2. From acetanilide. The analogous to previous section acetanilide (20.0 g, 0.15 mol) treated by chlorosulfonic acid (100 mL, 1.54 mol) and then $SOCl_2$ (43.0 mL, 0.60 mol) to afford **2**, which was purified as mentioned above (34.0 g, 58.4%), m.p. 168–170 °C.

A mixing test of the samples obtained by different given methods and with an authentic sample did not show a m.p. depression.

4.2.3. 2,4,6-Tris(chlorosulfonyl)chlorobenzene (3)

4.2.3.1. Preparation by PCl_5. A mixture of 2,4,6-tris(chlorosulfonyl)phenol (**1**) (55.7 g, 0.14 mol) and PCl_5 (60.0 g, 0.29 mol) in toluene (450 mL) was refluxed for 4 h and evolved HCl was absorbed with H_2O. The solvent was evaporated in vacuum at 30–45 °C and the residue like sour cream was cooled. The precipitate was filtered off, washed with ice H_2O up to pH 7 and dried in the vacuum desiccator to afford **3** (55.7 g, 95.4%), m.p. 168–169 °C ($CHCl_3$) (lit. m.p. 170–171 °C [16b]).

4.2.3.2. Preparation by $POCl_3$ with Py. A mixture of 2,4,6-tris(-chlorosulfonyl)phenol (**1**) (10 g, 26.0 mmol) and pyridine (0.6 mL, 7.45 mmol) in $POCl_3$ (20 mL) was refluxed until the gas evolution stopped (about 2 h). The cooled reaction mixture was poured into H_2O. The obtained oil was mashed to precipitate formation, that was filtered off, washed with H_2O up to pH 7 and dried in the vacuum desiccator over NaOH and H_2SO_4 to afford **3** (9.54 g, 91%), m.p. 165–169 °C ($CHCl_3$).

A mixing test of the samples obtained by different given methods did not show a m.p. depression.

4.2.4. Potassium 2,4,6-tris(fluorosulfonyl)phenolate (4)

4.2.4.1. From 2,4,6-tris(chlorosulfonyl)phenol (1). $KF{\cdot}2H_2O$ (61.0 g, 0.65 mol) was calcinated on the open flame and poured without cooling quickly by portions into a warm solution of 2,4,6-tris(chlorosulfonyl)phenol (**1**) (41.8 g, 0.10 mol) in dioxane (170 mL). The mixture was heated under reflux and stirring for 0.5 h, diluted with H_2O (about 100 mL), K_2CO_3 was added till the foaming terminated (pH 7–8) and dioxane was evaporated in vacuum. The residue was crystallized from H_2O (the hot solution was treated with charcoal) to afford **4** (30.6 g, 80.8%) in the form of a snow-white crystals. M.p. > 250 °C. ^1H NMR ([D_6]acetone): δ = 8.6 (s, ArH) ppm. ^{19}F NMR ([D_6]acetone): δ = 55.6 (s, 2F, *o*-SO_2F), 68.9 (s, 1F, *p*-SO_2F) ppm. $C_6H_2F_3O_7S_3K$ (378.37): calcd. C 19.05, H 0.53, S 25.42; found C 19.18, H 0.68, S 25.15.

4.2.4.2. From 2,4,6-tris(chlorosulfonyl)chlorobenzene (3) by $KF{\cdot}2H_2O$. $KF{\cdot}2H_2O$ (68.7 g, 0.73 mol) was added by portions to the boiling solution of 2,4,6-tris(chlorosulfonyl)chlorobenzene (**3**) (49.5 g, 0.12 mol) in dioxane (130 mL). The mixture was stirred under reflux for 1 h. The sticky precipitate that adhered to the walls of the flask was scraped off periodically. Dioxane was removed under reduced pressure and the crude product was extracted with acetone. After solvent vacuum evaporation the residue was treated with H_2O and solution obtained was neutralized with K_2CO_3 up to pH 7–8. The precipitated potassium salt was crystallized from H_2O. The residue insoluble in hot water was filtered off quickly and extracted by CH_2Cl_2 to afford 2,4,6-tris(fluorosulfonyl)chlorobenzene (**6**) (5.2 g, 12%). The hot water solution after cooling afforded **4** (31.2 g, 68.0%).

4.2.4.3. From 2,4,6-tris(chlorosulfonyl)chlorobenzene (3) by anhydrous KF with 1.5 equiv. H_2O. A solution of H_2O (0.7 mL, 0.04 mol) in dioxane (10 mL) was added dropwise to a suspension of $KF{\cdot}2H_2O$ (15.3 g, 0.16 mol), that was beforehand calcinated on the open flame, in dioxane (15 mL). 2,4,6-Tris(chlorosulfonyl)chlorobenzene (**3**) (11.0 g, 0.027 mol) was added and mixture was boiled with stirring for 30 min. After cooling, acetone (50 mL) and K_2CO_3 (up to foam termination) were added, the solvents were evaporated in vacuum and the residue was washed several times with acetone. After removing acetone, the residue was crystallized from H_2O to afford the potassium salt **4** (7.3 g, 71%).

4.2.4.4. From lithium 2,4,6-tris(fluorosulfonyl)phenolate (8). To a stirred solution of lithium 2,4,6-tris(fluorosulfonyl)phenolate (**8**) (18.8 g, 54.27 mmol) in H_2O (40 mL) was added a solution of KBr (6.64 g, 55.6 mmol) in H_2O (10–15 mL). The precipitate was filtered off, washed with H_2O, dried at 100 °C to afford **4** (20.0 g, 97%).

The samples obtained by different given methods have identical ^1H and ^{19}F NMR spectra.

4.2.5. 2,4,6-Tris(fluorosulfonyl)phenol (5)

4.2.5.1. From potassium 2,4,6-tris(fluorosulfonyl)phenolate (4). A solution of potassium 2,4,6-tris(fluorosulfonyl)phenolate (**4**) (104.6 g, 0.27 mol) in MeOH (250 mL) was saturated with dry HCl at 20 °C. The precipitated KCl was filtered off, the solvent was removed under reduced pressure to afford **5** (92 g, 97.8%), m.p. 143–144 °C ($CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.0 (br. s, 1H, OH), 8.86 (s, 2H, ArH); ([D_6]acetone): δ = 8.44 (s, ArH) ppm. ^{19}F NMR ([D_6]acetone): δ = 55.6 (s, 2F, *o*-SO_2F), 68.7 (s, 1F, *p*-SO_2F) ppm. ^{13}C NMR ([D_6]acetone): δ = 118.8 (m, 1C, 4-C), 124.6 (d, $^2J_{C,F}$ = 25.2 Hz, 2C, 2-C, 6-C), 139.1 (s, 2C, 3-C, 5-C), 163.1 (s, 1C, 1-C) ppm. $C_6H_3F_3O_7S_3$ (340.27); calcd. C 21.18, H 0.89, S 28.27; found C 21.09, H 0.90, S 28.38.

4.2.5.2. From 2,4,6-tris(fluorosulfonyl)chlorobenzene (6). A solution of 2,4,6-tris(fluorosulfonyl)chlorobenzene (**6**, 0.05 g, 0.14 mmol) in MeOH (2 mL) was heated under reflux (about 3.5 h). The solvent was removed under reduced pressure to afford phenol **5** (0.047 g, 99.0%), m.p. 141–143 °C ($CHCl_3$).

A mixing test of the samples obtained by different given methods did not show a m.p. depression.

4.2.6. 2,4,6-Tris(fluorosulfonyl)chlorobenzene (6)

4.2.6.1. Preparation with PCl_5. A mixture of potassium 2,4,6-tris(fluorosulfonyl)phenolate (**4**, 10.0 g, 26.43 mmol) and PCl_5 (11.0 g, 52.8 mmol) in toluene (90 mL) was refluxed for 3.5 h. The solvent was condensed in vacuo, the residue was pressed out, washed with ice-water till pH 7 and finally the precipitate was

dried in a vacuum desiccator over P_4O_{10} to afford **6** (8.5 g, 89.6%), m.p. 186.8–189.3 °C ($CHCl_3$, twice), R_f = 0.8 (benzene). ^1H NMR ([D_6]acetone): δ = 9.20 (s, ArH) ppm. ^{19}F NMR ([D_6]acetone): δ = 59.6 (s, 2F, *o*-SO_2F), 66.6 (s, 1F, *p*-SO_2F) ppm. ^{13}C NMR ([D_8]THF): δ = 132.9 (d, $^2J_{C,F}$ = 31.2 Hz, 1C, 4-C), 136.7 (d, $^2J_{C,F}$ = 28.6 Hz, 2C, 2-C, 6-C), 137.6 (s, 2C, 3-C, 5-C), 140.8 (s, 1C, 1-C) ppm. $C_6H_2ClF_3O_6S_3$ (358.73): calcd. C 20.09, H 0.56, Cl 9.88, S 26.82; found C 20.23, H 0.41, Cl 10.08, S 26.64.

4.2.6.2. Preparation with $POCl_3$ and pyridine. A mixture of potassium 2,4,6-tris(fluorosulfonyl)phenolate (**4**, 3.0 g, 7.93 mmol) and pyridine (0.2 mL, 2.48 mmol) in $POCl_3$ (3 mL) was refluxed for 2 h and poured out onto ice. The obtained oil was rubbed with a glass stick until solidification. The latter was filtered off, washed with ice-water till pH 7 and dried under reduced pressure over P_4O_{10} to afford **6** (2.56 g, 90%), R_f = 0.8 (benzene). M.p. 177–180 °C (toluene).

A mixing test of the samples obtained by different given methods did not show a m.p. depression.

4.2.7. 2,4,6-Tris(fluorosulfonyl)aniline (7)

$KF{\cdot}2H_2O$ (1.5 g, 15.94 mmol) was calcinated on an open flame and poured without cooling in portions into a warm solution of 2,4,6-tris(chlorosulfonyl)aniline (**2** 1.0 g, 2.57 mmol) in dioxane (4 mL) with H_2O (0.08 mL, 4.44 mmol). The mixture was refluxed for about 1.5–2 h. After addition of H_2O the precipitate formed was filtered off and dried to afford aniline **7** (0.68 g, 77.9%). M.p. 203.5–205.5 °C (benzene) (lit. m.p. 196–198 °C [12c]). ^1H NMR ([D_6]DMSO): δ = 8.3 (s, 2H, NH_2), 8.6 (s, 2H, ArH) ppm. ^{19}F NMR ([D_6]DMSO): δ = 61.4 (s, 2F, *o*-SO_2F), 68.5 (s, 1F, *p*-SO_2F) ppm. ^{13}C NMR ([D_6]DMSO): δ = 116.5 (d, $^2J_{C,F}$ = 27.3 Hz, 1C, 4-C), 116.9 (d, $^2J_{C,F}$ = 26.3 Hz, 2C, 2-C, 6-C), 140.6 (s, 2C, 3-C, 5-C), 149.3 (s, 1C, 1-C) ppm.

A mixing test with an authentic sample [12c] does not show an m.p. depression.

4.2.8. Lithium 2,4,6-tris(fluorosulfonyl)phenolate (8)

4.2.8.1. From potassium 2,4,6-tris(fluorosulfonyl)phenolate (4). A solution of LiCl (3.98 g, 93.9 mmol) in propanol-2 (86 mL) was added to a boiling solution of potassium 2,4,6-tris(fluorosulfonyl)phenolate (**4**, 32.13 g, 84.9 mmol) in propanol-2 (250 mL). After cooling the precipitated KCl was filtered off, the solvent was removed under reduced pressure. The colourless powder obtained was washed with anhydrous $CHCl_3$ and dried in vacuo (0.1 Torr) at 110–120 °C to afford **8** (28.5 g, 96.9%), m.p. > 250 °C. ^1H NMR ($CDCl_3$): δ = 8.39 (s, ArH) ppm. ^{19}F NMR (CD_3CN): δ = 54.3 (s, 2F, *o*-SO_2F), 66.7 (s, 1F, *p*-SO_2F) ppm. $C_6H_2F_3O_7S_3Li$ (346.22); calcd. C 20.82, H 0.58, S 27.78; found C 20.93, H 0.80, S 27.68.

4.2.8.2. From 2,4,6-tris(fluorosulfonyl)phenol (5). A mixture of 2,4,6-tris(fluorosulfonyl)phenol (**5**, 5 g, 14.7 mmol) and, Li_2CO_3 (1.4 g, 18.95 mmol) in MeOH (20 mL) was kept for 18–24 h at 20–25 °C. The excess of Li_2CO_3 was filtered off, MeOH was removed under reduced pressure. The residue was washed with anhydrous $CHCl_3$, toluene, dried by azeotropic distillation with toluene, filtered off and dried in vacuo (0.1 Torr) at 70 °C to afford **8** (5.08 g, 99.8%). ^1H NMR ([D_6]acetone): δ = 8.36 (s, ArH) ppm. ^{19}F NMR ([D_6]acetone): δ = 55.5 (s, 2F, *o*-SO_2F), 68.9 (s, 1F, *p*-SO_2F) ppm.

4.2.8.2.1. Crystallization of lithium 2,4,6-tris(fluorosulfonyl)phenolate (8) hydrate dimer for X-ray investigation. Anhydrous lithium 2,4,6-tris(fluorosulfonyl)phenolate (**8**) was dissolved in mixture of diethyl ether and hexane. The mother liquor was stored at room temperature under a ventilated hood for several days to precipitate colourless crystals of $[Li(OC_6H_2(2,4,6\text{-}SO_2F)_3{\cdot}H_2O]_2$.

4.2.9. Cesium 2,4,6-tris(fluorosulfonyl)phenolate (9)

To a stirred solution of 2,4,6-tris(fluorosulfonyl)phenol (**5**, 2.0 g, 5.88 mmol) in H_2O (25 mL) a solution of Cs_2SO_4 (1.12 g, 3.1 mmol) in H_2O (10 mL) was added. The precipitate was filtered off, washed with H_2O to afford **9** (2.13 g, 76.7%). ^1H NMR ([D_6]acetone): δ = 8.24 (s, ArH) ppm. ^{19}F NMR ([D_6]DMSO): δ = 57.1 (s, 2F, *o*-SO_2F), 70.8 (s, 1F, *p*-SO_2F) ppm. $C_6H_2CsF_3O_7S_3$ (472.17); calcd. C 15.26, H 0.43, F 12.06, S 20.37; found C 15.17, H 0.63, F 12.10, S 20.14.

4.2.10. Barium 2,4,6-tris(fluorosulfonyl)phenolate (10)

To a stirring solution of 2,4,6-tris(fluorosulfonyl)phenol (**5**, 0.6 g, 1.76 mmol) in H_2O (1.0 mL) a solution of $BaCl_2{\cdot}2H_2O$ (0.52 g, 2.13 mmol) in H_2O (0.3 mL) was added. The precipitate was filtered off, washed with water and dried under reduced pressure (0.1 Torr) to afford **10** (0.59 g, 70.3%). ^1H NMR ([D_6]acetone): δ = 8.24 (s, ArH) ppm. ^{19}F NMR ([D_6]acetone): δ = 55.6 (s, 2F, *o*-SO_2F), 67.7 (s, 1F, *p*-SO_2F) ppm. $C_{12}H_4BaF_6O_{14}S_6$ (815.86); calcd. C 17.67, H 0.49, S 27.45; found C 17.52, H 0.60, S 27.21.

4.2.11. Hexaaquamagnesium bis(2,4,6-tris(fluorosulfonyl)phenolate)) trihydrate (11)

A mixture of 2,4,6-tris(fluorosulfonyl)phenol (**5**, 1.54 g, 4.52 mmol) with magnesium shavings (0.10 g, 4.12 mmol) in H_2O (5 mL) was stirred until gas evolution was no more observed. After filtration, the solution was concentrated under reduced pressure (0.1 Torr), formed precipitate was filtered off to afford **11** (1.25 g, 64%). ^1H NMR ([D_6]acetone): δ = 4.55 (br. s, 9H, H_2O), 8.38 (s, 2H, ArH) ppm. ^{19}F NMR ([D_6]acetone): δ = 55.0 (s, 2F, *o*-SO_2F), 68.0 (s, 1F, *p*-SO_2F) ppm. $C_{12}H_{22}F_6MgO_{23}S_6$ (864.98); calcd. C 16.66, H 2.56, S 22.24; found C 16.68, H 2.49, S 21.96.

4.2.12. Hexaaquazinc bis(2,4,6-tris(fluorosulfonyl)phenolate)) pentasesqui hydrate (12)

A mixture of 2,4,6-tris(fluorosulfonyl)phenol (**5**, 1.15 g, 3.38 mmol) with zinc powder (0.20 g, 3.06 mmol) in H_2O (1.5 mL) was stirred until gas evolution was no more observed. After filtration, the solution was concentrated under reduced pressure (0.1 Torr), formed precipitate was filtered off to afford **12** (0.77 g, 48%). ^1H NMR ([D_6]acetone): δ = 4.10 (br. s, 11.5H, H_2O), 8.30 (s, 2H, ArH) ppm. ^{19}F NMR ([D_6]acetone): δ = 55.2 (s, 2F, *o*-SO_2F), 68.1 (s, 1F, *p*-SO_2F) ppm. $C_{12}H_{27}F_6O_{25.5}S_6Zn$ (951.08); calcd. C 15.15, H 2.86, S 20.23; found C 14.87, H 2.95, S 19.92.

4.2.13. Various pyridinium 2,4,6-tris(fluorosulfonyl)phenolate derivatives (13–15). General procedure

To a stirred solution of 2,4,6-tris(fluorosulfonyl)phenol (**5**, 2.0 g, 5.88 mmol) in MeCN (30 mL) a solution of a corresponding pyridine (5.88 mmol) in MeCN (10 mL) was added. The solution was stirred for 5 min, MeCN was removed under reduced pressure (0.1 Torr) to afford **13–15** in quantitative yields.

4.2.13.1. Pyridinium 2,4,6-tris(fluorosulfonyl)phenolate (13). Pyridine was used. M.p. 175.8–177.2 °C (propanol-2). ^1H NMR ([D_6]DMSO): δ = 8.00 (m, 2H, 3,5-ArH (Py)), 8.24 (s, 2H, ArH), 8.52 (m, 1H, 4-ArH (Py)), 8.89 (m, 2H, 2,6-ArH (Py)) ppm. ^{19}F NMR ([D_6]DMSO): δ = 57.2 (s, 2F, *o*-SO_2F), 70.9 (s, 1F, *p*-SO_2F) ppm. $C_{11}H_8F_3NO_7S_3$ (419.38); calcd. C 31.50, H 1.92, N 3.34, S 22.94; found C 31.72, H 1.98, N 3.34, S 22.95.

4.2.13.2. 2,4,6-Trimethylpyridinium 2,4,6-tris(fluorosulfonyl)phenolate (14). 2,4,6-Trimethylpyridine (collidine) was used. M.p. 201.8–204.7 °C (propan-2-ol). ^1H NMR ([D_6]acetone): δ = 2.48 (s, 3H, 4-CH_3-Py), 2.62 (s, 6H, 2,4-CH_3-Py), 7.57 (s, 2H, 3,5-ArH (Py)), 8.23 (s, 2H, ArH) ppm. ^{19}F NMR ([D_6]DMSO): δ = 55.2 (s, 2F, *o*-SO_2F), 68.9 (s, 1F, *p*-SO_2F) ppm. $C_{14}H_{14}F_3NO_7S_3$ (461.46); calcd. C 36.44, H 3.06, N 3.04, S 20.85; found C 36.45, H 2.85, N 2.98, S 20.78.

*4.2.13.3. 4-(N,N-Dimethylamino)pyridinium 2,4,6-tris(fluorosulfonyl)phenolate (**15**).* 4-(*N*,*N*-Dimethylamino)pyridine (DMAP) was used. M.p. 179.8–181.5 °C. ^{1}H NMR ([D$_6$]acetone): δ = 3.36 (s, 6H, NMe$_2$), 7.14 (d, $^2J_{H,H}$ = 7.4 Hz, 2H, 3,5-ArH (Py)), 8.30 (d, $^2J_{H,H}$ = 7.4 Hz, 2H, 2,6-ArH (Py)), 8.39 (s, 2H, ArH) ppm. ^{19}F NMR ([D$_6$]acetone): δ = 54.8 (s, 2F, *o*-SO$_2$F), 67.7 (s, 1F, *p*-SO$_2$F) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 39.5 (s, 2C, NMe$_2$), 106.9 (d, $^2J_{C,F}$ = 27 Hz, 1C, 4-C), 107.2 (s, 2C, 3-C, 5-C (Py)), 124.6 (d, $^2J_{C,F}$ = 21 Hz, 2C, 2-C, 6-C), 138.9 (s, 2C, 3-C, 5-C), 139.1 (s, 2C, 2-C, 6-C (Py)), 167.4 (s, 1C, 1-C) ppm. $C_{13}H_{13}F_3N_2O_7S_3$ (462.44); calcd. C 33.77, H 2.83, N 6.06, S 20.80; found C 33.66, H 2.79, N 6.15, S 20.75.

*4.2.14. Tetraalkylammonium 2,4,6-tris(fluorosulfonyl)phenolates (**16**–**18**). General procedure*

To a stirred solution of 2,4,6-tris(fluorosulfonyl)phenol (**5**, 2.0 g, 5.88 mmol) in H_2O (120 mL) a solution of a corresponding tetraalkylammonium iodide or hydroxide (6.17 mmol) in H_2O or MeOH (60 mL) was added. The formed precipitate was filtered off, washed with water to afford the tetraalkylammonium 2,4,6-tris(fluorosulfonyl)phenolate (**16**–**18**).

*4.2.14.1. Tetramethylammonium 2,4,6-tris(fluorosulfonyl)phenolate (**16**).* Tetramethylammonium iodide was used. Yield 81%. m.p. 240–242.7 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 3.09 (s, 12H, CH$_3$), 8.24 (s, 2H, ArH) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = 57.2 (s, 2F, *o*-SO$_2$F), 70.9 (s, 1F, *p*-SO$_2$F) ppm. $C_{10}H_{14}F_3NO_7S_3$ (413.41); calcd. C 29.05, H 3.41, N 3.39, S 23.27; found C 29.17, H 3.34, N 3.48, S 23.35.

*4.2.14.2. Tetraethylammonium 2,4,6-tris(fluorosulfonyl)phenolate (**17**).* Tetraethylammonium iodide was used. Yield 93%. m.p. 168–170 °C (propanol-2). ^{1}H NMR ([D$_6$]DMSO): δ = 1.16 (t, $^2J_{H,H}$ = 7.3 Hz, 12H, CH$_3$), 3.20 (q, $^2J_{H,H}$ = 7.3 Hz, 8H, CH$_2$) 8.24 (s, 2H, ArH) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = 55.2 (s, 2F, *o*-SO$_2$F), 68.8 (s, 1F, *p*-SO$_2$F) ppm. $C_{14}H_{22}F_3NO_7S_3$ (469.52); calcd. C 35.81, H 4.72, N 2.98, S 20.49; found C 35.79, H 4.79, N 3.07, S 20.35.

*4.2.14.3. Tetrabuthylammonium 2,4,6-tris(fluorosulfonyl)phenolate (**18**).* Tetrabuthylammonium hydroxide 0.1 M solution in MeOH was used. Yield 95%. m.p. 91.6–93.6 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 0.93 (t, $^2J_{H,H}$ = 7.2 Hz, 12H, CH$_3$), 1.30 (m, $^2J_{H,H}$ = 7.5 Hz, 8H, CH$_2$), 1.56 (m, 8H, CH$_2$), 3.15 (m, 8H, CH$_2$) 8.24 (s, 2H, ArH) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = 57.1 (s, 2F, *o*-SO$_2$F), 70.8 (s, 1F, *p*-SO$_2$F) ppm. $C_{22}H_{38}F_3NO_7S_3$ (581.74); calcd. C 45.42, H 6.58, N 2.41, S 16.54; found C 45.55, H 6.68, N 2.49, S 16.31.

Acknowledgment

The generous financial support of this work by the DFG (Grant 436 UKR 113) is gratefully acknowledged.

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