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Oxidation of Electron-Deficient Sulfides to Sulfones Using HOF·CH_3CN[†]

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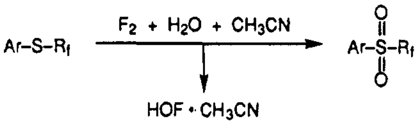
Introduction

The direct oxidation of sulfides to sulfones is a well-known, easy process for many alkyl and aryl substrates, but complications can arise with less reactive, electron-deficient sulfides, particularly perfluoroalkylated ones. Only a few methods for converting perfluoroalkyl sulfides to sulfones have been reported, and they typically require reagents like chromic anhydride or concentrated H_2O_2/trifluoroacetic acid/trifluoroacetic anhydride,[1] although even these potent oxidants often are not very efficient. Some time ago we introduced the HOF·CH_3CN complex reagent, made by simply adding elemental fluorine to aqueous acetonitrile,[2] and it proved to be an excellent oxygen transfer agent in direct aliphatic[3] and aromatic[4] hydroxylations, epoxidations,[5] and hydroxyl, carbonyl,[6] and amine oxidations.[7] The complex also can be used to quantitatively oxidize thiophenes[8] and common hydrocarbon sulfides[9] in a matter of seconds.

The latter finding prompted us to try oxidizing perfluoroalkyl sulfides to the corresponding sulfones with HOF·CH_3CN. We report here its successful use to convert aryl perfluoroalkyl sulfides to sulfones, $ArSO_2R_f$, some of which are useful second-order, nonlinear optical materials.[10]

Results and Discussion

The *n*-perfluoroalkyl sulfide substrates, perfluoro-*n*-butyl *p*-tolyl sulfide (**1**) and perfluoro-*n*-octyl *p*-tolyl sulfide (**2**), were prepared by reacting *p*-thiocresol with the corresponding perfluoroalkyl iodide in the presence of equimolar 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[11] Under conditions sufficient to convert hydrocarbon sulfides to sulfones,[9] namely 2.2 equiv of HOF·CH_3CN (10% excess) for 5 min, **1** and **2** were essentially inert. With a 4- to 5-fold excess of HOF·CH_3CN (8–10 equiv), however, the corresponding sulfones **3** and **4** were obtained in over 90% yield after 20 min at room temperature. When less than about a 4-fold excess of reagent was used, sulfone was still the main product but accompanied by up to 20% of the sulfoxide intermediate.



1	Ar = *p*-$CH_3C_6H_4$; R_f = n-C_4F_9	**3**	(95%)
2	Ar = *p*-$CH_3C_6H_4$; R_f = n-C_8F_{17}	**4**	(90%)
5	Ar = R_f = C_6F_5	**6**	(98%)
7	Ar = *p*-FC_6H_4 ; R_f = $C(CF_3)_3$	**9**	(94%)
8	Ar = *p*-FC_6H_4 ; R_f = $C(CF_3)_2CF_2CF_2CF_3$	**10**	(74%)

Bis(perfluoroaryl) sulfides, such as bis(pentafluorophenyl) sulfide (**5**), were somewhat less reactive than **1** or **2**, but a 7-fold excess of HOF·CH_3CN at room temperature for 20 min did afford the sulfone **6**[12] in nearly quantitative yield. By contrast, less than 2% of **5** was converted to **6** when it was treated with *m*-chloroperoxybenzoic acid in CH_2Cl_2 for 18 h or with hot 30% H_2O_2/CH_3CO_2H.

The sterically hindered aryl perfluoroalkyl sulfides **7** or **8**, which were prepared by reacting *p*-fluorobenzensulfenyl chloride[13] with perfluoroisobutylene or perfluoro-2-methylpent-2-ene and KF in DMF,[14] proved even less susceptible to oxidation. To achieve full conversion to sulfone, a 30–40 excess of HOF·CH_3CN for 1 h at room temperature was required. Under these conditions, **7** and **8** were converted to **9** and **10** in 94 and 74% yields, respectively.

These results with oxidation-resistant sulfides again demonstrate the unusual oxidative power and versatility of the HOF·CH_3CN complex,[15] which is the only known oxidant possessing a truly permanent electrophilic oxygen.

Experimental Section

^1H NMR spectra were recorded with $CDCl_3$ as solvent and Me_4Si as internal standard. The ^{19}F NMR spectra were measured at 338.8 MHz and are reported in parts per million upfield from $CFCl_3$, which also served as internal standard. IR spectra were recorded as neat films in $CHCl_3$ solution or in KBr pellets.

General Procedures for Preparation of the Aryl Perfluoroalkyl Sulfides. The sulfides **1** and **2** were prepared by mixing under nitrogen 1 g of *p*-thiocresol, 20 mL of dry benzene, and 1 equiv of DBU.[11] The mixture was cooled to about 5 °C, and then an equimolar amount of the corresponding perfluoroalkyl iodide was added. The reaction then was stirred overnight at room temperature, added to water, and extracted with $CHCl_3$. The organic extract was dried over $MgSO_4$, filtered, and evaporated. The products were usually flash chromatographed and obtained in over 95% purity.

The more sterically hindered sulfides **7** and **8** were prepared by reacting first a CH_2Cl_2 solution of *p*-fluorothiophenol under

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[15] Bis(perfluoroalkyl) sulfides, $F(CF_2)_nS(CF_2)_mF$, however, are inert to oxidation by HOF·CH_3CN under any conditions tested so far.

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nitrogen with a 10% molar excess of sulfuryl chloride in the presence of a catalytic amount of triethylamine. After standing overnight at room temperature, the mixture was diluted with CCl_4, filtered, concentrated, and distilled to give the expected *p*-fluorobenzenesulfenyl chloride in 80% yield: bp 45 °C/2 mm Hg; ^{1}H NMR δ 7.7 (m, 2H), 7.1 (m, 2H). This sulfenyl chloride was then reacted with the appropriate perfluoroolefin and KF as described below.

Perfluorobutyl *p*-tolyl sulfide (1) was obtained in 60% yield as an oil: ^{1}H NMR δ 7.53 and 7.22 (AB m, J = 8.1 Hz, 4H), 2.38 (s, 3H); ^{19}F NMR δ −81.5 (t, J = 9 Hz, 3F), −87.9 (t, J = 10 Hz, 2F), −120.6 (m, 2F), −126.0 (m, 2F); MS, *m/z* 342 (M^+).

Perfluorooctyl *p*-tolylsulfide (2)[16] was obtained in 50% yield as an oil: ^{1}H NMR δ 7.53 and 7.21 (AB m, J = 8.1 Hz, 4H), 2.38 (s, 3H); ^{19}F NMR δ −81.5 (t, J = 10 Hz, 3F), −87.56 (dt, J = 10, 3 Hz, 2F), −119.54 (m, 2F), −121.56 (m, 2F), −122.3 (m, 2F), −123.15 (m, 2F), −126.66 (m, 2F); MS, *m/z* 542 (M^+), 123 $(CH_3C_6H_4S)^+$.

***p*-Fluorophenyl perfluoro-*tert*-butyl sulfide (7)** was obtained by adding 12 g of perfluoroisobutylene (*CAUTION: EXTREMELY TOXIC GAS.* Should be handled only by an experienced worker in a well-ventilated hood!) to 3.6 g of dry KF in 200 mL of dry DMF followed by a slow addition at 0 °C of 8.4 g of *p*-fluorobenzenesulfenyl chloride obtained by the procedure outlined above. After 1 h the reaction was purged with nitrogen and the off gas was thoroughly scrubbed with methanol (which converts any unreacted perfluoroisobutylene to methyl ethers). Methanol was then added to the reaction which was stirred for 30 min before workup. The crude mixture was distilled to give **7** in 60% yield: bp 50-52 °C/4.5 mmHg; ^{1}H NMR δ 7.7 (m, 2H), 7.1 (m, 2H); ^{19}F NMR δ −64.7 (s, 9F), −107.2 (s, 1F); MS, *m/z* 346 (M^+), 127 $(FC_6H_4S)^+$.

***p*-Fluorophenylperfluoro-2-methyl-2-pentylsulfide (8)** was prepared similarly in 75% yield from perfluoro-2-methylpent-2-ene (HFP dimer): bp 58−59 °C/1.5 mmHg; ^{1}H NMR δ 7.7 (m, 2H), 7.1 (m, 2H); ^{19}F NMR δ −65.5 (s, 6F), −80.78 (t, 14 Hz, 3F), −105.35 (m, 2F), −107.2 (s, 1F), −122.5 (m, 2F); MS, *m/z* 446 (M^+), 127 $(FC_6H_4S)^+$.

General Procedure for Working with Fluorine. Fluorine is a strong oxidant and a very corrosive material. An appropriate vacuum line made from copper or monel in a well ventilated area should be constructed for working with this element. Additional experimental information on handling fluorine is recommended.[17] For the occasional user, however, various premixed mixtures of F_2 in inert gases are commercially available, which simplifies handling. The reactions can be carried out in glass vessels.

General Procedure for Producing $HOF\cdot CH_3CN$ Complex. Mixtures of 10−15% F_2 diluted with nitrogen were prepared in a secondary container before the reaction was started. This mixture was then added at a rate of about 400 mL/min to a cold (−10 °C) and vigorously stirred mixture of 400 mL of CH_3CN and 40 mL of H_2O. The formation of the oxidant was monitored by reacting aliquots with acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. The concentration of oxidant used in this work was about 0.25 M, although concentrations of more than 1 M oxidizing reagent can be generated in this manner.

General Oxidation Procedure. The aryl perfluoroalkyl sulfide (0.5−1.5 g) was dissolved in about 30−50 mL of CH_2Cl_2, cooled to 0 °C, and added in one portion to the reaction vessel in which the oxidizing agent had been prepared. At least a 4-fold excess of 0.25 M $HOF\cdot CH_3CN$ was used. The cooling bath was removed, and after the reaction was completed the solution was neutralized with saturated sodium bicarbonate solution and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent distilled. The crude product was either flash chromatographed or recrystallized.

Perfluorobutyl *p*-tolyl sulfone (3) was obtained in 95% yield as a yellow oil from **1** by using 9 molar equiv of $HOF\cdot CH_3CN$ for 20 min: IR 1371, 1352, 1239, 1171, 1141 cm^{-1}; ^{1}H NMR δ 7.92 and 7.48 (AB m, J = 8.1 Hz, 4H), 2.52 (s, 3H); ^{19}F NMR δ −81.3 (t, J = 10 Hz, 3F), −112.2 (t, J = 9 Hz, 2F), −121.24 (m, 2F), −126.5 (m, 2F); MS, *m/z* 374 (M^+). Anal. Calcd for $C_{11}H_7F_9O_2S$: C, 35.31; H, 1.89. Found: C, 35.34; H, 1.97.

Perfluorooctyl *p*-tolyl sulfone (4) was obtained in 90% yield using 10 molar equiv of $HOF\cdot CH_3CN$ for 10 min: mp 78 °C (from EtOH); IR 1357, 1202, 1172, 1149 cm^{-1}; ^{1}H NMR δ 7.92 and 7.47 (AB m, J = 8.1 Hz, 4H), 2.52 (s, 3H); ^{19}F NMR δ −81.1 (dt, J = 10, 2.5 Hz, 3F), −111.9 (t, J = 13 Hz, 2F), −120.1 (m, 4F), −121.8 (m, 2F), −122.0 (m, 2F), −123.0 (m, 2F), -126.4 (m, 2F); MS, *m/z* 574 (M^+). Anal. Calcd for $C_{15}H_7F_{17}O_2S$: C, 31.37; H, 1.23. Found: C, 31.62; H, 1.32.

Bis(pentafluorophenyl) sulfone (6)[12] was obtained in 98% yield using 15 molar equiv of $HOF\cdot CH_3CN$ for 20 min: mp 122 °C (from EtOH); IR 1303, 1178 cm^{-1}; ^{19}F NMR δ −136 (d, J = 20 Hz, 4F), −141.4 (m, 2F), −157.9 (t, J = 20 Hz, 4F); MS, *m/z* 398 (M^+).

***p*-Fluorophenyl perfluoro-*tert*-butyl sulfone (9)**[1a] was formed in 94% yield: mp 56 °C (from MeOH); IR 780, 1380, 1415, 3120 cm^{-1}; ^{1}H NMR δ 7.3 (m, 2H), 8.1 (m, 2H); ^{19}F NMR δ −62.1 (s, 9F), −97.5 (heptet, J = 4 Hz, 1 arom F); MS *m/z* 378 $(M)^+$, 159 $(FC_6H_4SO_2)^+$, 95 $(FC_6H_4)^+$, 69 $(CF_3)^+$.

***p*-Fluorophenyl perfluoro-2-methyl-2-pentyl sulfone (10)** was formed in 74% yield after a 1 h reaction between **8** and $HOF\cdot CH_3CN$: mp 44 °C (from MeOH); IR 780, 1385, 1420, 3120 cm^{-1}; ^{1}H NMR δ 7.3 (m, 2H), 8.1 (m, 2H); ^{19}F NMR δ −59.3 (heptet, J = 9 Hz, 6F), −80.6 (t, J = 14 Hz, 3F), −97.7 (heptet, J = 5 Hz, 1 arom F), −103.0 (m, 2F), −121.3 (m, 2F); MS *m/z* 459 $(M - F)^+$, 159 $(FC_6H_4SO_2)^+$, 95 $(FC_6H_4)^+$, 69 $(CF_3)^+$. Anal. Calcd for $C_{12}H_4F_{14}O_2S$: C, 30.14; H, 0.84. Found: C, 30.01; H, 0.89.

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