Oxidation of Sulfur-Containing Compounds with HOF·CH_3CN

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The HOF·CH_3CN complex, easily prepared by passing F_2 through aqueous acetonitrile, is an exceptionally efficient oxygen transfer agent. All types of sulfides have been oxidized to sulfones in excellent yields, in a few minutes at room temperature. The reaction proceeds through the formation of sulfoxides which at low temperatures of around −75 °C could be isolated in good yields. It was demonstrated through a reaction with thianthrene 5-oxide (**20**) that HOF·CH_3CN is strongly electrophilic in nature. Sulfides with an electron-depleted sulfur atom such as perfluoroalkyl or aryl sulfides, which could not be well oxidized by any other method, were also efficiently converted to the corresponding sulfones in minutes. Thiophenes are generally hard to oxidize to the corresponding *S*-dioxides since the conditions required by the orthodox oxidants encourage consecutive typical ene and diene reactions. HOF·CH_3CN requires short reaction times and low temperatures, thus enabling the isolation of thiophene dioxides, some of which could not be made by any other way. It seems that apart from unprotected amines, other functional groups such as aromatic rings, ketones, hydroxyls, and ethers do not interfere, since the sulfur atom reacts considerably faster.

The HOF·CH_3CN complex developed about 10 years ago[1] is one of the most powerful electrophilic oxidants organic chemistry has to offer. It is easily made by simply bubbling 10−15% fluorine in nitrogen through aqueous acetonitrile and is quick to react with substituents, under the mildest possible conditions.[2] We have shown that it readily epoxidizes olefins,[3] including electron-depleted ones,[4] and oxidizes aromatic and aliphatic amines to the corresponding nitro derivatives.[5] It also transforms alcohols[6] and ethers[7] to the respective aldehydes and ketones which then could be further oxidized to form the corresponding acids and esters via a Baeyer−Villiger type of reaction. Complexation with acetonitrile is essential, since it stabilizes the hypofluorous acid for several hours at room temperature, in sharp contrast to the noncomplexed molecule which is unstable at temperatures above −70 °C and hence of little use for synthetic purposes.[8] Its oxidizing power is derived from the fact that the oxygen is bonded to the only atom with higher electronegativity, fluorine, turning it into a strong electrophile. Associated with all these reactions is the formation of HF, and this is an additional driving force. It facilitates the process to a point that most reactions are completed at room temperature or below, almost instantaneously. In this report we evaluate the effect of this ecologically friendly[9] oxidizer on sulfur-containing organic molecules.[10]

Oxidizing sulfides to sulfones is a well established procedure. The transformation, however, requires either lengthy treatment with oxidants which contain polluting heavy metals such as $KMnO_4$[11] and osmium tetraoxide/*N*-oxides,[12] or the use of various peroxides including dimethyldioxirane.[13] In addition the reactions may require many hours and high temperatures. The HOF·CH_3CN complex is an excellent oxidant for sulfur atoms, and it rapidly oxidizes most sulfides to the corresponding sulfone in very high yields at room temperature or below.

Sulfides with electron-donating aromatic rings such as methyl *p*-tolyl sulfide (**1**) and 1,1,2,2-tetrahydroperfluorooctyl *p*-tolyl sulfide (**2**), as well as sulfides with electron-withdrawing aromatic rings, e.g. methyl 4-nitrophenyl sulfide (**3**), were oxidized to the corresponding sulfones **4**−**6** in quantitative yield in 4−6 min. Aliphatic sulfides are equally quickly oxidized to sulfones. Butyl sulfide (**7**), *tert*-butyl methyl sulfide (**8**) and even the sterically hindered *tert*-butyl sulfide (**9**) required short reaction times to be converted to the corresponding sulfones **10**−**12** in good yields. The reaction with **9** indicates that the oxidizing species is probably the noncomplexed HOF, whose complexation equilibrium constant is 3,[14] since the complex itself is too big to approach easily the sulfur atom situated between the two bulky *tert*-butyl groups. No surprises were recorded when two sulfur atoms were present in the same molecule as with 2-methyl-1,3-dithiane (**13**). The corresponding disulfone **14** was obtained at room temperature in a few minutes and in higher than 90% yield.

In all of these reactions we have used about 2.1 mol/equiv of the HOF·CH_3CN, each equivalent serving as a donor of one oxygen atom. Under these conditions, practically no sulfoxide is formed. Still it is unrealistic

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[6] Rozen, S.; Bareket, Y.; Kol, M. *Tetrahedron* **1993**, *49*, 8169.

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[8] Andrews, L. A.; Bonnett, R.; Appleman, E. H. *Tetrahedron* **1985**, *41*, 781.

[9] Unlike many other oxidants, which use some kind of undesirable inorganic residue, including heavy metals, the only byproduct of forming and using this reagent is HF, and this can be efficiently trapped by $Ca(OH)_2$ to form the harmless CaF_2.

[10] For preliminary communications on the oxidation of various types of sulfur-containing compounds see: (a) Rozen, S; Bareket, Y. *Tetrahedron Lett.*, **1994**, *35*, 2099. (b) Beckerbauer, R.; Smart, B. E.; Bareket, Y.; Rozen, S. *J. Org. Chem.* **1995**, *60*, 6186. (c) Rozen, S.; Bareket, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1959.

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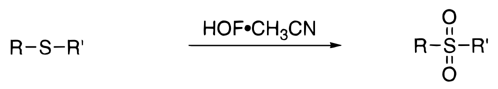
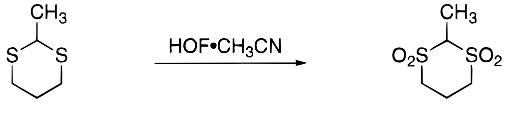
$$F_2 + H_2O + CH_3CN \longrightarrow HF + HOF{\bullet}CH_3CN$$

$$CH_3CN + HOF \xrightleftharpoons{K = 3} HOF{\bullet}CH_3CN$$



1	R = 4-$CH_3C_6H_4$; R' = CH_3	**4**
2	R = 4-$CH_3C_6H_4$; R' = $CH_2CH_2(CF_2)_5CF_3$	**5**
3	R = 4-$NO_2C_6H_4$; R' = CH_3	**6**
7	R = R' = Bu	**10**
8	R = *t*-Bu ; R' = CH_3	**11**
9	R = R' = *t*-Bu	**12**

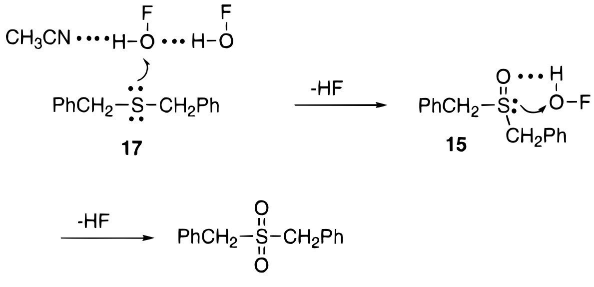


13 **14**

to assume that the corresponding sulfoxide is not an intermediate. On the other hand, if the reaction is electrophilic, the sulfide should be oxidized more easily then the sulfoxide.

Using 1 mol equiv of HOF·CH_3CN on benzyl sulfoxide (**15**) was enough to fully convert it to benzyl sulfone (**16**). Since, however, the reactions of sulfides and sulfoxides with HOF·CH_3CN are both quite fast, it was not easy to determine which one reacted faster. This was resolved by reacting 2 mol equiv of the oxidant with a mixture of 1 mol equiv each of benzyl sulfide (**17**) and sulfoxide (**15**). After 2 to 3 min a full consumption of HOF·CH_3CN was recorded. The resulting mixture constituted 0.6 mol equiv sulfone, 0.24 mol equiv sulfoxide, and only 0.15 mol equiv of the starting sulfide, indicating that the latter reacts considerably faster than the sulfoxide. When only 1 mol equiv of HOF·CH_3CN was applied to **17**, however, 45% was converted to the sulfone **16**, 45% remained unchanged, and only 10% sulfoxide was isolated. These conflicting observations require some explanation, since on the one hand it seems that the sulfide reacts faster than sulfoxide, while on the other hand the latter does not accumulate but is transformed to sulfone faster than is the sulfide.

We believe that sulfides do react initially faster than sulfoxides. HOF·CH_3CN possesses an acidic hydrogen and a fluorine atom capable of hydrogen bonding, since X-ray crystallography shows that the hydrogen atom of this reagent is the one complexed to the acetonitrile.[15] This encourages the formation of clusters of the reagent molecules through hydrogen bonding and is also responsible for its interaction of the reagent with the oxygen of the newly formed sulfoxide. This close proximity allows the continuation of the oxidation to the respective sulfone before the reagent has a chance to depart from the sulfoxide vicinity and react with another sulfide molecule. To give experimental backing for this hypothesis, we repeated the oxidation of **17**, dissolved this time in methanol in order to provide additional centers for hydrogen bonding of both the HOF·CH_3CN and the resulting sulfoxide. As a result the ratio of sulfoxide: sulfone increased from 1:4.5 to 1:2. Repeating the experiment with water-prediluted HOF·CH_3CN resulted in a still higher ratio of **15**:**16** of 1:1.4. With both reagent and sulfide prediluted with water and methanol respectively, the ratio was inverted and three times more sulfoxide was formed than sulfone.

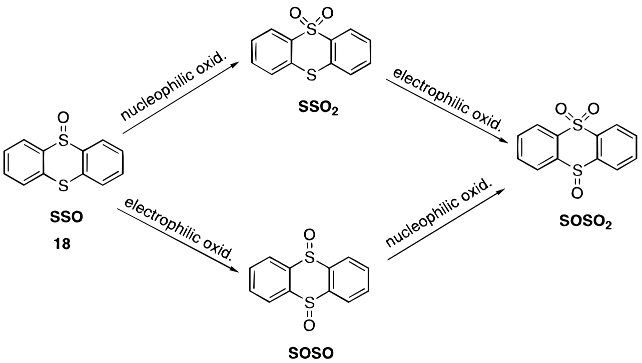


17 **15** **16**

The amount of the sulfoxide **15** could be further increased by lowering the reaction temperature to −78 °C. Such reaction temperatures could be achieved by diluting the acetonitrile solution of the hypofluorous acid with propionitrile. This presumably achieves an equilibrium between the aceto- and propionitrile complexes of HOF. In any event, at this temperature the oxidation of the resulting sulfoxide **15** to sulfone slows down to such an extent that after 10 min **17** was converted to **15** in higher than 90% yield (50% conversion) along with only traces (less than 2%) of the sulfone **16**.

Further support for the initial electrophilic attack of HOF·CH_3CN is derived from its reaction with thianthrene 5-oxide (**18**). Analyzing the ratio of the products SOSO, SSO_2, and $SOSO_2$ has become an acceptable standard for determination of the electrophilicity of oxidizers, since the two sulfur atoms presented are expected to have substantially different electron densities.[16] A parameter of X_{SO} was defined as:

$$X_{SO} = \frac{N_{SSO_2} + N_{SOSO_2}}{N_{SSO_2} + N_{SOSO} + 2N_{SOSO_2}}$$



When the X_{SO} value approaches unity the oxidizer is considered to be nucleophilic, while values of less then 0.5 are indicative of the reagent's electrophilic nature. In a series of experiments we found that at room temperature the X_{SO} value for HOF·CH_3CN is about 0.45 in agreement with its electrophilic character. This value

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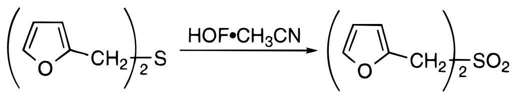
(15) Dunkelberg, O.; Haas, A.; Klapdor, M. F.; Mootz, D.; Poll, W.; Appelman, E. H. *Chem Ber.* **1994**, *127*, 1871.

(16) May, B. L.; Yee, H.; Lee, D. G. *Can. J. Chem.* **1994**, *72*, 2249. Adam, W.; Golsch, D.; Gorth, F. C. *Chem. Eur. J.* **1996**, *2*, 255.

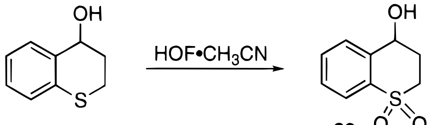
was not considerably lower because of the reagent's tendency to aggregate around the formed sulfoxide through hydrogen bonding as discussed above. When, however, the measurement was conducted at −78 °C, the second stage of the oxidation (sulfoxide → sulfone) is considerably slowed down and the X_{SO} value was reduced to 0.26 which is in line with the strong electrophilicity of the oxidizing reagent.

We checked several other functional groups in the presence of sulfides in order to evaluate the chemoselectivity of HOF·CH$_3$CN. Although it is known that aromatic rings may react with oxidizing agents to give various epoxides and quinones,[17] the reaction with the sulfur atom is much faster. For example, from compound **1** only sulfones were isolated leaving the aromatic ring untouched. Even heterocyclics such as furan derivatives were not effected. By adding slightly less than 2 mol equiv of the oxidant and supplementing the balance at the end of the reaction, furfuryl sulfide **19** was transformed into the corresponding sulfone **20** in 85% yield. The sulfur atom reacts much faster then the hydroxyl moiety as well. Reacting thiochroman-4-ol (**21**) with 2.2 mol equiv of HOF·CH$_3$CN produced, in higher than 90% yield, thiochroman-4-ol *S,S*-dioxide (**22**), which previously has had to be made through the reduction of the 4-keto derivative, since oxidation of the sulfur atom is difficult without affecting the hydroxyl group.[18] Next we examined allyl sulfide (**23**). Applying a small excess of HOF·CH$_3$CN for a short time transformed this sulfide into allyl sulfone (**24**),[19] leaving the double bond untouched. Only when 8.5 mol/equiv (slightly more than twofold excess) of the oxidizing complex was employed for 10 min did a reaction on both the sulfur atom and the double bonds take place, forming 2,3-epoxypropyl sulfone (**25**) in 70% yield readily converted to the corresponding glycol **26**. Ethers are also known to react with HOF·CH$_3$CN,[7] but again the sulfur atom is considerably more reactive and methoxymethyl phenyl sulfide (**27**) was transformed into the corresponding sulfone **28** in almost quantitative yield. It seems that only amino groups can complicate the sulfide−sulfone transformation. 3-Aminophenyl methyl sulfide (**29**) gave an inseparable mixture of products arising from indiscriminate attack on both nitrogen and sulfur. An attempt to slow down the reaction on the amine by protecting it as its hydrochloride salt did not improve the outcome.

While there are a number of alternatives for oxidizing sulfides,[20] there is practically none for clean oxidation of very electron deficient ones. There have been reports of attempts to oxidize perfluoroalkyl sulfides to sulfones with oxidants such as chromic anhydride or concentrated H$_2$O$_2$ in trifluoroacetic acid/trifluoroacetic anhydride, but even these potent oxidants were not very efficient.[21] The HOF·CH$_3$CN complex did succeed where the other oxidants failed, although large excesses were required and reaction times were usually longer between 10 to 30 min.



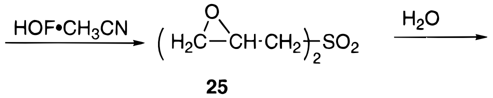
19 **20**



21 **22**

$$(CH_2{=}CH{-}CH_2)_2S \xrightarrow{HOF\bullet CH_3CN} (CH_2{=}CH{-}CH_2)_2SO_2$$

23 **24**



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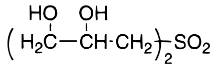
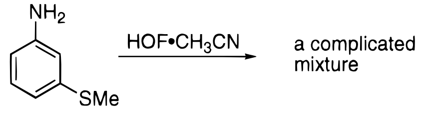


$$(H_2C(OH){-}CH(OH){-}CH_2)_2SO_2$$

26

$$MeOCH_2SPh \xrightarrow{HOF\bullet CH_3CN} MeOCH_2SO_2Ph$$

27 **28**



29

Thus, perfluorobutyl *p*-tolyl sulfide (**30**)[22] was treated at room temperature with 9 mol equiv (4.5 fold excess) of HOF·CH$_3$CN for 20 min to furnish the sulfone **31**. Similarly, perfluorooctyl *p*-tolyl sulfide (**32**) was converted to the sulfone **33**. These sulfones were the only isolated compounds in their respective reactions, and their purity approached analytical values. The mass balance, however, was only 95 and 85% correspondingly. This apparently was partially due to a parallel slow attack on the aromatic ring.[17] Replacing the electron-donating methyl group with an electron-withdrawing one such as bromine eliminated this problem, and *p*-bromophenyl perfluorobutyl sulfide (**34**) was converted to the sulfone **35** in 95% yield. Similar results were obtained with even more electron-depleted sulfides, as represented by 3,4-dichlorophenyl perfluorobutyl sulfide (**36**) oxidized to the corresponding sulfone **37**.

Pentafluorophenyl sulfone (**38**) is a known compound. It was prepared by reacting pentafluorobenzene with pentafluorophenyl sulfonyl fluoride at 110 °C with SbF$_5$ as a catalyst.[23] The yields were moderate and perfluorobiphenyl was a major byproduct. We tried to oxidize the commercial pentafluorophenyl sulfide (**39**) with MCPBA for 18 h at room temperature and with 30% H$_2$O$_2$ in boiling acetic acid but, apart from traces of the corresponding sulfoxide, only the starting material was quantitatively recovered. Applying a sevenfold excess of HOF·CH$_3$CN at room temperature for 20 min resulted in the formation of the desired sulfone **38** in 95% yield.

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(18) Lotspeich, F. J. *J. Org. Chem.* **1965**, *30*, 2068.

(19) Serra A. C.; Silva Correa, C. M. M.; Vieira, M. A. M. S. A.; Gomes, M. A. *Tetrahedron* **1990**, *46*, 3061.

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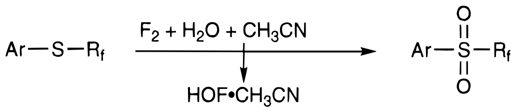
(22) All aryl perfluoroalkyl sulfides mentioned in this study were prepared according to a published procedure: Ono, N.; Miyake H.; Saito, T.; Kaji, A. *Synthesis* **1980**, 952.

(23) Furin, G. G.; Yakobson, G. G. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk,* **1976**, *3*, 120 (*Chem. Abstr.* **1976**, *85*, 77801).



30 Ar = *p*-$CH_3C_6H_4$; R_f = n-C_4F_9 **31**

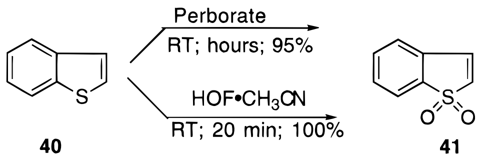
32 Ar = *p*-$CH_3C_6H_4$; R_f = n-C_8F_{17} **33**

34 Ar = 4-BrC_6H_4 ; R_f = n-C_4F_9 **35**

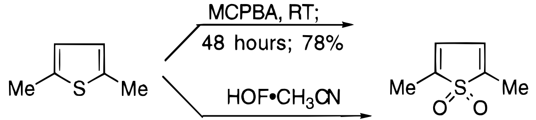
36 Ar = 3,4-$Cl_2C_6H_3$; R_f = n-C_4F_9 **37**

39 Ar = R_f = C_6F_5 **38**

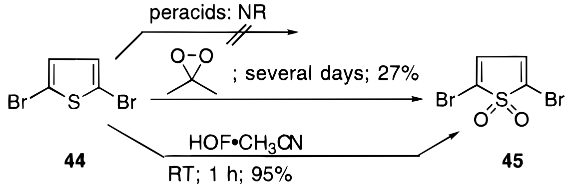
Sulfur-containing compounds of a different type are the thiophenes. Oxidizing the heteroatom of this system is challenging since there are two opposing factors involved. On the one hand the reaction has to overcome a substantial aromatic stabilization, requiring relatively harsh conditions. On the other hand, the nonaromatic *S,S*-dioxide products are sensitive to Diels–Alder and other ene and diene reactions which are strongly facilitated by high temperatures and prolonged reaction times. Indeed, the lack of easy availability of such dioxide compounds is the main reason for their underdeveloped chemistry despite the high interest they inspire.[24] One of the advantages of HOF·CH_3CN as an oxidant is that it is strong enough to act quickly under the mildest possible conditions. In the past we exploited this unique combination to oxidize, for the first time, sensitive amino acids to the corresponding α-nitro ones.[25] It proved valuable also in the case of the oxidation of thiophenes. Benzothiophene (**40**) is actually not difficult to oxidize to the *S,S*-dioxide **41** and either perborate or MoO_5·HMPA were able to accomplish this transformation.[26] Treating **40** with HOF·CH_3CN at 0 °C resulted in similar yields of **41**, but the reaction was complete in less than 20 min. 2,5-Dimethylthiophene (**42**) was also oxidized in the past to **43** with either MCPBA (hours, 78% yield) or dimethyldioxirane (90% yield). Higher than 95% yield of **43** was obtained when HOF·CH_3CN was used. Oxidation of somewhat electron-depleted rings such as 2,5-dibromothiophene (**44**) could no longer be achieved with various peracids and it took days for dimethyldioxirane to form **45** in 27% yield. HOF·CH_3CN achieved this transformation in 95% yield although 1 hour was required. The 2,5-dichlorothiophene (**46**), whose sulfur atom is more electron-depleted, is beyond the oxidizing power of the traditional oxidizers, but HOF·CH_3CN oxidized it at room temperature to 2,5-dichlorothiophene *S,S*-dioxide (**47**) in 70% yield in about 30 min. Similarly, HOF·CH_3CN was able to oxidize for the first time, both ethyl 2-methyl-5-thiophenecarboxylate (**48**) and 3-acetyl-2,5-dimethylthiophene (**49**) to the corresponding *S,S*-dioxides (**50** and **51**) in 20 min and in excellent yields.



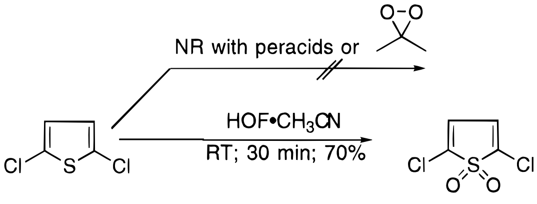
40 **41**



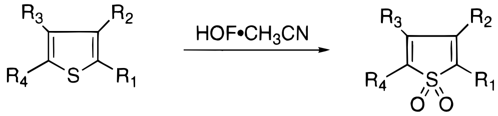
42 **43**



44 **45**



46 **47**



48 R_1 = COOEt; R_2 = R_3 = H; R_4 = Me **50**

49 R_1 = R_4 = Me; R_2 = $COCH_3$; R_3 = H **51**

It seems, however, that in some cases, efficient and clean oxidation requires substituents on both sides of the thiophene ring, otherwise the unsubstituted double bond starts to react, giving either Diels–Alder or epoxidation products. Thus, 2-cyano- (**52**) and 3-bromothiophene (**53**) gave mainly unidentified dimeric products, while 2,3-dibromothiophene (**54**) produced a mixture of two compounds, the desired 2,3-dibromothiophene *S,S*-dioxide (**55**) in 40% yield and the 2,3-dibromo-4,5-epoxythiophene *S,S*-dioxide (**56**) in 45% yield. Other combinations of thiophene with two bromines, **57** and **58**, gave the desired *S,S*-dioxides (**59** and **60**, respectively) in excellent yields. HOF·CH_3CN was even able to oxidize tetrabromothiophene (**61**) to the tetrabromothiophene *S,S*-dioxide (**62**) in 20 min in 70% yield. It should be noted that unprotected amino groups are not compatible with the oxidation of thiophenes. When methyl 2-carboxylate-3-aminothiophene (**63**) was treated with the HOF·CH_3CN complex, only the corresponding 3-nitro derivative **64** was obtained in about 75% yield.

Experimental Section

^1H NMR spectra were recorded at 200 MHz with $CDCl_3$ as solvent and Me_4Si as an internal standard. ^{19}F NMR spectra were recorded at 338.8 MHz and are reported in ppm's upfield from $CFCl_3$. GC/MS was used to record the mass spectra. FTIR spectra were recorded as neat films in $CHCl_3$ solution or in KBr pellets.

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(24) Raasch, M. S.; Benders, P. H.; Reinhoudt D. N.; Trompenaars, W. P. In *Chemistry of Heterocyclic Compounds*; Gronowitz, S., Ed.; John Wiley & Sons: New York, 1985; Vol. 44, part 1, pp 571, 671. Gronowitz, S.; Nikitidis, G.; Hallberg A.; Stalhandske, C. *Acta Chem. Scand.* **1991**, *45*, 636.

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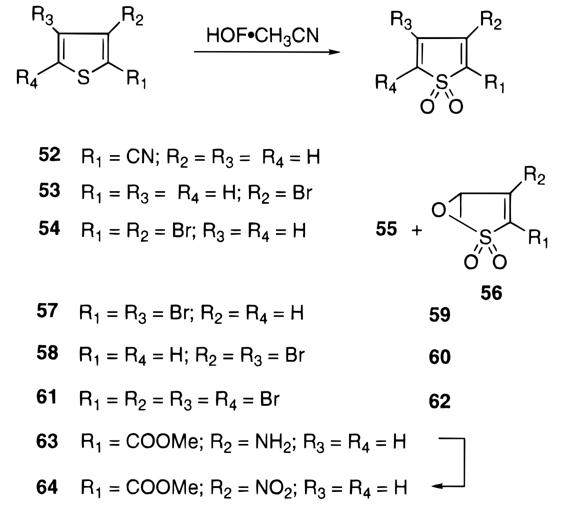
(26) (a) McKillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299. (b) Chien, C. S.; Kawasaki, T.; Sakamoto, M. *Chem. Pharm. Bull.* **1985**, *33*, 5071.



General Procedure for Working with Fluorine. Fluorine is a strong oxidizer 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. For more experimental details see reference.[27] For the occasional user, however, various premixed mixtures of F_2 in inert gases are commercially available, simplifying the whole process. The reactions themselves can be carried out in glass vessels. If elementary precautions are taken, work with fluorine is relatively simple and we have had no bad experiences working with it.

General Procedure for Producing the Oxidizing HOF·CH_3CN. Mixtures of about 10% F_2 with nitrogen were used in this work. The gas mixture was prepared in a secondary container before the reaction was started. This mixture was then passed at a rate of about 400 mL/min through a cold (−15 °C) mixture of 400 mL of CH_3CN and 40 mL of H_2O. The formation of the oxidizing reagent was monitored by reacting aliquots with an acidic aqueous solution of KI. The liberated iodine was titrated with thiosulfate. Concentrations of 0.2−0.3 mol/liter were routinely achieved. When working in small scale it is possible to achieve concentrations of more than 1.0 mol/L, and the solution has a half-life time of 3−4 h at rt.

General Oxidation Procedures. Sulfides: About 8 mmol of a sulfide was dissolved in 10 mL of $CHCl_3$ at 0 °C and added to about 20 mmol (50% excess) of a cold (−5 °C to 0 °C) aqueous CH_3CN solution of HOF•CH_3CN in one portion. The oxidizing power was usually lost after 5−10 min. The reaction mixture was then neutralized with saturated sodium bicarbonate solution, extracted with CH_2Cl_2, and washed again with $NaHCO_3$ and water until neutral. The organic layer was dried over $MgSO_4$, the solvent evaporated, and the sulfone isolated and purified by either recrystallization from EtOH or short chromatography. Known products were compared with either an authentic sample or with spectral properties reported in the literature. An excellent agreement was always found. We report here the appropriate analytical data only for new compounds or for those not well defined in the literature.

1,1,2,2-Tetrahydroperfluorooctyl *p*-tolyl sulfide (2) was prepared according to reference 22 and obtained in 95% yield as an oil. ^{1}H NMR: 7.2 (4H, AB, $J = 8.1$ Hz), 3.06 (2H, m), 2.37 (2H, m), 2.34 (3H, s). ^{19}F NMR: −81.3 (3F, dt, $J_1 = 9$, $J_2 = 2$ Hz), −114.7, −122.4, −123.4, −123.8, −126.7 (each 2F, m). MS: (*m*/*e*) 470 (M)$^+$.

Methyl *p*-tolyl sulfone (4)[28] was obtained in 100% yield, mp 88 °C. IR: 1300, 1143 cm^{-1}. MS: (*m*/*e*) 170 (M)$^+$.

1,1,2,2-Tetrahydroperfluorooctyl *p*-tolyl sulfide (5) was obtained in 100% yield, mp 92 °C. IR: 1317, 1150 cm^{-1}. ^{1}H NMR: 7.6 (4H, AB, $J = 8.1$ Hz), 3.3 (2H, m), 2.62 (2H, m), 2.48 (3H, s). ^{19}F NMR: −81.3 (3F, dt, $J_1 = 10$, $J_2 = 2$ Hz), −114, −122.4, −123.4, −123.6, −126.7 (each 2F, m). MS: (*m*/*e*) 502 (M)$^+$, 155. Anal. Calcd for $C_{15}H_{11}F_{13}O_2S$: C, 35.87; H, 2.21. Found: C, 35.94, H, 2.09.

Methyl *p*-nitrophenyl sulfone (6)[29] was obtained in 90% yield, mp 142 °C. IR: 1320, 1154 cm^{-1}. ^{1}H NMR: 6.3 (4H, AB, $J = 8.1$ Hz), 3.13 (3H, s). MS: (*m*/*e*) 201 (M)$^+$.

Butyl sulfone (10), which is commercially available, was obtained in 75% yield, mp 45 °C.

Methyl *tert*-butyl sulfone (11)[30] was obtained in 75% yield, mp 83 °C. IR: 1285, 1117 cm^{-1}. ^{1}H NMR: 2.63 (3H, s), 1.44 (3H, s).

***tert*-Butyl sulfone (12)**[31] was obtained in 95% yield, mp 130 °C. IR: 1269, 1088 cm^{-1}. ^{1}H NMR: 1.45 (s). MS: (*m*/*e*) 121 (M − *t*-Bu)$^+$.

2-Methyl-1,3-dithiane *S*,*S*,*S*,*S*-tetraoxide (14)[32] was obtained in 95% yield, mp 258 °C. IR: 1326, 1150 cm^{-1}. ^{1}H NMR: (in DMSO-d_6) 5.13 (1H, q, $J = 7$ Hz), 3.48 (4H, m), 2.41 (1H, m), 2.07 (1H, m), 1.51 (3H, d, $J = 7$ Hz). MS: (*m*/*e*) 198 (M)$^+$, 134.

Furfuryl sulfone (20) was obtained in 85% yield, mp 72 °C. IR: 1313, 1153 cm^{-1}. ^{1}H NMR: 7.5 (2H, d, $J = 1.5$ Hz), 6.57 (2H, d, $J = 3.2$ Hz), 6.44 (2H, dd, $J_1 = 3.2$, $J_2 = 1.5$ Hz), 4.32 (4H, s). MS: (*m*/*e*) 162 (M − SO_2), 81. Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.09; H, 4.46. Found: C, 52.91; H, 4.34.

Thiochroman-4-ol *S*,*S*-dioxide (22)[18] was obtained in 95% yield, mp 93 °C. ^{1}H NMR: 7.82−7.45 (4H, m), 4.85 (1H, dd, $J_1 = 6$, $J_2 = 4$ Hz), 3.63 (1H, dt, $J_1 = 10$, $J_2 = 4$ Hz), 3.23 (2H, m), 2.63 (1H, m), 2.45 (1H, m). MS: (*m*/*e*) 198 (M)$^+$.

Allyl sulfone (24)[19] was obtained in 86% yield, oil. ^{1}H NMR: 5.9 (2H, m), 5.4 (4H, m), 3.72 (4H, d, $J = 7$ Hz). MS: (*m*/*e*) 146 (M)$^+$, 41.

2,3-Epoxypropyl sulfone (25) was obtained in 70% yield, oil. IR: 1310, 1128 cm^{-1}. ^{1}H NMR: 3.4 (4H, m), 3.25 (2H, m), 2.96 (2H, t, $J = 4.5$ Hz), 2.55 (2H, m). ^{13}C NMR: 56.85 (CH_2), 56.56 (CH_2), 46.1 (2CH_2), 45.6 (CH), 45.4 (CH). A mixture of two diastereoisomers. Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66; S, 17.99. Found: C, 39.82; H, 5.58;.S, 17.73

2,3-Dihydroxypropyl sulfone (26) was obtained in 95% yield (based on **25**), oil. IR: 3462, 1310, 1128 cm^{-1}. Anal. Calcd for $C_6H_{14}O_6S$: C, 33.64; H, 6.59; S, 14.96. Found: C, 33.36; H, 5.94; S, 15.24.

Methoxymethyl phenyl sulfone (28)[11] was obtained in 95% yield, mp 70 °C. IR: 1330, 1142 cm^{-1}. ^{1}H NMR: 7.72 (5H, m), 4.52 (2H, s), 3.66 (3H, s). MS: (*m*/*e*) 186 (M)$^+$.

Aryl Perfluoralkyl Sulfides. In general the starting sulfides were prepared according to reference 22. About 2 g of aryl mercaptan was dissolved in 40 mL of cold (+5 − +7 °C), dry benzene containing an equimolar amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The reaction was stirred under nitrogen for 10 min and subsequently treated with an equimolar amount of the appropriate perfluoroalkyl iodide. The reaction mixture was brought to room temperature and stirred under nitrogen for 15 h. Pouring into water, extraction with chloroform, drying the organic layer with $MgSO_4$, and rotevaporation of the solvents afforded the desired sulfide in 60−70% yield (after column chromatography), the rest being the respective disulfide. The oxidation of these sulfides was similar to that described above except that 10 mol equiv of HOF•CH_3CN (fivefold excess) was used at room temperature for 10−30 min.

Perfluorobutyl *p*-tolyl sulfone (31)[10] was obtained in 95% yield, oil. MS: (*m*/*e*) 374 (M)$^+$.

Perfluorooctyl *p*-tolyl sulfone (33)[10] was obtained in 85% yield, oil. MS: (*m*/*e*) 574 (M)$^+$.

***p*-Bromophenyl perfluorobutyl sulfone (35)** was obtained in 95% yield, mp 56 °C. IR: 1362, 1174 cm^{-1}. ^{1}H NMR: 7.86 (m). ^{19}F NMR: −77.18 (3F, m), −106.3 (2F, t, $J = 13$ Hz), −115.24 (2F, m), −120.16 (2F, m). MS: (*m*/*e*) 440 (M)$^+$. Anal. Calcd for $C_{10}H_4BrF_9O_2S$: C, 27.35; H, 0.92. Found: C, 26.94; H, 1.28.

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3,4-Dichlorophenyl perfluorobutyl sulfone (37) was obtained in 90% yield, mp 52 °C. IR: 1376, 1172 cm^{-1}. ^{1}H NMR: 8.11 (1H, d, $J = 2$ Hz), 7.78 (2H, m). ^{19}F NMR: −81.18 (3F, m), −111.36 (2F, t, $J = 13$ Hz), −121.13 (2F, m), −126.34 (2F, m). MS: (m/e) 428 (M)$^+$. Anal. Calcd for $C_{10}H_3Cl_2F_9O_2S$: C, 27.99; H, 0.70. Found: C, 27.83; H, 1.09.

Pentafluorophenyl sulfone (38)[23] was obtained in 95% yield, mp 122 °C. IR: 1303, 1178 cm^{-1}. ^{19}F NMR: −136 (4F, d, $J = 20$ Hz), −141.4 (2F, m), −157.9 (4F, d, $J = 20$ Hz). MS: (m/e) 398 (M)$^+$.

Thiophenes. All thiophenes used in this study are commercially available. The oxidation was carried out as described above, using usually a fourfold excess of $HOF{\cdot}CH_3CN$ at room temperature for 20 min. The appropriate analytical data for new thiophene *S*,*S*-dioxides, or ones not well defined in the literature, are listed below.

Benzothiophene *S*,*S*-dioxide (41)[26] was obtained in 98% yield, mp 140 °C. IR: 1287, 1150 cm^{-1}. ^{1}H NMR: 7.5 (4H, m), 7.24 (1H, d, $J = 7$ Hz), 6.71 (1H, d, $J = 7$ Hz). MS: (m/e) 166 (M)$^+$.

2,5-Dimethylthiophene *S*,*S*-dioxide (43)[26a] was obtained in 96% yield, mp 88 °C. IR: 1285, 1151 cm^{-1}. ^{1}H NMR: 6.3 (2H, q, $J = 0.8$ Hz), 2.1 (6H, d, $J = 0.8$ Hz). MS: (m/e) 144 (M)$^+$.

2,5-Dibromothiophene *S*,*S*-dioxide (45)[33] was obtained in 95% yield, mp 128 °C. IR: 1321, 1152 cm^{-1}. ^{1}H NMR: 6.9 (s). MS: (m/e) 274 (M)$^+$.

2,5-Dichlorothiophene *S*,*S*-dioxide (47) was obtained in 70% yield, mp 103 °C. IR: 1332, 1155 cm^{-1}. ^{1}H NMR: 6.69 (s). MS: (m/e) 185 (M)$^+$. Anal. Calcd for $C_4H_2Cl_2O_2S$: C, 25.97; H, 1.09; S, 17.33. Found: C, 26.05; H, 1.19; S, 16.95.

Ethyl 2-methyl-5-thiophenecarboxylate *S*,*S*-dioxide (50) was obtained in 90% yield, mp 140 °C. IR: 1703, 1309, 1140 cm^{-1}. ^{1}H NMR: 7.54 (1H, d, $J = 4.6$ Hz), 6.45 (1H, dd, $J_1 = 2.4$, $J_2 = 1.8$ Hz), 4.38 (2H, q, $J = 7.1$ Hz), 2.21 (3H, d, $J = 1.8$ Hz), 1.39 (3H, t, $J = 7.1$ Hz). MS: (m/e) 202 (M)$^+$. Anal. Calcd for $C_8H_{10}O_4S$: C, 47.52; H, 4.98; S, 15.85. Found: C, 47.36; H, 4.76; S, 15.57.

3-Acetyl-2,5-dimethylthiophene *S*,*S*-dioxide (51) was obtained in 80% yield, mp 124 °C. IR: 1700, 1286, 1163 cm^{-1}. ^{1}H NMR: 9.79 (1H, q, $J = 1.7$ Hz), 2.48 (3H, s), 2.43 (3H, s), 2.07 (3H, d, $J = 1.7$ Hz). MS: (m/e) 186 (M)$^+$. Anal. Calcd for $C_8H_{10}O_3S$: C, 51.60; H, 5.41. Found: C, 51.15; H, 4.97.

2,4-Dibromothiophene *S*,*S*-dioxide (59) was obtained in 85% yield, mp 94 °C. IR: 1309, 1147 cm^{-1}. ^{1}H NMR: 6.94 (1H, d, $J = 1$ Hz), 6.78 (1H, d, $J = 1$ Hz). MS: (m/e) 274 (M)$^+$. Anal. Calcd for $C_4H_2Br_2O_2S$: C, 17.54; H, 0.74; S, 11.70. Found: C, 17.81; H, 0.73; S, 11.3.

3,4-Dibromothiophene *S*,*S*-dioxide (60) was obtained in 85% yield, mp 106 °C. IR: 1305, 1150 cm^{-1}. ^{1}H NMR: 6.84 (s). MS: (m/e) 274 (M)$^+$. Anal. Calcd for $C_4H_2Br_2O_2S$: C, 17.54; H, 0.74; S, 11.70; Br, 58.34. Found: C, 17.47; H, 0.74; S, 11.41; Br, 57.97.

Tetrabromothiophene *S*,*S*-dioxide (62)[34] was obtained in 70% yield, mp 202 °C. IR: 1333, 1157 cm^{-1}. MS: (m/e) 432 (M)$^+$.

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