α-Fluorination of Methyl Phenyl Sulfoxide and Related Compounds by Molecular Fluorine: A Novel Method for the Introduction of Fluorine into Sulfoxides Bearing α-H Atoms[1)]

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Received October 19, 1995; accepted December 8, 1995

Direct formation of α-fluorosulfones from sulfoxides bearing α-H atoms merely by reaction with molecular fluorine (5% F_2/N_2) is reported, and a novel non-Pummerer-type mechanism is proposed for this α-fluorination reaction.

Key words α-fluorination; molecular fluorine; α-fluorosulfone; non-Pummerer-type reaction; hypofluorous acid

Fluorination of sulfides and related compounds (sulfoxides and sulfones) is of importance since the resulting α-fluorinated sulfur compounds can serve as useful intermediates for the synthesis of organofluorine compounds of medicinal importance.[2-4)] Among such compounds, fluoromethyl phenyl sulfone[5)] and the corresponding sulfoximine (α-fluoromethyl-*N*-methylphenylsulfoximine)[6)] are reagents which permit direct conversion of a ketone or an aldehyde to fluoromethylene derivatives. Except for the replacement reaction of α-chlorosulfides with potassium fluoride in the presence of 18-crown-6,[7)] all of the reported methods for the preparation of α-fluorinated sulfides use α-fluorination reaction of the corresponding sulfides or sulfoxides bearing α-H atoms. These methods are as follows: (1) direct fluorination of the sulfides with xenon difluoride,[8)] (2) conversion of the sulfoxides to the α-fluorosulfides with diethylaminosulfur trifluoride (DAST),[9,10)] and (3) fluorination of the sulfides with electrophilic fluorinating reagents (such as *N*-fluoropyridinium triflates[11)] or *N*-fluoro derivatives of 1,4-diazabicyclo[2.2.2]octane[12)]). However, all of these reagents are expensive (especially xenon difluoride) and require anhydrous conditions. Furthermore, since most α-fluorosulfides decompose during the post-treatment, they must be isolated as the corresponding sulfoxides or sulfones after appropriate oxidation.

It is desirable, therefore, to develop an easily handled fluorination reaction using an inexpensive fluorinating reagent in an ordinary organic solvent to give directly the stable α-fluorinated sulfur compounds (*e.g.* the sulfoxides or sulfones). The fluorination by molecular fluorine has the advantage—apart from the favorable price of the reagent[13)]—that the reaction can be performed without difficulty.[2-4,14,15)]

We now report a novel synthesis of α-fluoromethyl phenyl sulfone (**2a**) and the corresponding difluoromethyl and trifluoromethyl derivatives (**3a**[16)] and **4**[17)]) by reacting methyl phenyl sulfoxide (**1a**) with molecular fluorine (5% F_2/N_2) in acetonitrile. This reaction has two further advantageous characteristics: 1) the reaction is applicable to all kinds of phenylsulfinyl compounds having at least one hydrogen on the α-carbon and 2) though all of the direct α-fluorination reactions cited above[8-12)] involve the Pummerer-type reaction as the key step, the present reaction is a non-Pummerer-type one, and hence, mechanistically novel.

First, reaction of methyl phenyl sulfoxide (**1a**) with fluorine was examined in $CFCl_3$. Thus, fluorine (5% F_2/N_2: the approximate amounts of fluorine were estimated by using a flow meter) was passed through a $CFCl_3$ solution (20 ml) of **1a** (1 mmol) at −78 °C. After the addition was completed (it took 10—15 min), N_2 was bubbled through the reaction mixture to expel excess fluorine and the reaction was neutralized (pH 7) by the addition of ice-cold saturated aqueous sodium bicarbonate solution. After addition of water, the products were extracted with CH_2Cl_2 and separated by silica gel column chromatography. Irrespective of the amount of fluorine, the corresponding sulfone (**5a**) was obtained as the major product, together with small amounts (less than 2% yield each) of the fluorinated sulfones (**2a**, **3a** and **4**). If the same reaction was carried out at −20 °C, however, the relative amounts of fluorinated products (**2a**, **3a**, and **4**) to **5a** were increased appreciably. This fact suggests that, though some novel intermediate [it gives the unfluorinated sulfone (**5a**) only after treatment with water and hence, is the precursor of **5a**] is formed from **1a** and molecular fluorine, and survives at −78 °C in $CFCl_3$, it reacts further with fluorine at −20 °C to give the precursors of the α-fluorinated sulfones (**2a**, **3a** and **4**). Since the reaction carried out at −20 °C still gave the unfluorinated sulfone (**5a**), it is clear that the above intermediate and precursors are in equilibrium at −20 °C in $CFCl_3$.

In order to utilize the above observation as the basis to elaborate a novel and economical α-fluorination reaction, we then carried out the reaction at the same temperature (−20 °C) using acetonitrile as the solvent. The results obtained are summarized in Table 1.

The results suggest the formation of the sulfur (VI) difluoride (**6a**)[18)] from **1a** by oxidative fluorination (Chart. 1). At −20 °C, HF may be lost to give the dehydrofluorinated product (**7a**), followed by fluorine addition to give the precursor (**8a**) of the α-fluorinated product (**2a**). Repetition of a similar reaction sequence leads to **10a** (the precursor of **3a**) *via* **9a**, and **12a** (the precursor of **4**) *via* **11a**. Though we consider that all steps proceed irreversibly, it is not possible at present to exclude the possibility that some steps may be reversible [*cf.* (←) in Chart 1].

Formation of the fluorine adduct (**6a**) as the primary intermediate is supported by the formation of similar

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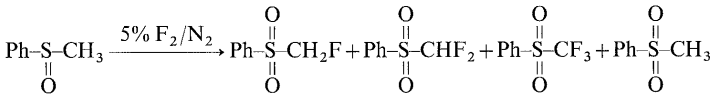
Table 1. Fluorination of Methyl Phenyl Sulfoxide (**1a**) by Molecular Fluorine[a]



1a **2a** **3a** **4** **5a**

Entry	Solvent	F_2 (mol eq)	Yield (%)[b]				Recovery
			2a	**3a**	**4**	**5a**	
1	CH_3CN	1	19	13	2	26	13
2	CH_3CN	2.5	21	12	8	23	0
3	CH_3CN/H_2O (10:1, v/v)	1	24	11	1	29	7
4	CH_3CN/H_2O (10:1, v/v)	2.5	20	8	5	26	0

a) Reaction conditions: Methyl phenyl sulfoxide (1.0 mmol) in the solvent (50 ml) was treated with 5% F_2/N_2 ($\leq$15 min) at -20 °C and then the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (-20 °C *ca.* r.t.). *b*) Isolated yields after silica gel column chromatography.

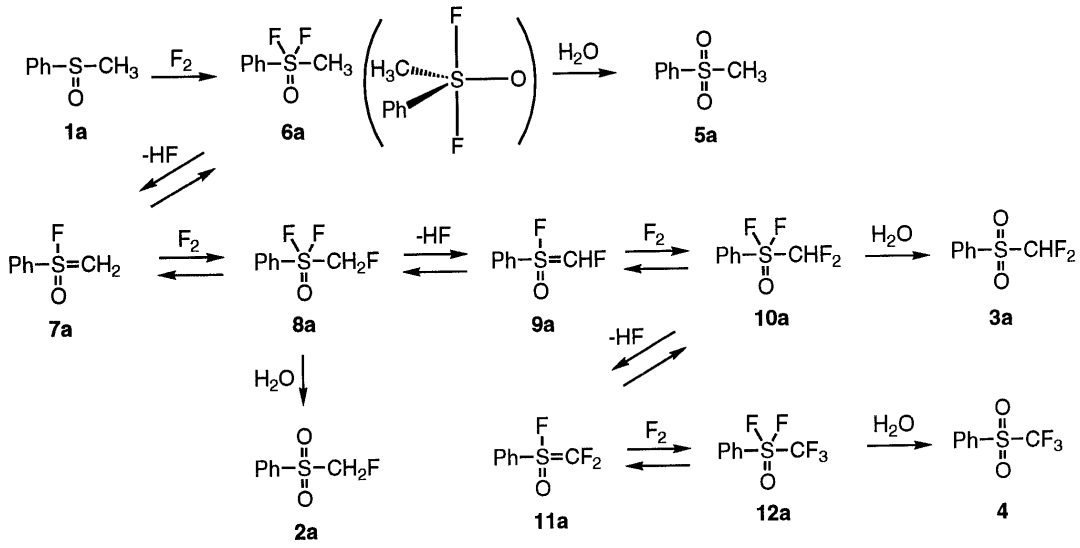


Chart 1

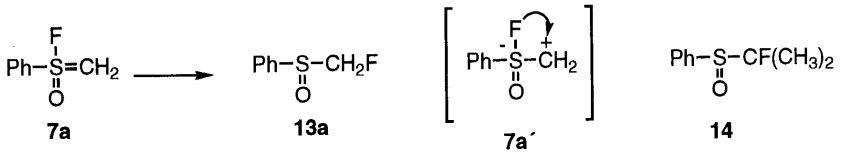


Chart 2

difluorides from diaryl sulfoxides under comparable conditions (F_2/helium, at -90 °C in $CFCl_3$), as reported by Ruppert.[19]

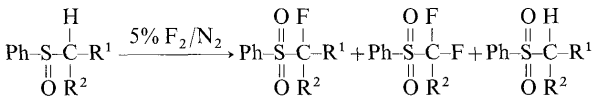
Remarkably, when the reaction was carried out in a mixture of CH_3CN–H_2O (10:1, v/v) as the solvent, the same products (**2a**—**5a**) were again obtained. This means that the reaction can be carried out in the presence of water. It should also be noted that in both solvents, the ratio of the products did not depend significantly on the amount of fluorine used. For example, if 1 mol eq of F_2 was used in this reaction, **2a** was still obtained as the major product and none of the corresponding sulfoxide (**13a**) was detected (*cf.* entries 1 and 3). This demonstrates that the Pummerer-type reaction (*cf.* **7a**→**7a′**→**13a**) is not involved in the α-fluorination reaction of **1a**.

Rozen *et al.* reported that, if fluorine was passed through a mixture of CH_3CN–H_2O (10:1, v/v) at -20 °C and the whole was kept for a few minutes, hypofluorous acid (HOF) was formed, and they utilized the resultant solution (Rozen's reagent) as a strong oxidant.[20] Actually, when **1a** was added to Rozen's reagent (prepared from 2.5 mol eq of F_2), **5a** was obtained in 85% yield and the fluorinated products were not detected. Hence it is clear that the reaction of **1a** to give **6a** and subsequent reactions with F_2 (*cf.* Chart 1) are much faster than that of fluorine with water to give HOF.

In order to examine the scope of the above fluorination reaction (2 mol eq of F_2 at -20 °C in CH_3CN), a series of phenylsulfenyl derivatives (**1b**—**1j**) was used as substrates. The results are summarized in Table 2.

The sulfoxides bearing either two H (**1b**—**1g**) or one H (**1h**) at the α-position gave the monofluorinated sulfones

Table 2. Fluorination of Various Alkyl Phenyl Sulfoxides (**1b**—**1k**) by Molecular Fluorine[a)]



1 **2** **3** **5**

Entry	Substrate	R^1	R^2	Yield (%)[b)]			Recovery
				2	**3**	**5**	
5	**1b**	H	Cl	43	—	25	—
6	**1c**	H	CO_2Et	57	8	2	—
7	**1d**	H	Me	44	—	12	—
8	**1e**	H	COPh	31	15	—	2
9	**1f**	H	$CH_2CH(Me)_2$	33	6	7	5
10[c)]	**1f**	H	$CH_2CH(Me)_2$	30	—	7	—
11	**1g**	H	CH_2CH_2Cl	46	—	9	5
12[d)]	**1h**	Me	CO_2Et	37	—	7	9
13[e)]	**1i**	H	Ph	—	—	—	31
14[f)]	**1j**	Me	Me	—	—	20	—
15	**1k**	CH_2–CH_2		5	—	62	7
16[g)]	**1k**	CH_2–CH_2		12	—	71	5

a) Reaction conditions: the substrate (1.0 mmol) in CH_3CN (50 ml) was reacted with 5% F_2/N_2 (2 mol eq ≤ 15 min) at −20 °C and the reaction was then quenched by the addition of aqueous saturated $NaHCO_3$ (−20 °C *ca.* r.t.). *b*) Isolated yields after silica gel column chromatography. *c*) The reaction was carried out in the presence of NaF (10 eq) and $PhSO_2F$ (**15**) was obtained in 18% yield. *d*) Oxidation of the corresponding sulfide with *m*-CPBA gave two diastereomers (3:2) which were separable by silica gel column chromatography. The major diastereomer thus obtained was used as the substrate. *e*) Small amounts of benzaldehyde, benzoic acid, and benzenesulfonic acid were isolated (each less than 5%). *f*) The monofluorinated sulfoxide (**14**) was isolated in *ca.* 2% yield. *g*) The reaction was carried out in the presence of Et_3N (1.1 eq to **1k**).

in satisfactory yields. In contrast, benzyl phenyl sulfoxide (**1i**) and isopropyl phenyl sulfoxide (**1j**) gave complex mixtures. In the former case, **1i** was recovered in 31% yield, while the unfluorinated sulfone (**5j**) was isolated in 20% yield in the latter case. While no fluorinated product was detected in the former case (entry 13), the monofluorinated sulfoxide (**14**) was formed in 2% yield as the only fluorinated product in the latter case (entry 14). The exceptional formation of the Pummerer-type rearrangement product (**14**) may be explained by assuming that the contribution of the ylide structure (*cf.* **7a′** in Chart 2: responsible for the Pummerer-type rearrangement) compared to other canonical forms (*cf.* **7a** in Chart 2: responsible for the fluorine addition) in the corresponding dehydrofluorinated intermediate is increased significantly due to the attachment of two methyl groups, which stabilize the carbocation center.

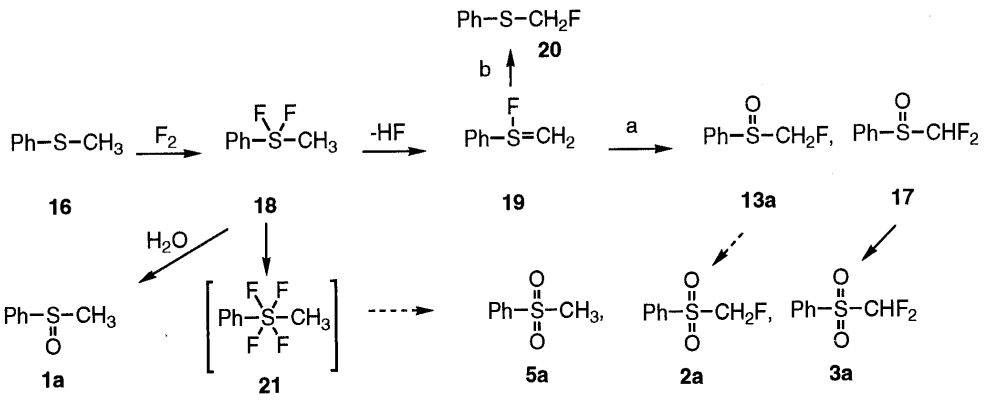
In order to examine the effect of HF, the reaction of **1f** in the presence of NaF was also carried out (entry 10). As a result, it was found that while the yields of **2f** and **5f** were almost unchanged, the formation of **3f** was suppressed. Instead, benzenesulfonyl fluoride (**15**)[21)] was isolated in 18% yield.[22)]

The same reaction of phenyl cyclopropyl sulfoxide (**1k**) gave rise mostly to the unfluorinated sulfone (**5k**), and the monofluorinated sulfone (**2k**) was isolated in 5% yield as the only fluorinated product (entry 15). Given that the α-proton in **1k** is far less acidic than that in the ordinary alkyl groups,[23)] the low yield of **2k** should be due to prohibition of the dehydrofluorination step.[24)] In accordance with this explanation, the amount of **2k** increased appreciably when the same reaction was carried out in the presence of 1 eq of triethylamine (entry 16).

Preliminary experiments carried out on related sulfides under the same conditions (at −20 °C in CH_3CN) were found to give the α-fluorinated sulfoxides as the major products. For example, the reaction of methyl phenyl sulfide (**16**) with F_2 (1 mol eq) gave, in addition to 34% recovery of the sulfide and formation (21%) of the unfluorinated sulfoxide (**1a**), mono- and difluorinated sulfoxides (**13a** and **17**) in 15% and 6% yields, respectively. Formation of these two fluorinated sulfoxides as the major fluorination products clearly suggests that this reaction proceeds through the monofluorine adduct (**18**) as the primary intermediate, followed by dehydrofluorination to give **19**, just as in the non-Pummerer-type mechanism shown in Chart 1.

Thorough chromatographic separation of the reaction products has revealed that, though the corresponding sulfones were obtained in very poor yields (**5a** in 1%, **2a** in 2% and **3a** in 1%), the monofluorinated sulfide (**20**) could not be isolated. It is therefore evident that, while one can not rigorously exclude the formation of the difluorine adduct (**21**) as another possible intermediate, the Pummerer-type mechanism (*cf.* **18**→**19**→**20**) is not operating.[25)] The low ratio of **2a**/**13a** in this reaction also supports our assumption that **13a** (*cf.* Chart 2) is not the precursor of **2a** in the fluorination reaction of **1a** (*cf.* Chart 1).

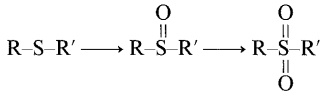
Finally, we should comment on the oxidations of sulfoxides to sulfones and of sulfides to sulfoxides by using Rozen's reagent ($HOF \cdot CH_3CN$). This reagent was originally developed by Rosen and his coworkers for the epoxidation of olefins.[20,26)] Though HOF was synthesized and identified by spectroscopic methods for the first time by Studier and Appelman by passing F_2 over ice at a



a: the non-Pummerer-type mechanism (*cf.* Chart 1). b: the Pummerer-type mechanism.

Chart 3

Table 3. Oxidation Reaction of Sulfides and Sulfoxides with $HOF \cdot CH_3CN$ Prepared by Passing F_2 through CH_3NH–H_2O (10 : 1, v/v) Solution at −20 °C



Entry	Substrate	R	R′	F_2 (mol eq)	Sulfoxide	Yield[a] Sulfone	Recovery
17	**22a**	Ph	Ph	2	—	93	—
18	**22a**	Ph	Ph	1	17	51	26
19	**22b**=**16**	Ph	CH_3	2	—	83	—
20	**22c**	Ph	CH_2Ph	2	42	54	—
21	**22c**	Ph	CH_2Ph	3	—	88	—
22	**22d**	Ph	$CH(CH_3)_2$	2	—	93	—
23	**22e**	^{t}Bu	CH_3	2	—	40	—
24	**23**=**1a**	Ph	CH_3	2	—	80	—
25	**24**=**5a**	Ph	CH_3	2	—	—	93

a) Isolated yield.

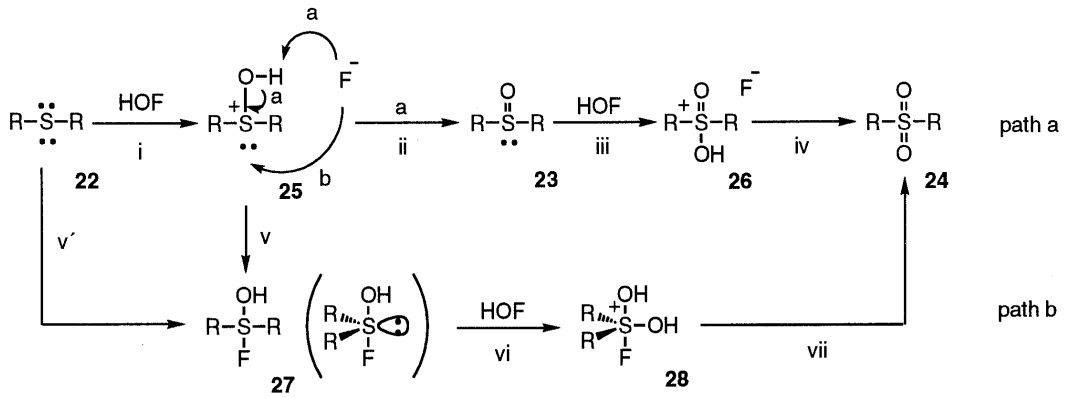


Chart 4

temperature of around −50 °C,[27] it was stable only at low temperatures. Rozen *et al.*, however, have found that when HOF is prepared by passing F_2 into acetonitrile containing water, the complex ($HOF \cdot CH_3CN$) thus formed can persist at temperatures up to 25 °C for several hours and can be used not only for the epoxidation of double bonds as mentioned above,[20,26] but also for hydroxylation of tertiary CH bonds,[28] oxidation of amines to the corresponding nitro derivatives,[29] and oxidation of alcohols to ketones as well as the Baeyer–Villiger oxidation of the latter.[30]

Since oxidation of sulfides and sulfoxides with Rozen's reagent has not been reported yet, we examined the oxidation reaction of several sulfur compounds with this reagent. The results are summarized in Table 3.

Formally, the oxidation reaction can be formulated through path a (**22**→**25**→**23**→**26**→**24**), just as in the case of electrophilic oxidation with organic peracids, *e.g.* *m*-chloroperbenzoic acid (*m*-CPBA) (Chart 4). However, in the reaction using an insufficient amount of HOF, the

yield of the sulfone significantly exceeded that of the sulfoxide. Generally, in the oxidation of sulfides with *m*-CPBA, the rate of formation of the sulfoxides is much faster than that of the sulfones.[31] Hence, we propose an alternative path (path b). In path b, the intermediates (**27**) may be formed from sulfides (**22**) *via* two steps (*cf.* i, v) or even one step (*cf.* v') and have, as in the case of **6a**, a trigonal bipyramidal structure with two electronegative substituents in axial positions, as shown in parenthesis.[18]

In conclusion, the present study not only provides a one-step synthesis of α-monofluorinated sulfones from phenylsulfenyl derivatives bearing at least one α-H atom, but also complements the existing methodology for the α-fluorination of sulfides and sulfoxides bearing α-H atoms, for which only the Pummerer-type rearrangement has so far been utilized as the key step.[7-11] At the same time, HOF–CH_3CN, originally developed by Rosen *et al.*, has been successfully applied to the oxidation of a variety of sulfides and sulfoxides.

Experimental

All melting points were determined on a Yanagimoto micro-hot stage and are uncorrected. IR spectra were measured on a JASCO A-102 spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL JNM-PMX 60 SI or Hitachi R-300 spectrometer with tetramethylsilane as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-DX-303 or JMS-AX-500 spectrometer.

The fluorine gas [5% (v/v) in N_2] was donated by Asahi Glass Co., Ltd. and the amount of fluorine was estimated by using a Kusano KG-2 flow meter. CH_3CN (special grade, Wako Pure Chemical Industries, Ltd.) was used as such as the solvent for the fluorination reaction. Merck Silica gel 60 (230—400 mesh ASTM) and Merck Silica gel 60 F_{254} were employed for flash chromatography and preparative thin layer chromatography (TLC), respectively.

Sulfides Most of the sulfides used in the present study were commercial samples and were used without further purification. A few sulfides which are not available commercially were prepared as follows.

Ethyl 2-Phenylthiopropanoate: ethyl thiophenylacetate (981 mg, 5.00 mmol) in THF (5 ml) was added to a stirred THF solution (25 ml) of LDA [prepared from diisopropylamine (510 mg, 5.04 mmol) and BuLi/hexane (1.56 M, 3.22 ml, 5.02 mmol)] kept at −78 °C. The mixture was stirred for 5 min at −78 °C, then methyl iodide (709 mg, 5.00 mmol) was added. The whole was stirred at −78 °C for 2 h, at 0 °C for 1 h, and at room temperatre for 5 h. After addition of saturated aqueous solution of NH_4Cl, the product was extracted with ether and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on a silica gel column (hexane–ether, 50 : 1, v/v) to give ethyl 2-phenylthiopropanoate (632 mg, 60%).

Typical Procedure for the Preparation of Sulfides *via* S–C Bond Formation: Isopropyl Phenyl Sulfide (**22d**): Under an argon atmosphere, lithium thiophenoxide (1.0 M solution of THF, 20 ml: 20 mmol) was added under stirring to a solution of 2-bromopropane (2.46 g, 20 mmol) in THF (100 ml) at 0 °C. After the addition was completed, the ice bath was removed and stirring was continued for 12 h. After the addition of 100 ml of water, the product was extracted with ether and dried over $MgSO_4$. Evaporation of the solvent gave the crude sulfide (2.42 g).

Isoamyl phenyl sulfide, 3-chloropropyl phenyl sulfide and phenylthioacetophenone were synthesized in the same manner from the tosylate of isoamyl alcohol, 1,3-dichloropropane, and bromoacetophenone, respectively.

Sulfoxides Most of the sulfoxides used in the present study were commercial samples and were used without further purification. Some sulfoxides which are not commercially available were prepared from the corresponding sulfides by oxidation with *m*-CPBA.

Typical Procedure for the Preparation of the Sulfoxides from the Corresponding Sulfides: Benzyl Phenyl Sulfoxide (**1i**): Under ice-cooling, *m*-CPBA (810 mg, 4.69 mmol) was added to a stirred solution of benzyl phenyl sulfide (801 mg, 4.00 mmol) in CH_2Cl_2 (20 ml). After the addition was completed, the mixture was stirred at 0 °C for 2 h and then at room temperature for 12 h. After addition of a saturated aqueous solution of $Na_2S_2O_3$ (10 ml), the stirring was continued for 1 h. After addition of a 5% aqueous solution of K_2CO_3, the product was extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on a silica gel column (hexane–AcOEt, 3 : 1, v/v) to give first benzyl phenyl sulfone (**5i**: mp 145—147 °C,[32] 43.5 mg, 5%) and then benzyl phenyl sulfoxide (**1i**: mp 121—123 °C,[32] 688 mg, 80%).

Ethyl 2-Phenylsulfinylpropanoate (**1h**): According to the typical oxidation procedure, ethyl 2-phenylthiopropanoate was oxidized by *m*-CPBA (1.1 eq). The crude products were separated by silica gel column chromatography. Elution with hexane–AcOEt (5 : 1, v/v) gave the sulfone (**5h**, 5%), the sulfoxide (**1h**-less polar: 47%), and its diastereomer (**1h**-more polar: 31%). The major diastereomer was used for the fluorination reaction.

1h-Less Polar: oil. High-resolution MS *m/z* 226.0666. (M^+; calcd for $C_{11}H_{14}O_3S$: 226.0664). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.17 (3H, t, J=7.2 Hz, CH_3), 1.49 (3H, d, J=7.3 Hz, CH_3), 3.50 (1H, br q, J=7.3 Hz, C<u>H</u>(CH_3)CO_2Et), 4.10 (2H, m, C<u>H</u>$_2$$CH_3$), 7.4—7.75 (5H, m, arom). ^{13}C-NMR (75 MHz, $CDCl_3$): 9.69, 14.04, 61.86, 65.80, 124.73, 129.149, 131.65, 142.02, 168.55.

1h-More Polar: oil. High-resolution MS *m/z* 226.0637. (M^+; calcd for $C_{11}H_{14}O_3S$: 226.0664). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.21 (3H, t, J=7.2 Hz, CH_3), 1.32 (3H, d, J=7.0 Hz, CH_3), 3.81 (1H, q, J=7.0 Hz, C<u>H</u>(CH_3)CO_2Et), 4.10 and 4.13 (each 1H, 9, d, J=7.2, 3.5 Hz, C<u>H</u>$_2$$CH_3$), 7.4—7.75 (5H, m, arom.). ^{13}C-NMR (75 MHz, $CDCl_3$): 8.93, 14.00, 61.72, 63.68, 125.11, 128.94, 131.74, 140.33, 167.70.

3-Chloropropyl phenyl sulfoxide (**1g**) was prepared according to the above procedure, oil, 49% (overall yield from 1,3-dichloropropane). High-resolution MS *m/z* 202.0228. (M^+; calcd for $C_9H_{11}ClOS$: 202.0219). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.10 (2H, m, CH_2), 2.95 (2H, m, C<u>H</u>$_2$SO), 3.62 (2H, m, C<u>H</u>$_2$Cl), 4.10 and 4.13 (each 1H, d, J=7.2, 3.5 Hz, C<u>H</u>$_2$$CH_3$), 7.4—7.8 (5H, m, arom.). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.72, 43.14, 53.43, 123.55, 128.95, 130.72, 143.00.

In the above reactions, the corresponding sulfones were obtained in minor amounts. The use of excess amounts of *m*-CPBA (>2.5 mol eq) in the oxidation reactions, afforded the sulfones as the major products in high yields.

Ethyl 2-Phenylsulfonylpropionate (**5h**): oil. High-resolution MS *m/z* 243.0691 (M^+; Calcd for $C_{11}H_{15}O_4S$: 243.0691. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.17 (3H, t, J=7.0 Hz) 1.58, (3H, d, J=7.4 Hz) 4.07 (1H, q, J=7.4 Hz) 4.13 (2H, q, J=7.0) 7.35—8.2 (5H, m, arom.).

General Procedure for the Fluorination of the Sulfoxides Exemplified by Using Methyl Phenyl Sulfoxide (1a) as the Substrate A solution of **1a** (140 mg, 1 mmol) in CH_3CN (50 ml) was cooled to −20 °C under bubbling of nitrogen. At this temperature, 5% F_2/N_2 was passed through the solution under vigorous stirring until 2 mmol (2 mol eq) of F_2 had passed through the flow meter (*ca.* 10 min). After the addition was completed, nitrogen was passed through the solution for 5 min. The reaction mixture was poured into ice-water (10 ml) and the pH of the solution was adjusted to 7—8 by the addition of a saturated aqueous solution of $NaHCO_3$. The whole was stirred until the temperature reached room temperature. The product was extracted with CH_2Cl_2 (100 ml) and the organic layer was dried over $MgSO_4$. The residue obtained after evaporation of the solvent was chromatographed on a silica gel column [hexane–AcOEt (3 : 1, v/v)] to give first trifluoromethyl phenyl sulfone (**4**: oil, bp 101—102 °C/15 mmHg),[17] the difluoromethyl sulfone (**3a**: oil),[16] and the monofluoromethyl sulfone (**2a**: oil),[5] then the starting sulfoxide (**1a**) in the isolated yields listed in Table 1. The ratios of the products can also be determined by GLC (5% OV-17, column temperature 175 °C and injection temperature 200 °C with carrier gas: N_2 1.8 kg/cm^{-1}) and are in good accordance with the data shown in Table 1. Under these conditions, the retention times of **4**, **3a**, **2a** and **1a** were 0.6, 1.6, 3.4 and 5.0 min, respectively.

Fluorination of related sulfoxides was carried out according to the general fluorination procedure and the results are listed in Table 2. In general, the sulfones are eluted faster than the sulfoxides and, in each series of compounds, the more fluorinated ones are eluted faster than the less fluorinated ones.

Structures of several fluorinated sulfones and sulfoxides not reported so far were determined based on the following data:

1-Chloro-1-fluoromethyl Phenyl Sulfone (**2b**): oil. High-resolution MS *m/z* 207.9795. (M^+; Calcd for $C_7H_6ClFO_2S$: 207.9761). IR (neat): 1345, 1332 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 6.57 (1H, d, J=49.1 Hz, CHFCl), 7.65 (2H, dd, J=9.5, 7.3 Hz, arom.), 7.80 (1H, dt,

J=9.5, 1.3 Hz, arom.), 8.01 (2H, br d, J=7.3 Hz, arom.). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.43 (d, J=284.4 Hz, CHFCl), 129.47, 130.64, 131.99, 135.69.

1-Fluoroethyl Phenyl Sulfone (**2d**): oil. High-resolution MS m/z 188.0293 (M^+; Calcd for $C_8H_9FO_2S$: 188.0307). IR (neat): 1448, 1322 cm^{-1}, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.71 (3H, dd, J=23.3, 6.6 Hz, CH_3), 5.29 (1H, dq, J=48.0, 6.6 Hz, CHF), 7.61 (2H, dd, J=7.7, 7.3 Hz, arom.), 7.73 (1H, tt, J=7.7, 1.4 Hz, arom.), 7.95 (2H, br d, J=7.3 Hz, arom.). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.76 (d, J=20.7 Hz, CH_3), 99.78 (d, J=217.6 Hz, CHF), 129.64, 129.32, 134.63, 134.86.

Ethyl 2-Fluoro-2-phenylsulfonylpropanoate (**2h**) (**1h**-less polar was used as the substrate): oil. High-resolution MS m/z 260.0483 (M^+; calcd for $C_{11}H_{13}FO_4S$: 260.0519). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.22 (3H, t, J=7.1 Hz, CH_3), 1.97 (3H, d, J=21.6 Hz, C($C\underline{H}_3$)F), 4.22 (2H, m, O$C\underline{H}_2$), 7.59 (2H, t, J=7.7 Hz, arom.), 7.74 (1H, t, J=7.3 Hz, arom.), 7.93 (2H, d, J=8.1 Hz, arom.).

1-Fluorocyclopropyl Phenyl Sulfone (**2k**): oil. High-resolution MS m/z 200.0332 (M^+; Calcd for $C_9H_9FO_2S$: 200.0307). ^{1}H-NMR (300 MHz, $CDCl_3$): δ, 1.43 (2H, ddd, J=17.5, 9.0, 7.0 Hz, C$\underline{H}$ *cis* to F), 1.70 (2H, ddd, J=9.0, 8.0, 7.0 Hz, CH *trans* to F). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.57 (d, J=10.4 Hz), 89.93 (d, J=264.8 Hz, CF), 128.98, 129.33, 134.40, 136.72.

2-Fluoropropan-2-yl Phenyl Sulfoxide (**14**): oil. High-resolution MS m/z 187.0592 (M^++1; Calcd for $C_9H_{12}FOS$: 187.0593). IR (neat): 1442, 1370 cm^{-1}, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.40 (3H, d, J=21.2 Hz, CH_3), 1.74 (3H, d, J=21.6 Hz, CH_3), 7.28—7.55 (3H, m, arom.), 7.64—7.68 (2H, m, arom.). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.48 (d, J=21.9 Hz, CH_3), 22.23 (d, J=21.9 Hz, CH_3), 125.99, 128.81, 131.71, 138.85.

Oxidation Reaction of Sulfides and Sulfoxides with Rozen's Reagent (HOF–CH_3CN Complex) Exemplified by Using Diphenyl Sulfide (22a) as the Substrate A mixture of CH_3CN and water (10 : 1, v/v, 25 ml) was cooled to −20 °C under bubbling of N_2. At this temperature, 5% F_2/N_2 was passed into the solution under vigorous stirring until 2 mmol (2 mol eq to **22a**) of F_2 had passed through the flow meter (*ca.* 10 min), then N_2 was bubbled through the mixture for 5 min. A solution of **22a** (186 mg, 1.00 mmol) in CH_2Cl_2 (5 ml) was added to the above solution. The mixture was stirred for 5 min at −20 °C, NaF (100 mg, 2.38 mol) was added and the precipitates that appeared were filtered off. A saturated aqueous solution of $NaHCO_3$ was added to the mixture until the pH became 7 and the product was extracted with CH_2Cl_2 (100 ml). After usual work-up, the diphenyl sulfone (**24a**) was obtained in 93% yield as a sole product. mp 126—128 °C (CH_2Cl_2–pentane). mp and spectroscopic data were identical with those of a commercially available authentic sample.

Use of 1 mol eq of F_2 in the above reaction resulted in the formation of the sulfoxide (**23a**: 17%) and the sulfone (**24a**: 51%), together with recovery (26%) of the sulfide (**22a**). During the separation by silica gel column chromatography, the elution order is **22a**, **24a**, and **23a**.

Oxidation of related sulfoxides was carried out according to the general oxidation procedure with Rosen's reagent, and the results are listed in Table 3.

Acknowledgments This work was supported in part by a Grant-in-Aid for Scientific Research to A. T. (Grant No. 07772084) from the Ministry of Education, Science, Sports and Culture, Japan. We also thank Asahi Glass Co., Ltd. for providing 5% F_2/N_2 used in this work.

References and Notes

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