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Oxidation of disulfides with electrophilic halogenating reagents: concise methods for preparation of thiosulfonates and sulfonyl halides

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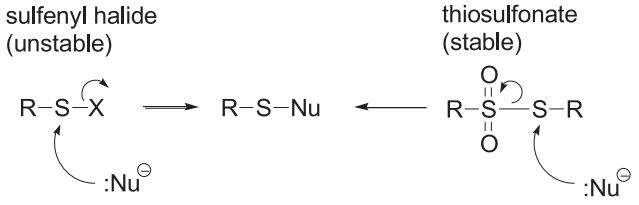
ABSTRACT

The reaction of aromatic or benzylic disulfides with 2.5 equiv of Selectfluor™ in acetonitrile/water (10:1) at room temperature efficiently produced the corresponding thiosulfonates. Conversely, the reaction of disulfides with 6.5 equiv of Selectfluor™ or thiosulfonates with 4.5 equiv of Selectfluor™ in refluxing acetonitrile/water (10:1) provided sulfonyl fluorides in high yields. Accufluor™ and FP-T300™ are also effective in preparing sulfonyl fluorides from disulfides under the similar reaction conditions. Sulfonyl chlorides or sulfonyl bromides were effectively obtained from the reaction of disulfides with 6 equiv of either *N*-chlorosuccinimide or *N*-bromosuccinimide in acetonitrile/water (10:1) at room temperature. Some other electrophilic chlorinating or brominating reagents are also able to be used instead of *N*-chlorosuccinimide or *N*-bromosuccinimide for the syntheses of sulfonyl halides from disulfides. These reactions of disulfides with electrophilic halogenating reagents are convenient methods to prepare thiosulfonates and sulfonyl halides.

1. Introduction

Thiosulfonates, which are stable compounds, can be used as strong electrophilic sulfenylating agents in organic synthesis.[1] Sulfenyl halides also act as electrophilic sulfenylating agents and have been widely used for this purpose (Scheme 1). However, they are unstable, difficult to handle, and must be prepared before use.[2] In spite of the synthetic utility of thiosulfonates,[3] the reagents are not so accessible because there are few methods to prepare them. Therefore, several research groups have recently developed new practical syntheses of thiosulfonates.[4]

Sulfonyl fluorides have seldom been used in organic syntheses. However, some, for example, phenyl methyl sulfonyl fluoride (PMSF) and 4-(2-aminomethyl)benzenesulfonyl fluoride hydrochloride (AEBSF), are strong protease inhibitors, and are frequently utilized in biochemistry (Fig. 1). Especially, PMSF has been essential and commonly used for the purification of enzymes from various tissues containing serine protease.[5]



Scheme 1. Electrophilic sulfenylating agents.

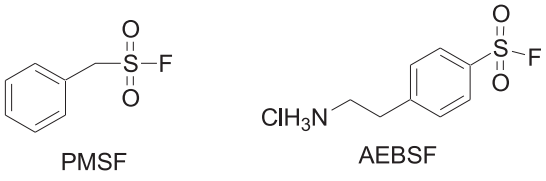


Fig. 1. Biologically important sulfonyl fluorides.

For such sulfonyl fluorides, there are few preparative methods.[6] The traditional method is nucleophilic substitution of sulfonyl chlorides using the fluoride ion ($^{n}Bu_4NF$ or KF/18-Crown-6).[6a–d] This method requires strict anhydrous conditions, otherwise

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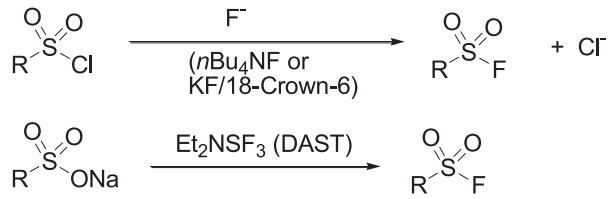
hydrolyzed compounds (sulfonic acids) are obtained as the major products.[6a–d] In 2009, Liskamp reported that the reaction of sodium sulfonates with *N*,*N*-diethylaminosulfur trifluoride (DAST) efficiently produces the corresponding sulfonyl fluoride.[6e] However, this method also required anhydrous conditions, because DAST is sensitive to water. Therefore, a more concise, less water-sensitive method for the preparation of sulfonyl fluoride was still needed (Scheme 2).



Scheme 2. Preparation of sulfonyl fluoride.

We recently found that the reaction of aromatic or benzylic disulfides with 2.5 equiv of Selectfluor™ {1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)} in acetonitrile/water (10:1) at room temperature efficiently produced the corresponding thiosulfonates, and the reaction of disulfides with 6.5 equiv of Selectfluor™ in refluxing acetonitrile/water (10:1) provided sulfonyl fluoride in high yields (Scheme 3). These results were published as a preliminary communication.[7]

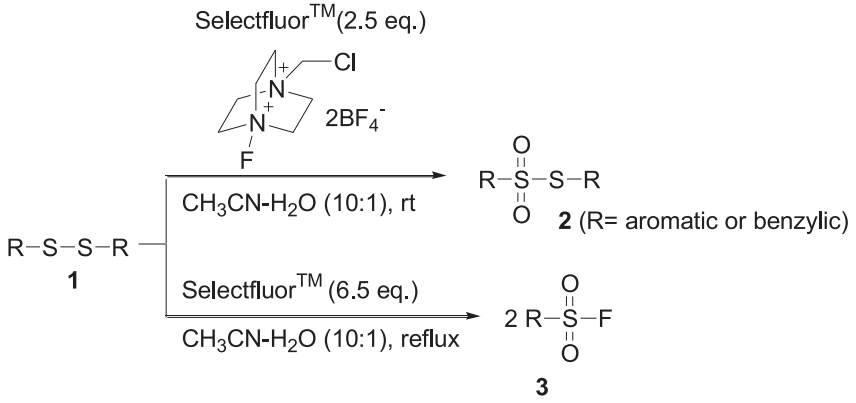
sulfonyl chlorides or sulfonyl bromides could be efficiently produced from the reactions of disulfides with electrophilic chlorinating or brominating reagents, including *N*-chlorosuccinimide (NCS, for sulfonyl chlorides) or *N*-bromosuccinimide (NBS, for sulfonyl bromides).

This paper describes in detail the reaction of disulfides with electrophilic halogenating reagents.

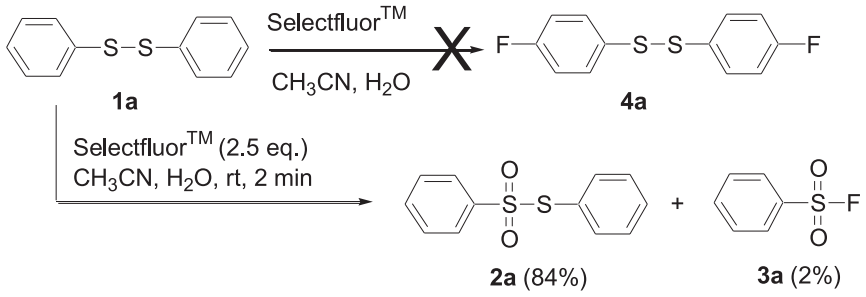
2. Synthesis of thiosulfonates from the reaction of disulfides with Selectfluor™

Selectfluor™ can be used for the reagent of electrophilic fluorination of aromatic compounds.[8a] Therefore we examined the reaction of diphenyl disulfide (**1a**) with 2.5 equiv of Selectfluor™ to prepare bis(*p*-fluorophenyl) disulfides (**4a**), during the course of our study of the synthesis of organofluorine compounds. Unfortunately, neither **4a** nor other fluorinated aromatic compounds were obtained at all. Phenyl benzenesulfonthiolate (thiosulfonate) (**2a**) was produced in high yield accompanied by a small amount of phenyl sulfonyl fluoride (**3a**) (Scheme 4).

Selectfluor™ is not only an electrophilic fluorinating reagent[8] but also a strong oxidant,[9] which explains why **1a** was further oxidized by Selectfluor™ to produce **2a** and **3a**. Based on this result, we theorized that the reaction of disulfides with Selectfluor™ might be an efficient method to prepare thiosulfonates. Initially, *p*-tolyl disulfide (**1b**) was chosen as a substrate and treated with 2.5 equiv of Selectfluor™ at room temperature to investigate any solvent effect (Table 1). In acetonitrile, the amount of water was



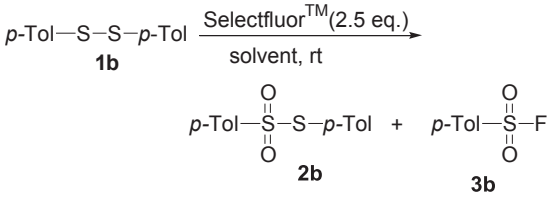
Scheme 3. Synthesis of thiosulfonates and sulfonyl fluoride by using Selectfluor™.



Scheme 4. Reaction of diphenyl disulfide with selectfluor™.

Further study of these reactions revealed that the sulfonyl fluorides can be synthesized from thiosulfonates in high yields. Other electrophilic fluorinating reagents are also applicable to the synthesis of sulfonyl fluorides from disulfides. We also found that found to be crucial to obtaining the corresponding thiosulfonate **2b** in high yield (runs 1–3). Acetonitrile/water (10:1) is the ideal (run 2). Neither aqueous methanol nor aqueous dimethylformamide afforded satisfactory results (runs 4 and 5).

Table 1
Reaction of di-*p*-tolyl disulfide with Selectfluor™ in several solvent-systems



Run	Solvent	Time	Ratio (%)[a]		
			1b	**2b**	**3b**
1	CH_3CN	1 h	52	26	22
2	CH_3CN/H_2O (10:1)	2 min	0	97	3
3	CH_3CN/H_2O (5:1)	24 h	11	87	2
4	CH_3OH/H_2O (10:1)	1 h	94	5	1
5	DMF/H_2O (10:1)	1 h	4	60	37

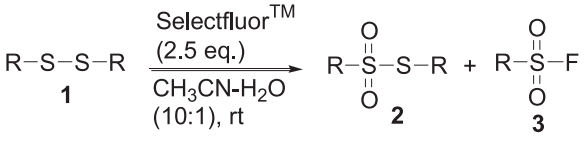
[a] Determined by 1H NMR (methyl protons). No products other than the thiosulfonate (**2b**) and the sulfonyl fluoride (**3b**) were detected in all cases.

Several disulfides were treated with 2.5 equiv of Selectfluor™ under optimal conditions [in acetonitrile/water (10:1), at room temperature] (Table 2). The corresponding thiosulfonates **2** were obtained in moderate to high yields accompanied by small amounts of the sulfonyl fluoride **3** in the cases of disulfides bearing aromatic or benzylic substituents (entries 1–5). For a disulfide having a relatively electron-deficient aromatic substituent, the reaction proceeded more slowly (entry 5). When aliphatic disulfides were used, the reaction rate was slow and inseparable mixtures of **1**, **2** and **3** were produced (runs 6 and 7).

Although the details of the reaction mechanism are not clear enough, one of the plausible reaction mechanisms for this Selectfluor™ disulfide oxidation is shown in Scheme 5. Initially, one of the sulfur atoms of **1** is fluorinated by Selectfluor™ to form a sulfonium ion (**A**), and successive substitution of the fluorine atom by water provides a thiosulfinate (**B**). The unchanged sulfur atom of **B** is further oxidized via a similar mechanism to produce an unstable disulfoxide (**C**), which immediately rearranges to form a stable thiosulfonate (**2**).[10]

According to this reaction mechanism, hydrogen fluoride must be produced, trapped by the amine generated from the Selectfluor™ consumed, to yield the corresponding ammonium fluorides. In fact, ammonium fluorides were detected in the resulting reaction mixture by ^{19}F NMR analysis (−155.7 and −189.1 ppm) as confirmation of this.

Table 2
Synthesis of thiosulfonate

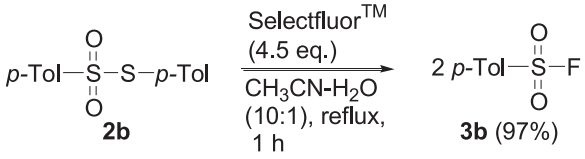


Entry	R	Time (min)	Yield (%)[a]		
			1	**2**	**3**
1	Ph	2	0	84	2
2	*p*-Tol	2	0	93	Trace
3	*p*-$MeOC_6H_4$	1	0	51	8
4	Bn	2	0	82	10
5	*p*-ClC_6H_4	20	3	72	10
6	$CH_3(CH_2)_9$	20	26[b]	36[b]	26[b]
7	Cyclohexyl	30	Mixture of **1**, **2**, and **3**[c]		

[a] Isolated yield except for entry 6.
[b] Based on GC–MS analysis using an internal standard.
[c] All attempts to determine the yields failed.

3. Synthesis of sulfonyl fluorides from the reaction of disulfides or thiosulfonates with electrophilic fluorinating reagents

The sulfonyl fluorides (**3**), which were obtained as byproducts of the reaction of the disulfides with 2.5 equiv of Selectfluor™ in aqueous acetonitrile, seem to be produced by further reaction of the thiosulfonates (**2**) with Selectfluor™ and water. To prove this hypothesis, the reaction of a thiosulfonate (**2b**) with 2.5 equiv of Selectfluor™ in aqueous acetonitrile was examined. The desired sulfonyl fluoride (**3b**) was obtained almost quantitatively under reflux conditions (Scheme 6).

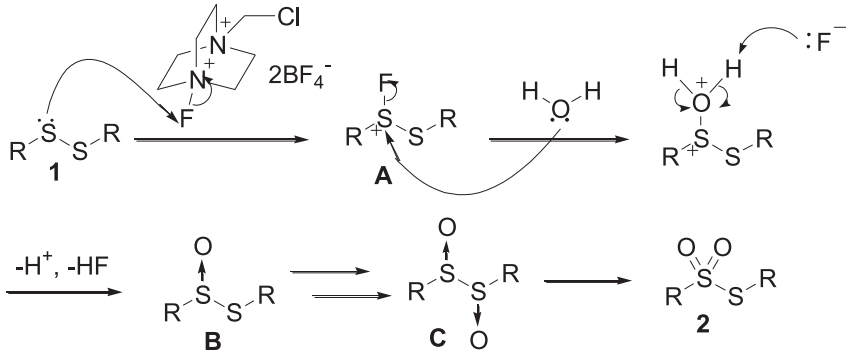


Scheme 6. Reaction of thiosulfonate (**2b**) with Selectfluor™.

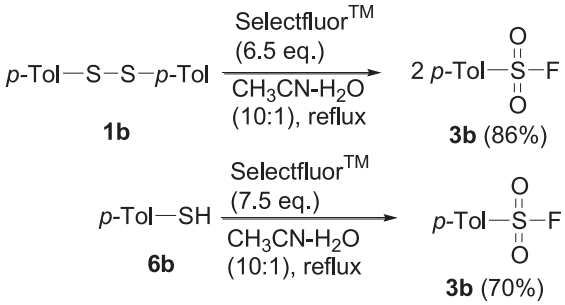
The reaction of di-*p*-tolyl disulfide (**1b**) or *p*-tolylthiol (**6b**) with Selectfluor™ in refluxing acetonitrile/water (10:1) also efficiently provided **3b** (Scheme 7).

It is interesting that the corresponding sulfonic acid was not obtained, even in the presence of water. This phenomenon strongly suggests that the fluorine–sulfur bond is constructed via a radical or electrophilic mechanism.

The reaction of several disulfides (1) with 6.5 equiv of Selectfluor™ in refluxing acetonitrile/water (10:1) was examined



Scheme 5. A plausible reaction mechanism from **1** to **2**.

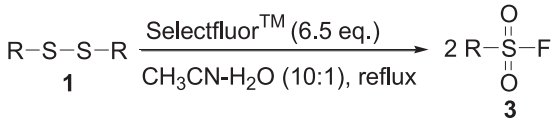


Scheme 7. Synthesis of sulfonyl fluoride (**3b**) from disulfide (**1b**) or thiol (**6b**).

(Table 3). The corresponding sulfonyl fluorides (**3**) were produced in moderate to high yields in all cases including aliphatic disulfides (entries 6 and 7).

Several sulfonyl fluorides (**3**) were also efficiently obtained from the reaction of the corresponding thiosulfonate (**2**) with 4.5 equiv

Table 3
Synthesis of sulfonyl fluorides from disulfides

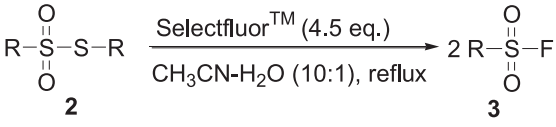


Entry	R	Time (h)	Yield (%)[a]
1	Ph (**3a**)	2.0	69
2	*p*-Tol (**3b**)	1.5	86
3	*p*-$MeOC_6H_4$ (**3c**)	1.0	77
4	Bn (**3d**)	1.5	88
5	*p*-ClC_6H_4 (**3e**)	3.0	96
6	Cyclohexyl (**3f**)	1.0	60
7	$CH_3(CH_2)_9$ (**3g**)	1.0	91

[a] Isolated yields.

of Selectfluor™ in refluxing aqueous acetonitrile (Table 4). These reactions are superior to existing methods for preparing sulfonyl fluorides[6] because the experimental procedure is quite simple and does not require strict anhydrous conditions.

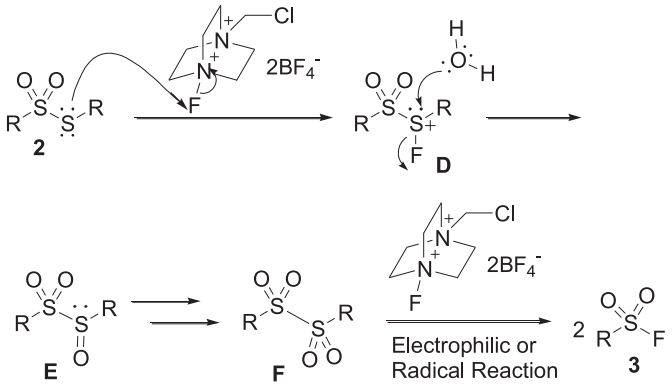
Table 4
Synthesis of sulfonyl fluorides from thiosulfonate



Entry	R	Time (h)	Yield (%)[a]
1	Ph (**3a**)	1.0	89
2	*p*-Tol (**3b**)	3.0	quant.
3	*p*-$MeOC_6H_4$ (**3c**)	1.0	90
4	Bn (**3d**)	1.5	98
5	*p*-ClC_6H_4 (**3e**)	4.7	72
6	Cyclohexyl (**3f**)	0.5	79

[a] Isolated yields.

A plausible reaction mechanism for the reaction of thiosulfonates (**2**) with Selectfluor™ is shown below (Scheme 8). A thiosulfonate sulfur atom is fluorinated by Selectfluor™, and the resulting sulfonium ion (**D**) is attacked by water to form **E**. Intermediate **E** is further oxidized by Selectfluor™ and water to



Scheme 8. A plausible reaction mechanism from **2** to **3**.

produce the disulfone (**F**). The radical or electrophilic reaction of **F** with Selectfluor™ provides the sulfonyl fluoride (**3**), however, the mechanism of this step is still unclear.

Following the plausible reaction mechanism described above, the electrophilic fluorinating ability of Selectfluor™ plays an important role. It is also important that Selectfluor™ is stable to water and can therefore be used in aqueous solutions. We expected that other water tolerant electrophilic fluorinating reagents, such as Accufluor™ [1-fluoro-4-hydroxy-1,4-diazoniabicyclo-[2,2,2]octane bis(tetrafluoroborate) on aluminum oxide] and FP-T300™ (1-fluoro-2,4,6-trimethyl-pyridinium trifluoromethanesulfonate) would be applicable to the preparation of thiosulfonates and sulfonyl fluorides. Actually, the reaction of *p*-tolyl disulfide (**1b**) with Accufluor™ or FP-T300™ in aqueous acetonitrile produced the sulfonyl fluoride (**3b**) in high yields (Scheme 9).[11] Unfortunately, the investigations of finding the suitable reaction conditions to selectively prepare the corresponding thiosulfonate (**2b**) using Accufluor™ or FP-T300™ were unsuccessful.

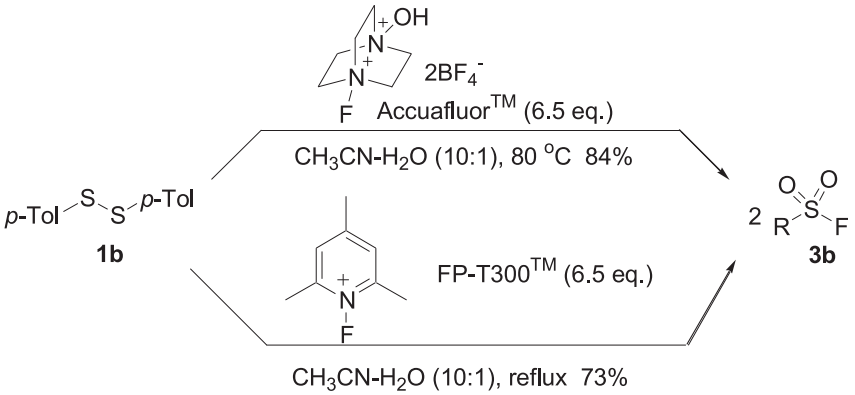
4. Reaction of disulfides with electrophilic chlorinating or brominating reagents

We expected that other water tolerant electrophilic halogenating reagents, such as *N*-chlorosuccinimide (NCS, an electrophilic chlorinating reagent) and *N*-bromosuccinimide (NBS, an electrophilic brominating reagent), would be applicable to the preparation of thiosulfonates and sulfonyl halides. It has been reported that the reaction of a disulfide with NCS and diluted hydrochloric acid provides the corresponding sulfonyl chloride.[12] The oxidative chlorination of disulfides with NCS/$BnMe_3NCl/H_2O$ affording sulfonyl chlorides was also recently reported.[13] However, the reaction of disulfides with simple NCS or NBS has not been reported. Therefore, the reaction of disulfides with NCS or NBS was examined.

Initially, *p*-tolyl disulfide (**1b**) was treated with varying amounts of NCS or NBS (1–6 equiv) in aqueous acetonitrile at room temperature (Table 5). Runs 1–6 made both the corresponding thiosulfonate and sulfonyl halide, and the sulfonyl halide was effectively obtained in runs 7 and 8. Although we have not succeeded in discovering the reaction conditions, which produce the thiosulfonate selectively, the reaction of disulfides with NCS or NBS are excellent methods for the preparation of sulfonyl halides.

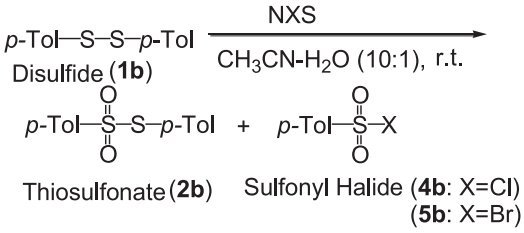
Several disulfides **1** were treated with 6 equiv of NCS in aqueous acetonitrile at room temperature (Table 6). The corresponding sulfonyl chlorides were obtained in high yields in all cases.

The desired sulfonyl bromides were effectively obtained from the oxidation of the disulfides **1** with NBS in aqueous acetonitrile at room temperature in most cases (Table 7). Unfortunately, *p*-methoxyphenylsulfonyl bromide (**5c**) was obtained in poor yield



Scheme 9. Reaction of **1b** with electrophilic fluorinating regents.

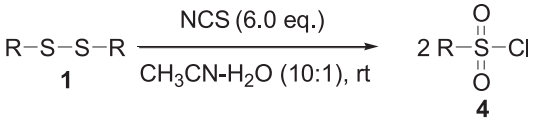
Table 5
Reaction of **1b** with NXS



Run	NXS	Equiv	Time (h)	Ratio (%)[a]		
				1b	**2b**	**4b** or **5b**
1	NCS	1.0	0.5	68	22	10
2	NBS	1.0	0.5	79	4	17
3	NCS	2.0	1.0	24	64	12
4	NBS	2.0	1.0	42	34	24
5	NCS	4.0	2.0	0	64	36
6	NBS	4.0	2.0	6	51	43
7	NCS	6.0	3.0	0	0	100
8	NBS	6.0	3.0	0	0	100

[a] Determined by ^{1}H NMR (methyl protons). No products other than the thiosulfonate (**2b**) and the sulfonyl halide (**4b**, **5b**) were detected in all cases.

Table 6
Synthesis of sulfonyl chloride (**4**)

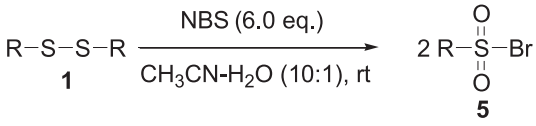


Entry	R	Time (h)	Yield (%)[a]
1	*p*-Tol (**4b**)	2.3	83
2	*p*-MeOC$_6$H$_4$ (**4c**)	2.3	88
3	Bn (**4d**)	2.5	84
4	*p*-ClC$_6$H$_4$ (**4e**)	2.3	85
5	Cyclohexyl (**4f**)	1.0	90
6	CH$_3$(CH$_2$)$_9$ (**4g**)	1.0	91

[a] Isolated yields.

under the reaction conditions (entry 2); however, **5c** was effectively produced when the reaction was performed in the dark (entry 3). Since sulfonyl bromide **5c** is photo sensitive, the **5c**, which was produced from the reaction of the disulfide **1c** under standard conditions easily decomposed during the NBS-reaction. Although the reaction effectively proceeded in the dark, the resulting sulfonyl bromide **5d** is unstable[14] and part of **5d** decomposed to benzyl bromide during silica-gel column chromatography purification.

Table 7
Synthesis of sulfonyl bromide (**5**)



Entry	R	Time (h)	Yield (%)[a]
1	*p*-Tol (**5b**)	3.0	79
2	*p*-MeOC$_6$H$_4$ (**5c**)	4.6	5
3[b]	*p*-MeOC$_6$H$_4$ (**5c**)	0.25	87
4[b]	Bn (**5d**)	2.5	—[c]
5	*p*-ClC$_6$H$_4$ (**5e**)	3.0	64
6	Cyclohexyl (**5f**)	3.0	94
7	CH$_3$(CH$_2$)$_9$ (**5g**)	2.7	quant.

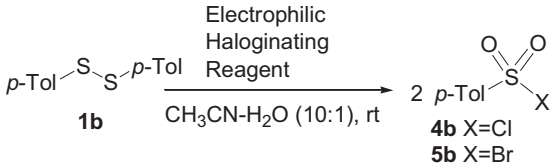
[a] Isolated yields.
[b] Reaction was performed in the dark.
[c] The mixture of sulfonyl bromide **5d** and benzyl bromide was obtained.

There have been no practical methods to prepare sulfonyl bromides. Therefore, they have seldom been used as reagents in organic synthesis. Our method is very practical, and seems to be an excellent preparation of sulfonyl bromides.

Other electrophilic chlorinating or brominating reagents [dichloramine T (*N*,*N*-dichloro-*p*-toluenesulfonamide) (run 2), *N*-chlorophthalimide (run 3), DBH (1,3-dibromo-5,5-dimethylhydantoin) (run 5), and *N*-bromophthalimide (run 6)] are also effective for the synthesis of sulfonyl halides from the disulfide (**1b**). The desired products were obtained in moderate to high yields (Table 8).

The mechanism of these reactions might be the same as for the reaction with Selectfluor™.

Table 8
Reaction of **1b** with electrophilic halogenating reagents



Run	Reagent	Equiv	Time (h)	Product	Yield (%)[a]
1	NCS	6.0	2.3	**4b**	83
2	Dichloramine T	6.0	1.0	**4b**	78
3	*N*-Chlorophthalimide	6.0	5.5	**4b**	41
4	NCS	6.0	3.0	**5b**	79
5	DBH	3.0	1.0	**5b**	94
6	*N*-Bromophthalimide	6.0	0.75	**5b**	63

[a] Isolated yields.

5. Conclusions

The oxidation of disulfides (**1**) with Selectfluor™ in the presence of water, produces the corresponding thiosulfonates (**2**), which further react with Selectfluor™ and water to provide the corresponding sulfonyl fluorides (**3**). Accufluor™ and FP-T300™ are also effective to prepare sulfonyl fluorides (**3**) from disulfides under the similar reaction conditions. Although the thiosulfonates (**2**) could not be selectively obtained from the reaction of the disulfides (**1**) with NCS or NBS in aqueous acetonitrile, the corresponding sulfonyl halides (**4**, **5**) were efficiently produced under the reaction conditions. Some other electrophilic chlorinating or brominating reagents are also able to be used instead of *N*-chlorosuccinimide or *N*-bromosuccinimide for the syntheses of sulfonyl halides (**4**, **5**) from disulfides (**1**).

6. Experimental

6.1. General

All reagents were obtained from Nacalai Tesque, Wako Pure Chemicals Industry, Kanto Kagaku, Kishida Reagents Chemicals Co, Tokyo Chemical Industry Co, or Aldrich, and were used without further purification. Melting points were measured using a Yanaco micromelting point apparatus (MP-J3), and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL (JNM-EX400) spectrometer in $CDCl_3$ solutions, using TMS or the residual $CHCl_3$ peak as an internal standard. The IR spectra were recorded using a Jasco IR-8300 FT-IR spectrophotometer. The mass spectra were recorded on a Shimadzu GCMS-QP1100EX spectrometer.

6.2. Representative experimental procedure to prepare thiosulfonates from disulfides

To a stirred solution of *p*-tolyl disulfide (**1b**) (246.3 mg, 1.0 mmol) in acetonitrile (2.0 mL) and water (0.2 mL), Selectfluor™ (885.5 mg, 2.5 mmol) was added at room temperature for over 20 min, and the resulting mixture was stirred. The reaction was monitored via thin layer chromatography (TLC). After the disulfide disappeared from the TLC, water (5 mL) was added, and the resulting mixture was extracted with ethyl acetate (15 mL×3). The extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel using *n*-hexane/ethyl acetate as the eluent gave the corresponding thiosulfonate (**2b**) (259.3 mg, 93%) as colorless crystals.

*6.2.1. Diphenyl thiosulfonate (**2a**).*[15,16] Colorless crystals, mp 41 °C (lit.[16] 41–42 °C). ^{1}H NMR ($CDCl_3$) δ: 7.63–7.28 (10H, m). ^{13}C NMR ($CDCl_3$) δ: 127.52, 127.78, 128.78, 129.40, 131.39, 133.62, 136.56, 142.87. MS (*m*/*z*): 250 (M^+). IR (KBr) cm^{-1}: 1310, 1133.

*6.2.2. 4,4′-Dimethylphenyl thiosulfonate (**2b**).*[16] Colorless crystals, mp 76.5 °C (lit.[16] 73–75 °C). ^{1}H NMR ($CDCl_3$) δ: 2.38 (3H, s), 2.42 (3H, s), 7.14 (2H, d, *J*=8.4 Hz), 7.21 (2H, d, *J*=8.4 Hz), 7.25 (2H, d, *J*=8.4 Hz), 7.46 (2H, d, *J*=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.46, 21.62, 124.54, 127.55, 129.33, 130.16, 136.45, 140.40, 144.55. MS (*m*/*z*): 278 (M^+). IR (KBr) cm^{-1}: 1327, 1142.

*6.2.3. 4,4′-Dimethoxyphenyl thiosulfonate (**2c**).*[16] Colorless crystals, mp 91.3 °C (lit.[16] 92–94 °C). ^{1}H NMR ($CDCl_3$) δ: 3.83 (3H, s), 3.87 (3H, s), 6.85 (2H, d, *J*=9.2 Hz), 6.88 (2H, d, *J*=9.2 Hz), 7.27 (2H, d, *J*=9.2 Hz), 7.51 (2H, d, *J*=9.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 55.46, 55.69, 113.81, 114.89, 118.90, 129.89, 134.91, 138.35, 162.18, 163.49. MS (*m*/*z*): 310 (M^+). IR (KBr) cm^{-1}: 1321, 1129.

*6.2.4. Dibenzyl thiosulfonate (**2d**).*[16,17] Yellow crystals, mp 101.5 °C (lit.[17] 102–104 °C). ^{1}H NMR ($CDCl_3$) δ: 4.03 (2H, s), 4.22 (2H, s), 7.26–7.37 (10H, m). ^{13}C NMR ($CDCl_3$) δ: 40.92, 69.03, 127.66, 128.31, 128.98, 129.34, 131.35, 134.81. MS (*m*/*z*): 122, 91, 65. IR (KBr) cm^{-1}: 3085, 1510, 1332.

*6.2.5. 4,4′-Dichlorophenyl thiosulfonate (**2e**).*[16] Colorless crystals, mp 137.5 °C (lit.[16] 134–136 °C). ^{1}H NMR ($CDCl_3$) δ: 7.31 (2H, d, *J*=8.4 Hz), 7.36 (2H, d, *J*=8.4 Hz), 7.43 (2H, d, *J*=8.4 Hz), 7.52 (2H, d, *J*=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 126.00, 128.92, 129.26, 129.91, 137.67, 138.56, 140.55, 141.28. MS (*m*/*z*): 159, 143, 111. IR (KBr) cm^{-1}: 1570, 1467.

6.3. Representative experimental procedure to prepare sulfonyl fluorides from disulfides

To a stirred solution of *p*-tolyl disulfide (**1b**) (246.3 mg, 1.0 mmol) in acetonitrile (10.0 mL) and water (1.0 mL), Selectfluor™ (2306 mg, 6.5 mmol) was added at room temperature for over 20 min, and the resulting mixture was heated under reflux. The reaction was monitored via TLC. After the disulfide and the corresponding thiosulfonate disappeared from the TLC, water (10 mL) was added, and the resulting mixture was extracted with ethyl acetate (20 mL×3). The extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel using *n*-hexane/ethyl acetate as the eluent gave the sulfonyl fluoride (**3b**) (299.0 mg, 86%) as colorless crystals.

6.4. A representative experimental procedure to prepare sulfonyl fluorides from thiosulfonates

To a stirred solution of 4,4′-dimethylphenyl thiosulfonate (**2b**) (278.0 mg, 1.0 mmol) in acetonitrile (10.0 mL) and water (1.0 mL), Selectfluor™ (1594 mg, 4.5 mmol) was added at room temperature for over 20 min, and the resulting mixture was heated under reflux for 1.5 h. The reaction was monitored via TLC. After the thiosulfonate disappeared from the TLC, water (10 mL) was added and the resulting mixture was extracted with ethyl acetate (20 mL×3). The extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel using *n*-hexane/ethyl acetate as the eluent gave the sulfonyl fluoride (**3b**) (347.8 mg, quant.) as colorless crystals.

*6.4.1. Benzenesulfonyl fluoride (**3a**).*[18] Pale yellow crystals, mp 87 °C (lit.[18] 88–89 °C). ^{1}H NMR ($CDCl_3$) δ: 7.64 (2H, t, *J*=7.8 Hz), 7.79 (1H, t, *J*=7.8 Hz), 8.03 (2H, d, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 128.37, 129.65, 133.04 (d, *J*=24.9 Hz), 135.56. ^{19}F NMR ($CDCl_3$) δ: −200.43. MS (*m*/*z*): 160 (M^+). IR (KBr) cm^{-1}: 1730, 1405, 1208.

*6.4.2. p-Tolylsulfonyl fluoride (**3b**).*[18] Pale yellow crystals, mp 39 °C (lit.[18] 41–43 °C). ^{1}H NMR ($CDCl_3$) δ: 2.49 (3H, s), 7.42 (2H, d, *J*=7.8 Hz), 7.90 (2H, d, *J*=8.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.75, 128.37, 129.95 (d, *J*=24.0 Hz), 130.23, 147.11. ^{19}F NMR ($CDCl_3$) δ: -200.12 (1F, s). MS (*m*/*z*): 174 (M^+). IR (KBr) cm^{-1}: 1410, 1205.

*6.4.3. 4-Methoxyphenylsulfonyl fluoride (**3c**).*[18] Yellow crystals, mp 93 °C (lit.[18] 93–94 °C). ^{1}H NMR ($CDCl_3$) δ: 3.92 (3H, d, *J*=2.0 Hz), 7.06 (2H, d, *J*=7.6 Hz), 7.95 (2H, d, *J*=7.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 55.86, 114.83, 123.94 (d, *J*=24.8 Hz), 130.78, 165.19. ^{19}F NMR ($CDCl_3$) δ: −199.03 (1F, s). MS (*m*/*z*): 190 (M^+). IR (KBr) cm^{-1}: 2852, 1405, 1213.

*6.4.4. Benzylsulfonyl fluoride (**3d**).*[19] Pale yellow crystals, mp 90 °C (lit.[19] 92 °C). ^{1}H NMR ($CDCl_3$) δ: 4.60 (2H, d, *J*=3.1 Hz), 7.40–7.49 (5H, m). ^{13}C NMR ($CDCl_3$) δ: 56.84 (d, *J*=17.4 Hz), 125.47, 129.33,

129.93, 130.66. ^{19}F NMR ($CDCl_3$) δ: −214.89 (1F, s). MS (m/z): 174 (M^+). IR (KBr) cm^{-1}: 1406, 1214.

*6.4.5. 4-Chlorophenylsulfonyl fluoride (**3e**).*[18] Colorless crystals, mp 48 °C (lit.[18] 36–37 °C). ^{1}H NMR ($CDCl_3$) δ: 7.61 (2H, d, J=8.5 Hz), 7.96 (2H, d, J=8.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 129.89, 130.13, 131.4 (d, J=26.5 Hz), 142.69. ^{19}F NMR ($CDCl_3$) δ: −199.90 (1F, s). MS (m/z): 194 (M^+). IR (KBr) cm^{-1}: 1412, 1213, 1089.

*6.4.6. Cyclohexylsulfonyl fluoride (**3f**).*[20] Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.26–1.37 (3H, m), 1.67–1.77 (3H, m), 1.94–1.97 (2H, m), 2.28–2.31 (2H, m), 3.28–3.34 (1H, m). ^{13}C NMR ($CDCl_3$) δ: 14.11, 24.62, 24.67, 26.42. ^{19}F NMR ($CDCl_3$) δ: −225.45 (1F, s). MS (m/z): 166 (M^+). IR (neat) cm^{-1}: 2944, 2254, 1399, 1199.

*6.4.7. Decylsulfonylfluoride (**3g**).*[20] Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ: 0.8–0.96 (3H, m), 1.27–1.97 (16H, m), 3.35 (2H, s). ^{13}C NMR ($CDCl_3$) δ: 14.08, 22.63, 23.38, 27.83, 28.68, 28.773, 29.13, 29.18, 29.37, 31.80. ^{19}F NMR ($CDCl_3$) δ: −213.04 (1F, s). MS (m/z): 224 (M^+). IR (neat) cm^{-1}: 2928, 1856, 1402, 1197.

6.5. Representative experimental procedure to prepare sulfonyl chloride from disulfides

To a stirred solution of *p*-tolyl disulfide (**1b**) (246.3 mg, 1.0 mmol) in acetonitrile (2.0 mL) and water (0.2 mL), *N*-chlorosuccinimide (802 mg, 6.0 mmol) was added, and the resulting mixture was stirred at room temperature for 3 h. Water (10 mL) was added and the resulting mixture was extracted with ethyl acetate (20 mL×3). The extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel using *n*-hexane/ethyl acetate as the eluent gave the sulfonyl chloride (**4b**) (304.7 mg, 83%) as colorless crystals.

*6.5.1. p-Toluenesulfnoyl chloride (**4b**).*[19] Mp 68 °C (lit.[19] 65–69 °C). ^{1}H NMR ($CDCl_3$) δ: 2.49 (3H, s), 7.41 (2H, d, J=8.4 Hz), 7.93 (2H, d, J=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.83, 127.06, 130.23, 141.71, 146.79. MS (m/z): 190 (M^+ for ^{35}Cl). IR (neat): 1591, 1375, 1299, 1172, 1079, 810, 653, 567, 525.

*6.5.2. p-Methoxybenzenesulfonyl chloride (**4c**).*[19] Colorless crystals, mp 38 °C (lit.[19] 39–42 °C). ^{1}H NMR ($CDCl_3$) δ: 3.93 (3H, s), 7.05 (2H, d, J=9.0 Hz), 7.98 (2H, d, J=9.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 55.96, 114.69, 129.54, 136.07, 164.85. MS (m/z): 206 (M^+ for ^{35}Cl). IR (neat) cm^{-1}: 3101, 2945, 2846, 1589, 1493, 1371, 1268, 1163, 1083, 1022, 832, 659, 566.

*6.5.3. Benzylsulfonyl chloride (**4d**).*[19] Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 4.87 (2H, s), 7.43–7.51 (5H, m). ^{13}C NMR ($CDCl_3$) δ: 70.90, 126.10, 129.21, 130.28, 131.38. MS (m/z): 190 (M^+ for ^{35}Cl), 192 (M^+ for ^{37}Cl). IR (neat) cm^{-1}: 2989, 2918, 1494, 1455, 1367, 1257, 1162, 908, 772, 696, 515.

*6.5.4. 4-Chlorobenzenesulfonyl chloride (**4e**).*[19] Colorless crystals, mp 53 °C (lit.[19] 50–52 °C). ^{1}H NMR ($CDCl_3$) δ: 7.61 (2H, d, J=8.8 Hz), 7.99 (2H, d, J=8.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 128.43, 130.04, 142.21, 142.59. MS (m/z): 211 (M^+ for ^{35}Cl). IR (neat) cm^{-1}: 1577, 1474, 1377, 1280, 1174, 1091, 1011, 826, 753, 603, 565, 468.

*6.5.5. Cyclohexanesulfonyl chloride (**4f**).*[19] Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.43–1.20 (3H, m), 1.78–1.68 (3H, m), 2.00 (2H, d, J=13.4 Hz), 2.43 (2H, d, J=12.4 Hz), 3.51 (1H, tt, J=12.4, 3.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 24.73, 25.07, 27.23, 74.93. MS (m/z): 99, 83. IR (neat) cm^{-1}: 2941, 2863, 1452, 1366, 1272, 1160, 994, 750, 589, 539, 483.

*6.5.6. Decanesulfonyl chloride (**4g**).*[21] Colorless crystals, mp 30 °C (lit.[21] 34 °C). ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t, J=6.3, 7.1 Hz), 1.52–1.27 (16H, m), 2.08–2.01 (2H, m), 3.66 (2H, t, J=7.8, 8.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.09, 22.64, 24.26, 27.56, 28.87, 29.15, 29.19, 29.37, 31.81, 65.48. MS (m/z): 207, 140. IR (neat) cm^{-1}: 2927, 2857, 1461, 1375, 1166, 755, 735, 591, 521.

6.6. Representative experimental procedure to prepare sulfonyl bromide from disulfides

In a 10 mL round bottom flask, *p*-tolyl disulfide (**1b**) (246.3 mg, 1.0 mmol) was dissolved in acetonitrile (2.0 mL) and water (0.2 mL). The round bottom flask was covered with aluminum foil to shield it from light. *N*-Bromosuccinimide (1068 mg, 6.0 mmol) was added to the mixture, and the resulting mixture was stirred at room temperature for 3 h. Water (10 mL) was added and the resulting mixture was extracted with ethyl acetate (20 mL×3). The extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel using *n*-hexane/ethyl acetate as the eluent gave the sulfonyl bromide (**5b**) (371.4 mg, 79%) as colorless crystals.

*6.6.1. p-Toluenesulfonyl bromide (**5b**).*[22] Colorless crystals, mp 95 °C (lit.[22] 95–96 °C). ^{1}H NMR ($CDCl_3$) δ: 2.49 (3H, s), 7.39 (2H, d, J=8.4 Hz), 7.89 (2H, d, J=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.85, 126.54, 130.13, 144.61, 146.86. MS (m/z): 155, 91. IR (neat) cm^{-1}: 1361, 1296, 1171, 1076, 808, 647, 567, 550.

*6.6.2. p-Methoxybenzenesulfonyl bromide (**5c**).*[22] Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 3.93 (3H, s), 7.03 (2H, d, J=9.1 Hz), 7.95 (2H, d, J=9.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 55.99, 114.53, 129.10, 139.18, 170.26. MS (m/z): 253 (M^+ for ^{81}Br), 251 (M^+ for ^{79}Br). IR (neat) cm^{-1}: 3100, 2943, 2846, 1586, 1491, 1360, 1266, 1157, 1079, 1018, 834, 655, 561.

*6.6.3. 4-Chlorobenzenesulfonyl bromide (**5e**).*[23] Colorless crystals, mp 53 °C (lit.[23] 56 °C). ^{1}H NMR ($CDCl_3$) δ: 7.59 (2H, d, J=8.4 Hz), 7.95 (2H, d, J=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 127.91, 129.91, 142.06, 145.33. MS (m/z): 144, 109. IR (neat) cm^{-1}: 1570, 1470, 1365, 1282, 1161, 1089, 1012, 826, 749, 691, 590, 463.

*6.6.4. Cyclohexanesulfonyl bromide (**5f**).* Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ: 1.45–1.21 (3H, m), 1.75–1.66 (3H,m), 1.99 (2H, d, J=13.7 Hz), 2.42 (2H, d, J=12.9 Hz), 3.49 (1H, tt, J=11.8, 3.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 24.80, 24.99, 27.55, 78.84. IR (neat) cm^{-1}: 2940, 2861, 1451, 1357, 1270, 1151, 995, 893, 742, 572, 525, 474. MS (ESI) (m/z): 251 [(M+Na)$^+$ for ^{81}Br], 249 [(M+Na)$^+$ for ^{79}Br]. HRMS (ESI) calcd for $C_6H_{11}{}^{79}BrO_2SNa$ [(M+Na)$^+$], 248.9555, found: 248.9549.

*6.6.5. Decanesulfonyl bromide (**5g**).* Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, t, J=7.0 Hz), 1.52–1.27 (16H, m), 2.04 (2H, m), 3.66 (2H, t, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.09, 22.64, 24.58, 27.28, 28.90, 29.16, 29.20, 29.37, 31.81, 69.66. IR (neat) cm^{-1}: 2939, 2860, 1451, 1354, 1212, 1154, 955, 848, 742, 571, 529. MS (ESI) (m/z): 309 [(M+Na)$^+$ for ^{81}Br], 307 [(M+Na)$^+$ for ^{79}Br]. HRMS (ESI) calcd for $C_{10}H_{21}{}^{79}BrO_2SNa$ [(M+Na)$^+$], 307.0338, found: 307.0331.

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