A New Route to Thio- and Selenosulfonates from Disulfides and Diselenides. Application to the Synthesis of New Thio- and Selenoesters of Triflic Acid

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Alkyl and aryl trifluoromethanethiosulfonates[1] (or selenosulfonates) were prepared in one step either from alkyl and aryl sulfenyl (or selenenyl) chlorides and sodium trifluoromethanesulfinate (**3**) or, more generally, from disulfides (or diselenides), **3**, and bromine. The second method involved trifluoromethanesulfonyl bromide as key intermediate. Benzenethiosulfonates were obtained in a similar way from disulfides, benzenesulfinate, and bromine but benzeneselenosulfonates could not be obtained by the same method from diselenides.

Introduction

Some years ago, we described new trifluoromethylation processes in which the trifluoromethyl radical was mildly generated either by single-electron reduction of bromotrifluoromethane[2] or by single-electron oxidation of sodium trifluoromethanesulfinate[3] (sodium "triflinate", a stable salt readily obtained from CF_3Br and cheap sources of $SO_2^{\bullet-}$).[4] Nevertheless, these two complementary techniques, though simple and efficient, must be applied to substrates which are not reactive under reductive or oxidative conditions. In order to circumvent such drawbacks, we looked for new sources of the $^{\bullet}CF_3$ radical under mild and "neutral" conditions (from a redox point of view).

Since our previous experiments[3] indicated that the trifluoromethanesulfonyl radical $CF_3SO_2^{\bullet}$ is very unstable (as confirmed by further independent calculations),[5] we planned to examine the photolytic behavior of trifluoromethanethiosulfonates (CF_3SO_2SR, **1**) and their seleno analogues (CF_3SO_2SeR, **2**), compounds in which the trifluoromethanesulfonyl moiety is linked by weak bonds to large atoms like sulfur or selenium. This strategy was successful (the results will be given in future papers), but first, we had to prepare such reagents. At the moment, only one perfluorinated trifluoromethaneselenosulfonate ($CF_3SO_2SeCF_3$) has been described (from a surprising isomerization of $CF_3Se(O)OSCF_3$)[6] and only few trifluoromethanethiosulfonates, essentially CF_3SO_2SPh[7] and $CF_3SO_2SCF_3$,[8] have been synthesized. Another one ($CF_3SO_2-S-CCl_2-CO-NPh^iPr$) has been claimed to exhibit herbicidal properties.[9] On the other hand, apart from their interest as generators of trifluoromethyl radicals, trifluoromethanethiosulfonates could be also stable and more potent sulfenylating agents than nonfluorinated thiosulfonates,[10−12] which have found attractive applications in cephem synthesis.[13,14] Like their nonfluorinated analogues,[15] trifluoromethaneselenosulfonates could be also useful tools in organic synthesis.

Results and Discussion

Though the successful preparation of *p*-tolyl *p*-toluenethiosulfonate from *p*-toluenesulfonic anhydride, *p*-methylthiophenol, and pyridine has been claimed in the literature,[16] the more usual course of the reactions between thiols and sulfonic anhydrides[17] or sulfonyl chlorides[10,11,18] does not lead to the formation of thiosulfonates but to disulfides as the major products. The reason is that thiosulfonates, in which the divalent sulfur atom is usually more electrophilic than the hexavalent

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(1) In *Chemical Abstracts*, alkanethiosulfonates are named alkanesulfonothioic acids *S*-alkyl (or -aryl) esters. As these compounds are often cited in this paper, it has been chosen to keep the simpler thiosulfonate nomenclature system.

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Scheme 1. Reaction of Thiols with Triflic Anhydride in the Presence of a Base

$$RSH + B^- \rightleftharpoons RS^- + BH$$
$$(CF_3SO_2)_2O + RS^- \longrightarrow CF_3SO_2SR + CF_3SO_3^-$$
$$CF_3SO_2SR + RS^- \longrightarrow RSSR + CF_3SO_2^-$$

Scheme 2. Reaction of Thiols with Triflic Anhydride in the Absence of a Base

$$(CF_3SO_2)_2O + RSH \longrightarrow CF_3SO_2SR + CF_3SO_3H$$
$$CF_3SO_2SR + RSH \longrightarrow CF_3SO_2H + RSSR$$
$$CF_3SO_2H + RSH \longrightarrow CF_3S(O)SR + H_2O$$
$$2CF_3S(O)SR \longrightarrow CF_3SSR + CF_3SO_2SR$$

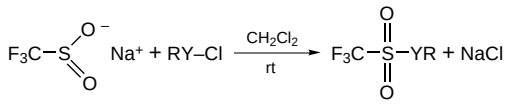
one,[10,18,19] react with thiols[20,21] and thiolates[22] as soon as they are formed. A recent paper indicates that fair yields of thiosulfonates can be reached, at low temperature, from lithium 1-propenethiolate and a very large excess of alkanesulfonyl chloride (20 equiv) since, with only 2 equiv, the corresponding disulfide is formed with an excellent yield.[23]

Indeed, in our hands, thiophenol, trifluoromethanesulfonic anhydride, and pyridine (or sodium hydride) failed to deliver phenyl trifluoromethanesulfonate (CF_3SO_2SPh, **1a**), even at −78 °C: only diphenyl disulfide was obtained along with pyridinium (or sodium) triflate and triflinate (Scheme 1).

Nevertheless, it should be noted that, in the absence of any base, phenyl trifluoromethyl disulfide (CF_3SSPh) is the major nonvolatile product along with diphenyl disulfide. CF_3SSPh has been previously obtained in one or two steps from very toxic reagents like trifluoromethanesulfenyl chloride (CF_3SCl)[24−26] or bis(trifluoromethyl) trisulfide (CF_3SSSCF_3).[27] In our experiment, it could result either from the reaction of thiophenol with $CF_3SO_2SCF_3$ (formed *in situ* by disproportionation of trifluoromethanesulfinic acid, as reported for nonfluorinated sulfinic acids[28]) or, more probably, from the disproportionation of the thiosulfinate $CF_3S(O)SPh$,[8] formed *in situ* from trifluoromethanesulfinic acid and thiophenol (Scheme 2).

Such an observation probably precludes any triflinic acid-based strategy for the synthesis of thio- or selenoesters of triflic acid.[13,28,29] Likewise, the oxidation of phenyl trifluoromethyl disulfide does not seem suited to our purpose since it would probably deliver CF_3SSO_2Ph rather than CF_3SO_2SPh.[30,31]

Table 1. Preparation of Trifluoromethanethio- and -selenosulfonates from Sulfenyl and Selenenyl Chlorides



3

1a–e (Y = S)
2a (Y = Se)

R	Y	product	reaction time	yield (%)[a]
Ph	S[b]	**1a**	15 min	84
Ph	Se	**2a**	5 min	95
4-$O_2NC_6H_4$	S	**1b**	15 min	93
CCl_3	S	**1c**	48 h	95
CO_2Me	S	**1d**	1 h	(96)
$C(Ph)_3$	S	**1e**	24 h	0

[a] Isolated yields except when mentioned in parentheses (yields from ^{19}F NMR analysis). [b] PhSCl prepared from thiophenol and *N*-chlorosuccinimide.[33]

Then, we turned our attention to the use of sodium triflinate (CF_3SO_2Na) which is now readily available.[4] Silver sulfinates are known to react with sulfenyl chlorides,[30] as do alkaline sulfinates[21] which are also able to substitute some relatively stable areneselenenyl bromides;[32] sodium triflinate itself has been employed to obtain one of the few trifluoromethanethiosulfonates known at the moment ($CF_3SO_2-S-CCl_2-CO-NPh^iPr$).[9] Consequently, we prepared several new trifluoromethanethiosulfonates (**1a**−**d**) and one trifluoromethaneselenosulfonate (**2a**) from sodium triflinate (**3**) and commercially available (or easily prepared) sulfenyl and selenenyl chlorides (Table 1). The reaction occurred rapidly at room temperature with good yields and can be carried out in pure dichloromethane instead of the biphasic system (CCl_4/H_2O) previously recommended.[9]

IR spectra confirmed that **1a**−**d** are true thiosulfonates (−S(O)$_2$−S−) (ν_{sym} = 1110−1120 cm^{-1}, ν_{asym} = 1370−1390 cm^{-1})[33] and not mixed sulfinyl−sulfenyl anhydrides (−S(O)−O−S−), in other words that sulfur is engaged in the CF_3SO_2 moiety as S(VI) and not as S(IV). The same is true for the seleno derivative **2a** (ν_{sym} = 1095 cm^{-1}, ν_{asym} = 1353 cm^{-1}). Compound **2a** can be isolated after filtration and evaporation, but its shelf-life is rather limited (<1 day). Nevertheless, as it will be reported in a subsequent paper, it can be used *in situ*.

However, sulfenyl and selenenyl chlorides are not very stable and few of them are commercially available. If arenesulfenyl chlorides can be obtained directly from the corresponding thiophenols,[34] other ones must be prepared by halogenation of the corresponding disulfides[34] or aryl benzyl sulfides.[35] Since disulfides and diselenides can themselves behave as sulfenylating or selenenylating agents, we then considered the opportunity to synthesize **1** and **2** directly from **3**, and these compounds which, on the other hand, are readily available from thiols,[36]

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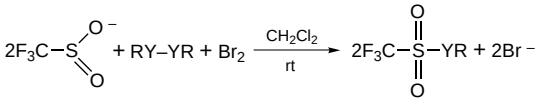
Table 2. Preparation of Trifluoromethanethio- and -selenosulfonates from Disulfides and Diselenides



3 **4a,f–k** **5a** **1a,f–j** (Y = S) **2a** (Y = Se)

R	Y	substr	RYYR/Br_2/**3**	product	yield (%)[a]
Ph	S	**4a**	1/1/2	**1a**	50
Ph	S	**4a**	1/1.5/3	**1a**	67
Ph	Se	**5a**	1/1/2	**2a**	(55)
4-ClC_6H_4	S	**4f**	1/1/2	**1f**	50
$PhCH_2$	S	**4g**	1/1/2	**1g**	90
n-C_8H_{17}	S	**4h**	1/1/2	**1h**	88
$-(CH_2)_2CO_2Et$	S	**4i**	1/1/2	**1i**	88
c-C_6H_{11}	S	**4j**	1/1/2	**1j**	65
t-Bu	S	**4k**	1/1/2	**1k**	0

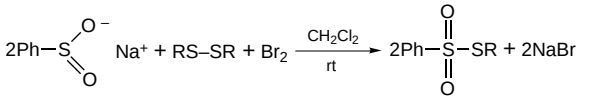
[a] Isolated yields except when mentioned in parentheses (yields from ^{19}F NMR analysis).

thioacetates,[37] thiocyanates,[38] or selenocyanates,[32b] as well as from alkyl halides[39] or arenediazonium salts.[40]

Indeed, some aryl areneselenosulfonates have been produced, very recently, by oxidation of aryl diselenides in the presence of arenesulfinates. However, with ammonium peroxydisulfate as oxidant,[41] the technique is not adaptable to the synthesis of **2** since peroxydisulfate oxidizes triflinate anion to $^{\bullet}CF_3$.[3a] When [bis(trifluoroacetoxy)iodo]benzene is used,[42] a 4-fold excess of sulfinate (over diselenide) is claimed and, moreover, the large amounts of side products (PhI, CF_3CO_2Na) are not in accordance with the recent "atom economy" concept. Concerning thiosulfonates, some have been already obtained from sodium methanesulfinate and disulfides, provided that the latter were activated with stoichiometric amounts of silver nitrate.[43] In this expensive technique, only one thiyl moiety of the disulfide leads to the desired product, the second one being lost as insoluble silver thiolate. Thus, we examined the possibility of activating disulfides (**4**) or diselenides (**5**) *in situ* by bromine (in the form of sulfenyl bromides or bromosulfonium bromides) to promote their reaction with **3**.

Indeed, when solutions of **3** and different disulfides (**4a,f**−**k**) in dichloromethane were treated dropwise with bromine at room temperature and then stirred at the same temperature for 8 h, the corresponding trifluoromethanethiosulfonates (**1a,f**−**j**) were obtained in fair to good yields. Provided that a molar ratio **3**/**4** ≥ 2 was used, both thiyl moieties of the disulfide delivered the corresponding thiosulfonate (Table 2). Aliphatic disulfides, which are more nucleophilic, delivered better yields than aromatic ones. In the latter case, however, the yield can be improved by increasing the amounts of **3** and bromine. Primary disulfides (**4g**−**i**) were more reactive than secondary ones (**4j**), and *tert*-butyl disulfide (**4k**), which is very hindered, failed to deliver **1k**. This result

Table 3. Preparation of Benzenethiosulfonates from Disulfides



(2 equiv) (1 equiv) (1 equiv)

6 **4a,g–i** **7a,g–i**

R	substrate	product	yield (%)
Ph	**4a**	**7a**	70
Ph-CH_2	**4g**	**7g**	90
n-C_8H_{17}	**4h**	**7h**	60
$-(CH_2)_2CO_2Et$	**4i**	**7i**	80

is consistent with the failure already reported for the reaction of *tert*-butyl disulfide with sodium methanesulfinate and silver nitrate.[43] The latter report also specified that, with other disulfides, the $-S(O)_2-S$ structure was obtained rather than the $-S(O)-O-S-$ one. In our process too, IR spectra were in accordance with the formation of the thiosulfonate structure only. Phenyl trifluoromethaneselenosulfonate (**2a**) has been prepared, in the same way, from diphenyl diselenide (**5a**), bromine, and **3**, but diphenyl ditelluride failed to deliver the expected tellurosulfonate.

Such a technique is not specific for the synthesis of trifluoromethanethiosulfonates and has been extended to the preparation of benzenethiosulfonates from sodium benzenesulfinate, disulfides, and bromine (Table 3). Nevertheless, diphenyl diselenide failed to deliver phenyl benzeneselenosulfonate under these conditions.

The order of introduction of the reagents was a crucial parameter, as illustrated by the three following experiments dealing with the preparation of octyl trifluoromethanethiosulfonate (**1h**). In the first one, bromine was dropped into a solution of di-*n*-octyl disulfide (**4h**) in dichloromethane before addition of sodium triflinate: the bromine color did not fade, even after a long time until **3** was introduced; when **3** was then added, this color disappeared quite instantaneously and, after 8 h of stirring, **1h** was obtained in a good yield. In the second experiment, bromine was dropped into a solution of **4h** *and* **3** in dichloromethane: the reaction medium remained colorless all through this sequence and, when quenched just after bromine addition, delivered **1h** in a 50% yield. When treatment was carried out after 8 h of stirring at room temperature, **1h** was isolated in 88% yield. In the third experiment, bromine was first added to a suspension of **3** in dichloromethane: the bromine color was discharged immediately upon addition. Then, **4h** was added and, after stirring as long as previously, **1h** was obtained in the same yield. The same result was obtained when pure trifluoromethanesulfonyl bromide (**8**), previously prepared from bromine and an aqueous solution of **3**,[44] was treated with **4h**.

The same observations have been made during the preparation of phenyl benzenethiosulfonate (**7a**): this compound was obtained in the same yield either by addition of bromine to a mixture of **6** and **4a** or when bromine was added dropwise to **6** followed by the addition of **4a** to the colorless resulting mixture.

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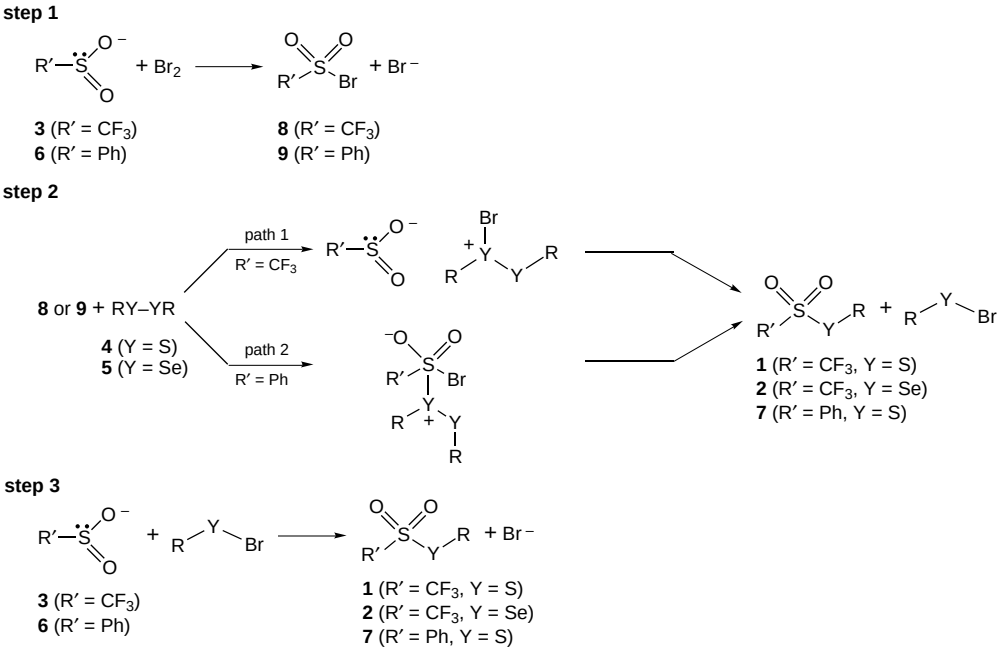
Scheme 3. Reaction Pathways from Disulfides (or Diselenides), 3, and Bromine



These experiments clearly demonstrated that **8** or benzenesulfonyl bromide (**9**) was the true reactive species and was formed more rapidly than sulfenyl bromides. Moreover, when taking into account the excellent yields of **1g** and **7g** resulting from dibenzyl disulfide (**4g**), it is suspected that bromine did not react with disulfides to a large extent since halogenation of **4g** is known to deliver benzyl halides rather than phenylmethanesulfenyl halides.[45] Concerning the reaction mechanism (Scheme 3), it can be suggested that **8** and **9**, which were obviously formed first in a very fast reaction from **3** and **6** (step 1), reacted rapidly with disulfides **4** (or diselenides **5**) to provide **1** (or **2**) and **7** along with sulfenyl bromides (or selenenyl bromides) (step 2). Then, the latter were substituted by **3** and **6** in a slow reaction (step 3); this proposal is consistent with the amount of **1h** (yield = 50%) obtained just after the introduction of bromine.

More precisely, **4** can attack **8** or **9**, during the second step, either at the bromine atom (path 1) or at the sulfur atom (path 2); these two routes lead to the same products. However, it can be suspected that **8**, which probably behaves as a strong electrophilic brominating agent like other perfluoroalkanesulfonyl bromides,[46] reacts more easily through path 1 whereas **9**, in which sulfur constitutes the most electrophilic center, probably reacts essentially through path 2. Such a difference could explain why the bulky diphenyl diselenide delivers **2a** through path 1 but does not react, through path 2, with **9**. Concerning the third step, it can be understood that the reaction of sulfinates **3** and **6** with sulfenyl bromides is a slow process because these intermediates are electromeric compounds in which the S−Br bond is not very cleanly polarized[47] (except when electron-withdrawing groups are present).[32]

The occurrence of sulfonium intermediates (step 2) could also explain why diethyl 2,2′-dithiodiacetate (**4l**, R = CH_2CO_2Et) did not react cleanly with **3** and bromine: the expected thiosulfonate **1l** was detected in low yield along with several byproducts. It could be suspected that the sulfonium species resulting from the reaction of **4l** and **8** deprotonated very easily and provided very reactive unsaturated products.

Conclusion

Thiosulfonates can be prepared at room temperature by an efficient, inexpensive, and easy to scale-up route, from sulfinates, disulfides, and bromine. Usually, selenosulfonates cannot be obtained by the same technique. However, with sodium trifluoromethanesulfinate and bromine, both disulfides and diselenides provide the corresponding chalcogenosulfonates, quite unknown at present. Some of these compounds can be also obtained from sulfenyl or selenenyl chlorides and sodium trifluoromethanesulfinate, but the scope of this method is not so wide. Such a simple access to new compounds illustrates the importance of now readily available sodium triflinate in fluorine chemistry. Our experiments, presently in progress, with thio- and selenoesters of triflic acid show that these compounds are very versatile and fruitful tools; they behave as precursors of the very lipophilic trifluoromethylthio and trifluoromethylseleno ethers, provide easily vinyl trifluoromethyl sulfones, and also allow the formal vicinal addition of trifluoromethyl and thiyl moieties to olefins. The results will be reported in future papers.

Experimental Section

Dichloromethane was distilled prior to use and stored over 3 Å molecular sieves. Other reagents were used as received. Unless stated otherwise, ^1H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ at 200, 188, and 50 MHz, respectively. Chemical shifts are given in ppm relative to TMS (^1H, ^{13}C) or $CFCl_3$ (^{19}F) used as internal references. Coupling constants are given in hertz. UV absorptions were determined in acetonitrile in a 1 cm long cell. IR spectra were recorded either on the pure compound (in KBr) or by a coupled GC-IR FT technique. Frequencies are given in cm^{-1}. Mass spectra were recorded at 70 eV.

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Table 4. Spectroscopic Features of CF_3SO_2SR (1a−d,f−j) and CF_3SO_2SePh (2a)

	NMR data				
		^{13}C NMR		UV data	
CF_3SO_2YR **1** (Y= S) or **2** (Y= Se)	^{19}F NMR δ (ppm)	CF_3 (quadruplet) δ(ppm), J_{C-F} (Hz)	SO_2-Y-C δ (ppm)	λ_{max} (nm)	ϵ (L mol^{-1} cm^{-1})
1a (R = Ph)	−75.80	120.11, 330.0	124.57	200.0	22325
				238.2	10930
1b (R = 4-$O_2NC_6H_4$)	−75.32	120.00, 329.7	131.80		
1c (R = CCl_3)	−75.20	119.36, 330.0	93.39		
1d (R = CO_2Me)	−75.95	119.30, 329.5[a]	158.73[a]		
1f (R = 4-ClC_6H_4)	−75.46	120.06, 330.0	122.94		
1g (R = $PhCH_2$)	−78.64	119.68, 327.9	132.12		
1h (R = *n*-C_8H_{17})	−78.96	119.65, 327.7	37.97	193.4	2105
				239.3	105
1i (R = $(CH_2)_2CO_2Et$)	−78.95	119.58, 327.6	34.49	194.5	2812
				237.0	625
1j (R = *c*-C_6H_{11})	−79.25	119.52, 327.7	53.72	192.0	1917
				239.2	94
2a (R = Ph)	−77.60	118.63, 332.0	125.41	200.1	12217
				243.8	7195

[a] From a preparation performed in $CDCl_3$.

Reaction of Trifluoromethanesulfonic Anhydride with Thiophenol. Degased dichloromethane (3 mL) was placed in a flask and kept under nitrogen; then triflic anhydride (1.69 g, 6 mmol) was added, followed by thiophenol (0.66 g, 6 mmol) which was introduced dropwise. After being stirred at room temperature for 24 h, the reaction was washed with water and the aqueous phase extracted with ether. The gathered organic phases were dried over magnesium sulfate. After filtration and evaporation under reduced pressure, the crude mixture was analyzed by GC-MS and NMR ^{19}F (with (trifluoromethoxy)-benzene as internal standard). The estimated crude yield of phenyl trifluoromethyl disulfide was 25%.

Phenyl Trifluoromethyl Disufide. ^{19}F NMR: δ −46.37. MS: *m*/*z* 210 ($M^{\bullet+}$), 141, 109, 77, 69.

General Procedure for the Synthesis of Trifluoromethanethiosulfonates (or Selenosulfonates) from 3 and Sulfenyl (or Selenenyl) Chlorides. A solution of the selected sulfenyl or selenenyl chloride (around 1 mmol) in dichloromethane was dropped, at room temperature, in approximately 5 min on a suspension of **3** (1 molar equiv) in dichloromethane. The resulting mixture was then stirred at room temperature and its composition followed by GC. After the time indicated in Table 1, the reaction medium was filtered and the filtrate evaporated at room temperature under reduced pressure. The crude thio- or selenosulfonates were usually sufficiently pure to be used in further reactions. They cannot be submitted to column chromatography but can be purified by distillation or recrystallization from petroleum ether.

General Procedure for the Synthesis of Trifluoromethanethiosulfonates (or Selenosulfonates) from 3, Bromine, and Disulfides (or Diselenides). The selected disulfide or diselenide (around 1 mmol) was added to a suspension of **3** in dichloromethane. Then, a 1 M solution of bromine in dichloromethane was added dropwise at room temperature, over approximately 5 min, at a rate which allowed the medium to remain colorless. The amounts of **3** and bromine, which can vary with the substrate, are indicated in Table 2, but usually, 2 molar equiv of **3** and 1 of bromine were used. Then, the resulting mixture was stirred at room temperature and its composition followed by GC. When a stable composition was reached (usually after 8 h), the reaction medium was filtered and the filtrate evaporated at room temperature under reduced pressure. The crude thio- or selenosulfonate was purified by distillation under reduced pressure or recrystallization in petroleum ether.

The same procedure was used to prepare benzenethiosulfonates.

Common Spectroscopic Features of CF3SO2SR (1a−d, f−j) and CF_3SO_2SePh (2a). See Table 4.

Additional Data for CF_3SO_2SR (1a−d,f−j) and CF_3SO_2SePh (2a). Phenyl Trifluoromethanethiosulfonate (1a). Mp: 38−39 °C. ^1H NMR: δ 7.73−7.45 (m, 5H). ^{13}C NMR: δ 136.88, 132.81, 130.06, 124.57, 120.11 (q, *J* = 330.0). MS: *m*/*z* 242 ($M^{\bullet+}$), 109, 69. IR FT: (KBr) 3088, 1370, 1204, 1106, 763, 689, 620; (GC-IRFT) 3076, 1393, 1215, 1119, 744, 687. Anal. Calcd for $C_7H_5F_3O_2S_2$: C, 34.71; H, 2.07; S, 26.45. Found: C, 34.71; H, 2.17; S, 26.26.

4-Nitrophenyl Trifluoromethanethiosulfonate (1b). Mp: 76−77 °C. ^1H NMR: δ 8.39−8.32 (m, 2H), 7.95−7.88 (m, 2H). ^{13}C NMR: δ 150.25, 137.59, 131.80, 124.79, 120.00 (q, *J* = 329.7). MS: *m*/*z* 287 ($M^{\bullet+}$), 154, 108, 69, 30. Anal. Calcd for $C_7H_4F_3NO_4S_2$: C, 29.27; H, 1.39; N, 4.88; S, 22.3. Found: C, 29.42; H, 1.34; N, 4.95; S, 21.75.

Trichloromethyl Trifluoromethanethiosulfonate (1c). Oil. ^{13}C NMR (75 MHz): δ 119.36 (q, *J* = 330.0), 93.39. MS: *m*/*z* 282 ($M^{\bullet+}$), 247, 151, 117, 79, 69.

Methoxycarbonyl Trifluoromethanethiosulfonate (1d). ^1H NMR (300 MHz): δ 4.04 (s). ^{13}C NMR (75 MHz): δ 158.73, 119.30 (q, *J* = 329.5), 57.3. Decomposition on GC columns.

4-Chlorophenyl Trifluoromethanethiosulfonate (1f). Oil. ^{13}C NMR: δ 139.95, 137.98, 130.43, 122.94, 120.06 (q, *J* = 330.0). MS: *m*/*z* 278 and 276 ($M^{\bullet+}$), 145 and 143, 108, 69. Anal. Calcd for $C_7H_4ClF_3O_2S_2$: C, 30.38; H, 1.45; Cl, 12.84; S, 23.15. Found: C, 30.13; H, 1.37; Cl, 12.94; S, 23.03.

Benzyl Trifluoromethanethiosulfonate (1g). Oil. ^1H NMR: δ 7.36 (s, 5H), 4.5 (s, 2H). ^{13}C NMR: δ 132.12, 129.46, 129.34, 129.10, 119.68 (q, *J* = 327.9), 41.99. MS: *m*/*z* 256 ($M^{\bullet+}$), 123, 122, 91. Anal. Calcd for $C_8H_7F_3O_2S_2$: C, 37.50; H, 2.73; S, 25.0. Found: C, 37.92; H, 2.74; S, 25.35.

***n*-Octyl Trifluoromethanethiosulfonate (1h).** Oil. ^1H NMR: δ 3.28 (t, *J* = 7.35, 2H), 1.79 (quint, *J* = 7.35 and 7.50, 2H), 1.28 (m, 10H), 0.89 (t, *J* = 6.5, 3H). ^{13}C NMR: δ 119.65 (q, *J* = 327.7), 37.97, 31.78, 29.28, 29.07, 28.90, 28.43, 22.69, 14.09. MS: *m*/*z* 221 (M − C_4H_9), 145, 69. IR: 2980, 2930, 2880, 1460, 1370, 1210, 1110, 740, 630. Anal. Calcd for $C_9H_{17}F_3O_2S_2$: C, 38.85; H, 6.11; S, 23.02. Found: C, 38.72; H, 6.11; S, 23.11.

Ethyl 3-((Trifluoromethanesulfonyl)thio)propionate (1i). Oil. ^1H NMR: δ 4.20 (q, *J* = 7.16, 2H), 3.48 (t, *J* = 6.41, 2H), 2.89 (t, *J* = 6.41, 2H), 1.29 (t, *J* = 7.16). ^{13}C NMR: δ 170.78, 119.58 (q, *J* = 327.6), 61.64, 34.49, 32.77, 14.15. MS: *m*/*z* 221 (M − OEt), 193, 133, 105, 69, 45, 29. IR: 1730, 1370, 1210, 1110, 620. Anal. Calcd for $C_6H_9F_3O_4S_2$: C, 27.07; H, 3.38; S, 24.06. Found: C, 27.09; H, 3.56; S, 23.09.

Cyclohexyl Trifluoromethanethiosulfonate (1j). Oil. ^1H NMR (300 MHz): δ 3.69 (tt, *J* = 10 and 4, 1H), 2.15 (m, 2H), 1.9−1.1 (m, 8H). ^{13}C NMR: δ 119.52 (q, *J* = 327.7), 53.72, 33.94, 25.77, 24.89. MS: *m*/*z* 248 ($M^{\bullet+}$), 179, 83. Anal. Calcd for $C_7H_{11}F_3O_2S_2$: C, 33.86; H, 4.47; S, 25.83. Found: C, 34.13; H, 4.51; S, 25.09.

Phenyl Trifluoromethaneselenosulfonate (2a). Mp: 61−64 °C dec. ^1H NMR (300 MHz): δ 7.79−7.76 (m, 2H), 7.58−7.43 (m, 3H). ^{13}C NMR: δ 137.44, 132.33, 130.10,

125.41, 118.63 (q, $J = 332.0$). IR FT (KBr) 2930, 1353, 1179, 1095, 758, 688, 614. Not stable enough for GC and elemental analysis.

Characteristics of Benzenethiosulfonates Mentioned in Table 3. Phenyl Benzenethiosulfonate (7a). Mp: 40−41 °C (lit. mp 43−44.5 °C,[48] 44.5−45.5 °C [16]). ^{1}H NMR: δ 7.63−7.28 (m). ^{13}C NMR: δ 142.83, 136.50, 133.72, 131.47, 129.50, 128.80, 127.73, 127.50. MS: m/z 250 ($M^{\bullet+}$), 141, 109, 77.

Benzyl Benzenethiosulfonate (7g). Oil. ^{1}H NMR: δ 7.81−7.77 (m, 2H), 7.53−7.37 (m, 3H), 7.26−7.09 (m, 5H), 4.22 (s, 2H). ^{13}C NMR: δ 144.67, 133.52, 133.49, 129.12, 128.96, 128.67, 127.92, 126.70, 40.28. MS: m/z 264 ($M^{\bullet+}$), 123, 91, 77.

***n*-Octyl Benzenethiosulfonate (7h).** Oil. ^{1}H NMR: δ 7.96−7.93 (m, 2H), 7.91−7.50 (m, 2H), 2.99 (t, $J = 7.3$, 2H), 1.58 (quint, $J = 7.3$, 2H), 1.20 (m, 10H), 0.86 (t, $J = 6.8$, 3H). ^{13}C NMR: δ 144.93, 133.62, 129.29, 126.94, 36.15, 31.70, 28.99, 28.85, 28.58, 28.50, 22.61, 14.10. MS: m/z 287 (M + 1), 145, 125, 77. Anal. Calcd for $C_{14}H_{22}O_2S_2$: C, 58.74; H, 7.69; S, 22.38. Found: C, 58.64; H, 7.76; S, 22.50.

Ethyl 3-(Benzenesulfonylthio)propionate (7i). Oil. ^{1}H NMR: δ 7.98−7.92 (m, 2H), 7.66−7.53 (m, 3H), 4.12 (q, $J = 7.13$, 2H), 3.20 (t, $J = 6.94$, 2H), 2.71 (t, $J = 6.94$, 2H), 1.23 (t, $J = 7.13$, 3H). ^{13}C NMR: δ 170.9, 144.5, 133.5, 129.4, 126.9, 61.0, 34.2, 30.7, 14.1. MS: m/z 229 (M − OEt), 133, 77. Anal. Calcd for $C_{12}H_{10}O_2S_2$: C, 48.17; H, 5.11; S, 23.36. Found: C, 47.81; H, 5.10; S, 23.22.

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