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Useful electrophilic trifluoromethylating agents; *S*-, *Se*- and *Te*-(trifluoromethyl)dibenzo-thio-, -seleno- and -telluro-phenium-3-sulfonates

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Abstract

Se, Se- and *Te*-(Trifluoromethyl)dibenzo-thio-, -seleno- and -telluro-phenium-3-sulfonates and their dimethyl and nitro derivatives have been synthesized in good yield by sulfonation of the corresponding (trifluoromethyl)dibenzocyclic chalcogen salts with fuming sulfuric acid or by sulfonation followed by nitration. The practical use of these power-variable trifluoromethylating agents has been demonstrated. Thus, they provide good yields of trifluoromethylated products, and the by-product (a salt of dibenzothiophene-3-sulfonic acid or an analog) was easily removed from the products by filtration or by washing with water. *S*-(Perfluoro-ethyl, -n-butyl- and -n-octyl)dibenzothiophenium-3-sulfonates have also been synthesized and a similar perfluoroalkylation using one of them has been accomplished.

Keywords: Electrophilic trifluoromethylating agents; Perfluoroalkylation; *S*-(Trifluoromethyl)dibenzothiophenium sulfonates; *Se*-(Trifluoromethyl)-dibenzoselenophenium sulfonates; *Te*-(Trifluoromethyl)dibenzotellurophenium sulfonates; NMR/IR spectroscopy

1. Introduction

Trifluoromethylated organic compounds are becoming important in the development of more effective medicines [1], agricultural chemicals [2] and new materials such as liquid crystals [3] because of the characteristics of the trifluoromethyl group such as high electronegativity, stability and lipophilicity [4].

Thus, there have been many studies on the synthesis of trifluoromethylated organic compounds [5,6]. We have developed a new class of electrophilic trifluoromethylating agents, *S*-, *Se*- and *Te*-(trifluoromethyl)dibenzo-thio-, -seleno- and -telluro-phenium triflates which vary in their trifluoromethylating power [7,8]. This power depends on the electron density of the trifluoromethyl group and thus increases both in the order Te < Se < S and electron-donating substituent < H < electron-withdrawing substituent in the dibenzoheterocyclic ring. The reagents can be selected on the basis of the nucleophilicity of the substrate. Thus, these power-variable reagents have a wide application in the preparation of trifluoromethylated organic compounds. However, the reagents produce a water-insoluble by-product, dibenzo-thio-, -seleno- or -telluro-phene, along with the trifluoromethylated products. Since all are water-insoluble, separation is difficult.

We have therefore introduced an $—SO_3^-$ substituent on the dibenzoheterocyclic ring to act as a counteranion and this makes the heterocyclic by-product water-soluble. This paper describes the synthesis of a series of counteranion-bound *S*-, *Se*- and *Te*-(trifluoromethyl)dibenzo-thio-, -seleno- and -telluro-phenium-3-sulfonates and their analogs, and their practical usefulness for trifluoromethylation.

2. Results and discussion

2.1. Synthesis of S-, Se- and Te-(trifluoromethyl)dibenzo-thio-, -seleno- and -telluro-phenium-3-sulfonates and their derivatives

We found that *S*-(trifluoromethyl)dibenzothiophenium triflate (**1**) was successfully sulfonated with fuming sulfuric acid of a high sulfur trioxide content. Thus, sulfonation of **1** with 60% fuming sulfuric acid at 40 °C for 5.5 h gave *S*-(trifluoromethyl)dibenzothiophenium-3-sulfonate (**8**) in 73% yield (see Scheme 1). The sulfonation occurred at the 3-position exclusively. Important in the preparation of **8** was how to isolate it from the reaction solution, i.e. fuming sul-

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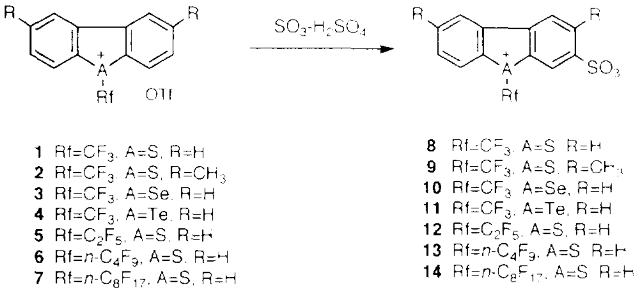
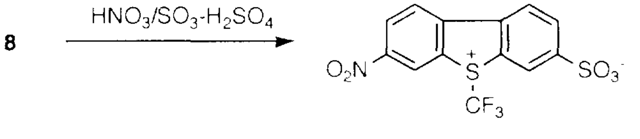


Scheme 1



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Scheme 2

furic acid solution, because product **8** is a water-soluble and reactive salt. As described under Experimental details, our procedure led successfully to the isolation of salt **8** as crystals in a good yield. The sulfonation of *Se*-(trifluoromethyl)dibenzoselenophenium triflate (**3**) was accomplished in 2 h at 40 °C using 60% fuming sulfuric acid to give *Se*-(trifluoromethyl)dibenzoselenophenium-3-sulfonate (**10**) in 72% yield. *Te*-(Trifluoromethyl)dibenzotellurophenium-3-sulfonate (**11**) was synthesized in 92% yield by sulfonation of *Te*-(trifluoromethyl)dibenzotellurophenium triflate (**4**) for 1 h at 40 °C with 20% fuming sulfuric acid.

Thus, the sulfonation proceeded more readily in the order **1**<**3**<**4**. This is opposite to the trifluoromethylating power order (**1**>**3**>**4**) [7] but can be explained by the electron deficiency of the dibenzoheterocyclic ring. As expected from the power order (**3**>**2**) [7], the sulfonation of *S*-(trifluoromethyl)-2,8-dimethyldibenzothiophenium triflate (**2**) proceeded smoothly to give *S*-(trifluoromethyl)-2,8-dimethyldibenzothiophenium-3-sulfonate (**9**) in 80% yield. *S*-(Trifluoromethyl)-7-nitrodibenzothiophenium-3-sulfonate (**15**) was synthesized in 75% yield by nitration of **8** with a mixture of concentrated nitric acid and 20% fuming sulfuric acid at room temperature (Scheme 2).

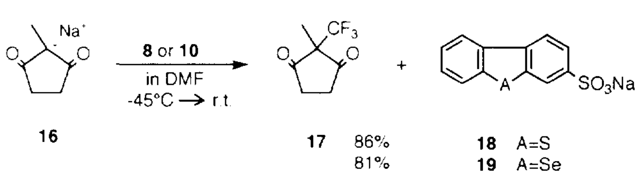
By analogy to the trifluoromethylating power order of the non-counteranion-bound (trifluoromethyl)dibenzoheterocyclic onium salts [7], the power of the counteranion-bound salts should increase in the order of **11**<**9**<**10**<**8**<**15**. *S*-(Perfluoro-ethyl-, -n-butyl- and -n-octyl)dibenzothiophenium-3-sulfonates (**12**, **13** and **14**) were synthesized in 86%, 67% and 85% yield by sulfonation of the corresponding triflates **5**, **6** and **7**, respectively, under similar conditions as for **1**.

2.2. Trifluoromethylation with S- and Se-(trifluoromethyl)dibenzo-thio- and -seleno-phenium-3-sulfonates and a nitro derivative

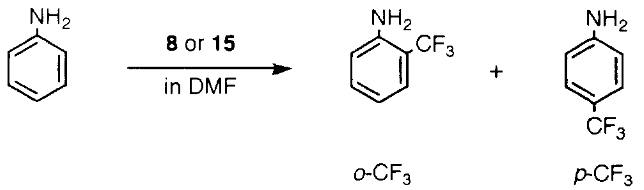
The sodium salt **16** of 2 methyl-1,3-cyclopentanedione was allowed to react with *S*-(trifluoromethyl)dibenzothiophenium-3-sulfonate (**8**) in DMF from −45 °C to room temperature for 2 h to give 86% of 2-methyl-2-(trifluoromethyl)-1,3-cyclopentanedione (**17**) and sodium dibenzothiophene-3-sulfonate (**18**). Similar treatment of sodium salt **16** with *Se*-trifluoromethyl salt **10** gave 81% of the CF_3 product **17** and sodium dibenzoselenophenium-3-sulfonate (**19**). The CF_3 product was easily separated from the by-product **18** or **19** by filtration or by washing with water since **18** and **19** are insoluble in organic solvents and soluble in water (Scheme 3).

The reactions of **8** and its nitro derivative **15** with aniline to give *o*- and *p*-trifluoromethylated anilines were examined (Scheme 4). The results obtained are listed in Table 1, together with those for non-counteranion-bound salts, *S*-(trifluoromethyl)dibenzothiophenium triflate (**1**) and its mononitro and dinitro derivatives **20** and **21** [7].

As expected from the strong electron-withdrawing effect of a nitro group ($\sigma_m = 0.71$), the nitro derivative **15** is much more reactive than **8**. Thus, the reaction of **15** was complete in less than 0.5 h at 80 °C in DMF (Run 7), whereas that of **8** took 7 h to bring to completion under the same conditions (Run 2). However, both **8** and **15** gave the same yield of *o*- and *p*-CF_3-anilines (36%–37% for *o*- and 18% for *p*-CF_3-aniline). These yields were the same as those obtained with non-counteranion-bound salt **1** (Run 5). A comparison between Runs 1 and 4 and Runs 2 and 5 shows that the reactivity of **8** was almost the same as **1**. This indicates that the sulfonate anion substituent hardly affects the trifluoromethylating power of the (trifluoromethyl)dibenzoheterocyclic onium salts, as expected from its weak electron-withdrawing effect ($\sigma_m = 0.05$ for SO_3^-). However, the nitro derivative **15** was less reactive than the non-counteranion-bound nitro triflate **20** as seen from a comparison between Runs 6 and 8. This lowered reactivity of **15** was

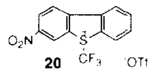
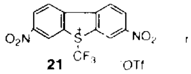


Scheme 3.



Scheme 4.

Table 1
Controlled trifluoromethylation of aniline with a series of (trifluoromethyl)dibenzothiophenium salts

Run No. [a]	CF_3^+	Temp [b] (°C)	Time (h)	Yield of CF_3-aniline (%) [c]		Remaining CF_3^+ (%) [c]
				o-CF_3 [d]	p-CF_3 [e]	
1	**8**	80	1	27	14	27
2	**8**	80	7	36	18	1
3 [f]	**1**	r.t.	0.5	0	0	100
4 [f]	**1**	80	1	31	15	27
5 [g]	**1**	80	7	39	18	5
6	**15**	r.t.	0.5	3	1	92
7	**15**	80	0.5	37	18	0
8 [f]	 **20**	r.t.	0.5	18	17	71
9 [f]	 **21**	r.t.	0.5	54	20	5

[a] Dimethylformamide (DMF) was used as a reaction solvent for all the reactions.

[b] r.t. = room temperature.

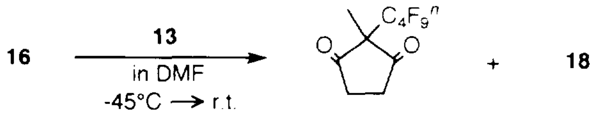
[c] The yields of $CF_3C_6H_4NH_2$ and the remainder of CF_3^+ were determined by an ^{19}F NMR spectroscopic technique. See Experimental details.

[d] *o*-(Trifluoromethyl)aniline.

[e] *p*-(Trifluoromethyl)aniline.

[f] See Ref. [7b] for these data.

[g] This experiment was carried out according to the procedure described in Ref. [7b], which was the same as for Run 4 except for the reaction time.



22 77%

Scheme 5

probably due to the low solubility of **15** compared to the nitro triflate **20**. The nitro derivative **15** is barely soluble in DMF, while **20** is soluble. Thus, the apparent power order was estimated as **1** ≈ **8** < **15** < **20** < **21**.

2.3. *Perfluorobutylation with S-(perfluoro-n-butyl)-dibenzothiophenium-3-sulfonate*

The sodium salt **16** was treated with the *S*-perfluorobutyl salt **13** under the same conditions as for **8** to give 2-methyl-2-(perfluorobutyl)-1,3-cyclopentanedione (**22**) (77%) (see Scheme 5). The by-product, dibenzothiophene-3-sulfonate (**18**), was easily removed by filtration or by washing with water. Thus, perfluorobutylation was achieved in a similar manner to trifluoromethylation.

3. Experimental details

3.1. *General*

Melting points were uncorrected. ^1H and ^{19}F NMR spectra were recorded with a 200 MHz NMR spectrometer. ^{19}F NMR chemical shifts are reported in ppm downfield from CCl_3F as internal reference. Mass spectra were recorded at 70 eV.

3.2. *Materials*

The trifluoromethylating agents **1–4** and the perfluorooctylating agent **7** were prepared according to reported methods [7]. The perfluoroethylating agent **5** [1] and perfluorobutylating agent **6** [2] were prepared in the same manner as compound **7**. Reagents **1**, **3**, **5**, **6** and **7** were available commercially from Daikin Chemical Sales, Ltd. (Japan). Dimethylformamide (DMF) was dried by the usual method. Other commercially available compounds were used without further purification.

3.3. *Preparation of S-(trifluoromethyl)dibenzothiophenium-3-sulfonate (8)*

Triflate **1** (7.90 g, 19.7 mmol) was added to 5.5 ml of 60% fuming sulfuric acid which was stirred and cooled by means of an ice bath. After the exothermic reaction had ceased, the mixture was stirred at 40 °C for 5.5 h. With cooling by an ice bath or a Dry Ice/acetone bath, 150 ml of diethyl ether and a small amount of methanol (5.5 ml) were carefully added to the stirred reaction mixture when a vigorous exothermic reaction occurred on mixing. The resulting lower oily layer was separated from the upper solution by decanting and then washed repeatedly with diethyl ether. Addition of acetone to the oily layer then resulted in a white precipitate of **8** which was collected by filtration. The yield was 4.76 g (73%). A sample for analysis was obtained by recrystallization from methanol.

Compound **8**: m.p. 160–165 °C (with dec.) (CH_3OH). ^1H NMR (CD_3OD) δ: 7.91 (1H, td, $J=8$, 1 Hz, 7-H); 8.10 (1H, td, $J=8$, 1 Hz, 8-H); 8.41 (1H, dd, $J=8$, 1 Hz, 2-H); 8.48 (1H, dd, $J=8$, 1 Hz, 9-H); 8.49 (1H, d, $J=8$ Hz, 1-H); 8.53 (1H, d, $J=8$ Hz, 6-H); 8.88 (1H, d, $J=1$ Hz, 4-H) ppm.

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[1] Compound **5**: m.p. 172–175 °C (with dec.) (CH_3CN/Et_2O). ^1H NMR (CD_3CN) δ: 7.87 (2H, td, $J=8$, 1 Hz); 8.09 (2H, td, $J=8$, 1 Hz); 8.37 (4H, dd, $J=8$, 1 Hz) ppm. ^{19}F NMR (CD_3CN) δ: −76.9 (3F, s, CF_3); −78.1 (3F, s, SO_2CF_3); −97.1 (2F, s, SCF_2) ppm. IR (KBr) (cm^{-1}): 1334; 1260; 1239; 1165; 1030; 929; 768; 636; 516. Mass spectrum (FAB): m/z 303 ($M^+ - OSO_2CF_3$); 264 ($303 - C_2F_5$). Analysis: Calc. for $C_{15}H_8F_8O_3S_2$: C, 39.83; H, 1.78%. Found: C, 39.90; H, 1.71%.

[2] Compound **6**: m.p. 175–180 °C (with dec.) (CH_3CN/Et_2O). ^1H NMR (CD_3CN) δ: 7.86 (2H, tm, $J=7$ Hz); 8.10 (2H, td, $J=7$, 1 Hz); 8.37 (4H, dm, $J=7$ Hz) ppm. ^{19}F NMR (CD_3CN) δ: −77.9 (3F, s, SO_2CF_3); −79.8 (3F, m, CF_3); −92.1 (2F, m, SCF_2); −115.4 (2F, m, $SCF_2\mathit{CF_2}$); −124.6 (2F, m, $\mathit{CF_2}CF_3$) ppm. IR (KBr) (cm^{-1}): 1451; 1348; 1254; 1215; 1144; 1028; 771; 724; 637; 516. Mass spectrum (FAB) m/z: 403 ($M^+ - OSO_2CF_3$); 184 ($403 - C_4F_9$). Analysis: Calc. for $C_{17}H_8F_{12}O_3S_2$: C, 36.97; H, 1.46%. Found: C, 36.72; H, 1.40%.

^{19}F NMR (CD_3OD) δ: -53.9 (s) ppm. IR (KBr) (cm^{-1}): 3510; 3465; 3096; 1652; 1456; 1235; 1117; 1077; 1035; 665; 617. Mass spectrum (FAB) *m/z*: 333 ($M^+ + 1$); 264 ($M^+ + 1 - CF_3$). Analysis: Calc. for $C_{13}H_7F_3O_3S_2 \cdot H_2O$: C, 44.57; H, 2.59%. Found: C, 44.19; H, 2.57%.

*3.4. Preparation of Se-(trifluoromethyl)dibenzoselenophenium-3-sulfonate (**10**)*

Triflate **3** (0.898 g, 2 mmol) was added to 0.56 ml of 60% fuming sulfuric acid which was stirred and cooled by means of an ice bath. After the exothermic reaction ceased, the mixture was stirred at 40 °C for 2 h. The post-treatment was carried out in the same way as for **8**. The yield was 0.548 g (72%). A sample for analysis was obtained by recrystallization from methanol.

Compound **10**: m.p. 175–178 °C (with dec.) (CH_3OH). ^{1}H NMR (DMSO-d_6) δ: 7.77 (1H, td, $J=8$, 1 Hz, 7-H); 7.92 (1H, td, $J=8$, 1 Hz, 8-H); 8.07 (1H, dd, $J=8$, 1 Hz, 2-H); 8.36 (1H, d, $J=8$ Hz, 1-H); 8.38 (1H, dd, $J=8$, 1 Hz, 6-H); 8.47 (1H, dd, $J=8$, 1 Hz, 9-H); 8.78 (1H, d, $J=1$Hz, 4-H) ppm. ^{19}F NMR (DMSO-d_6) δ: -46.5 (s) ppm. IR (KBr) (cm^{-1}): 3464; 1183; 1117; 1076; 1028; 773; 743; 705; 656; 615. Mass spectrum (FAB) *m/z*: 383; 381; 379; 378; 377 ($M^+ + 1$); 314; 312; 310; 309; 308 ($M^+ + 1 - CF_3$). Analysis: Calc. for $C_{13}H_7F_3O_3SSe \cdot H_2O$: C, 39.31; H, 2.28%. Found: C, 38.90; H, 2.14%.

*3.5. Preparation of Te-(trifluoromethyl)dibenzotellurophenium-3-sulfonate (**11**)*

Triflate **4** (0.498 g, 1 mmol) was added to 0.272 ml of 20% fuming sulfuric acid stirred at room temperature. The reaction mixture was then stirred at 40 °C for 1 h. In a similar manner to the case of **8**, a large amount of diether ether and a small amount of methanol were carefully added to the reaction mixture with cooling by a Dry Ice/acetone bath. The resulting precipitates of **11** were collected by filtration and washed with acetone and diethyl ether. The yield was 0.394 g (92%).

Compound **11**: m.p. 271–275 °C. ^{1}H NMR (DMSO-d_6) δ: 7.67 (1H, td, $J=8$, 1 Hz, 7-H); 7.80 (1H, td, $J=8$, 1 Hz, 8-H); 7.95 (1H, dd, $J=8$, 1.6 Hz, 2-H); 8.23 (1H, dd, $J=8$, 1 Hz, 9-H); 8.26 (1H, d, $J=8$ Hz, 1-H); 8.28 (1H, d, $J=8$ Hz, 6-H); 8.53 (1H, d, $J=1.6$ Hz, 4-H) ppm. ^{19}F NMR (DMSO-d_6) δ: -43.6 (s) ppm. IR (KBr) (cm^{-1}) 3422; 1152; 1120; 1078; 1022; 774; 730; 702; 653; 616. Mass spectrum (FAB) *m/z*: 431; 429; 427; 426 ($M^+ + 1$); 362; 360; 358; 357; 356 ($M^+ + 1 - CF_3$). Analysis: Calc. for $C_{13}H_7F_3O_3STe \cdot 1.5H_2O$: C, 34.33; H, 2.22%. Found: C, 34.00; H, 2.05%.

*3.6. Preparation of S-(trifluoromethyl)-2,8-dimethyldibenzothiophenium-3-sulfonate (**9**)*

Triflate **2** (0.215 g, 0.5 mmol) was added to 0.262 ml of 20% fuming sulfuric acid stirred at room temperature. The mixture was then stirred for 1 h at 40 °C. The post-treatment was carried out in the same way as for **8**. The yield was 0.151 g (80%). A sample for analysis was obtained by recrystallization from methanol/diethyl ether.

Compound **9**: m.p. 188–190 °C (with dec.) (CH_3OH/Et_2O). ^{1}H NMR (DMSO-d_6) δ: 2.56 (3H, s, 8-CH_3); 2.77 (3H, s, 2-CH_3); 7.67 (1H, dd, $J=8$, 1 Hz, 7-H); 8.30 (1H, s, 1-H); 8.32 (1H, s, 9-H); 8.51 (1H, d, $J=8$ Hz, 6-H); 8.95 (1H, s, 4-H) ppm. ^{19}F NMR (DMSO-d_6) δ: -53.7 (s) ppm. IR (KBr) (cm^{-1}): 3450; 1207; 1103; 1068; 1035; 712; 626. Mass spectrum (FAB) *m/z*: 361 ($M^+ + 1$). Analysis: Calc. for $C_{15}H_{11}F_3O_3S_2 \cdot 0.5H_2O$: C, 48.78; H, 3.27%. Found: C, 49.08; H, 3.10%.

*3.7. Preparation of S-(trifluoromethyl)-7-nitrodibenzothiophenium-3-sulfonate (**15**)*

Salt **8** (1.0 g, 3.0 mmol) was added in several portions to a mixture of 1.0 ml of 20% fuming sulfuric acid and 0.3 ml of conc. nitric acid. The reaction mixture was stirred for 16 h at room temperature. Then, under cooling by an ice bath, diethyl ether was added carefully to the reaction mixture. After the exothermic reaction ceased, the resulting precipitate of **15** was separated from the solution by decanting and washed with a small amount of methanol and a large amount of diethyl ether. The precipitate was then collected by filtration and washed with a 10:1 mixture of dichloromethane and methanol. The yield was 0.852 g (75%). A sample for analysis was obtained by recrystallization from DMSO/H_2O/CH_3CN.

Compound **15**: dec. 196–210 °C (DMSO/H_2O/CH_3CN). ^{1}H NMR (DMSO-d_6) δ: 8.27 (1H, dd, $J=1.2$, 8.1 Hz, 2-H); 8.65 (1H, d, $J=8.1$ Hz, 1-H); 8.75 (1H, d, $J=8.6$ Hz, 9-H); 8.86 (1H, dd, $J=2.1$, 8.6 Hz, 8-H); 9.05 (1H, d, $J=1.2$ Hz, 4-H); 9.64 (1H, d, $J=2.1$ Hz, 6-H) ppm. ^{19}F NMR (DMSO-d_6) δ: -50.9 (s) ppm. IR (KBr) (cm^{-1}): 3460; 3097; 1599; 1534; 1351; 1228; 1114; 1076; 1034; 809; 757; 670; 633. Mass spectrum (FAB) *m/z*: 378 ($M^+ + 1$); 307 ($M^+ - 1 - CF_3$). Analysis: Calc. for $C_{13}H_6F_3NO_5S_2 \cdot H_2O$: C, 39.50; H, 2.04; N, 3.54%. Found: C, 39.25; H, 2.11; N, 3.44%.

*3.8. Preparation of S-(perfluoroethyl)dibenzothiophenium-3-sulfonate (**12**)*

Triflate **5** (0.452 g, 1 mmol) was added to 0.28 ml of 60% fuming sulfuric acid stirred at room temperature. The reaction mixture was stirred for 6 h at 40 °C. In a similar manner to the case of **8**, with cooling by a Dry Ice/acetone bath, a large amount of diethyl ether and a small amount of methanol were carefully added into the reaction mixture when a vigorous exothermic reaction occurred on mixing. The resulting lower oily layer was separated from the upper solution by decanting and washed repeatedly with diethyl ether. The oily layer was dissolved in the minimum amount of methanol and then diethyl ether was added to the solution to give the precipitate of **12**, which was collected by filtration. The yield was 0.33 g (86%). A sample for analysis was obtained by recrystallization from methanol/diethyl ether.

Compound **12**: m.p. 174–178 °C (with dec.) (CH_3OH/Et_2O). ^1H NMR (DMSO-d_6) δ: 7.87 (1H, td, $J=8$, 1 Hz, 7-H); 8.07 (1H, td, $J=8$, 1 Hz, 8-H); 8.22 (1H, dd, $J=8$, 1 Hz, 2-H); 8.51 (1H, d, $J=8$ Hz, 1-H); 8.53 (1H, dd, $J=8$, 1 Hz, 6-H); 8.63 (1H, d, $J=8$ Hz, 9-H); 8.91 (1H, s, 4-H) ppm. ^{19}F NMR (DMSO-d_6) δ: −76.6 (3F, s, CF_3); −97.8 (1F, AB system, dm, $J=201$ Hz, SCF_A); −98.5 (1F, AB system, dm, $J=201$ Hz, SCF_B) ppm. IR (KBr) (cm^{-1}): 3093; 1330; 1244; 1214; 1195; 1113; 1032; 932; 750; 662; 611; 520. Mass spectrum (FAB) m/z: 383 ($M^+ + 1$); 264 ($M^+ + 1 - C_2F_5$). Analysis. Calc. for $C_{14}H_7F_5O_3S_2$: C, 43.98; H, 1.85%. Found: C, 43.82; H, 1.72%.

3.9. Preparation of S-(perfluoro-n-butyl)dibenzothiophenium-3-sulfonate (13)

Salt **13** was prepared by the same procedure as for **12** using triflate **6** (1.10 g, 2 mmol) and 0.56 ml of 60% fuming sulfuric acid. The yield was 0.65 g (67%).

Compound **13**: m.p. 190–198 °C (with dec.) (CH_3OH/Et_2O). ^1H NMR (DMSO-d_6) δ: 7.87 (1H, t, $J=8$ Hz, 7-H); 8.07 (1H, t, $J=8$ Hz, 8-H); 8.23 (1H, dd, $J=8$, 1 Hz, 2-H); 8.51 (1H, d, $J=8$ Hz, 1-H); 8.53 (1H, d, $J=8$ Hz, 6-H); 8.62 (1H, d, $J=8$ Hz, 9-H); 8.88 (1H, s, 4-H) ppm. ^{19}F NMR (DMSO-d_6) δ: −79.6 (3F, t, $J=9$ Hz, CF_3); −93.3 (1F, dt, AB system, $J=200$, 13 Hz, SCF_A); −94.5 (1F, dt, AB system, $J=200$, 13 Hz, SCF_B); −116.4 (2F, m, CF_2); −125.1 (2F, m, CF_2) ppm. IR (KBr) (cm^{-1}): 3091; 1349; 1230; 1205; 1144; 1112; 1029; 725; 695; 661; 616; 518. Mass spectrum (FAB) m/z: 483 ($M^+ + 1$); 264 ($M^+ + 1 - C_4F_9$). Analysis: Calc. for $C_{16}H_7F_9O_3S_2$: C, 39.84; H, 1.46%. Found: C, 39.77; H, 1.41%.

3.10. Preparation of S-(perfluoro-n-octyl)dibenzothiophenium-3-sulfonate (14)

Triflate **7** (2.26 g, 3 mmol) was added to 0.84 ml of 60% fuming sulfuric acid stirred at room temperature. The reaction mixture was stirred for 4.5 h at 40 °C and then for 12 h at room temperature. With cooling by an ice bath, a large amount of diethyl ether was added carefully into the reaction mixture when a vigorous exothermic reaction occurred on mixing. The resulting paste was separated from the solution by decanting and washed with diethyl ether. Addition of methanol to the paste then resulted in a precipitate of **14**, which was collected by filtration and washed with a mixture of diethyl ether and methanol. The yield was 1.75 g (85%).

Compound **14**: dec. 150–180 °C. ^1H NMR (DMSO-d_6) δ: 7.87 (1H, t, $J=8$ Hz, 7-H); 8.07 (1H, t, $J=8$ Hz, 8-H); 8.22 (1H, dd, $J=8$, 1 Hz, 2-H); 8.51 (1H, d, $J=8$ Hz, 1-H); 8.53 (1H, d, $J=8$ Hz, 6-H); 8.62 (1H, d, $J=8$ Hz, 9-H); 8.88 (1H, s, 4-H) ppm. ^{19}F NMR (DMSO-d_6) δ: −79.7 (3F, t, $J=9$ Hz, CF_3); −93.0 (1F, d, AB system, $J=200$ Hz, SCF_A); −94.3 (1F, d, AB system, $J=200$ Hz, SCF_B); −115.3 (2F, m, CF_2); −120.8 (4F, m, $CF_2 \times 2$); −121.1 (2F, m, CF_2); −121.9 (2F, m, CF_2); −125.2 (2F, m, CF_2) ppm. IR (KBr) (cm^{-1}): 3428; 3090; 1208; 1152; 1031; 661; 616. Mass spectrum (FAB) m/z: 683 ($M^+ + 1$); 264 ($M^+ + 1 - C_8F_{17}$). Analysis: Calc. for $C_{20}H_7F_{17}O_3S_2 \cdot H_2O$: C, 34.30; H, 1.30%. Found: C, 34.29; H, 1.02%.

3.11. Trifluoromethylation of the sodium salt of 2-methyl-1,3-cyclopentanedione with S- and Se-(trifluoromethyl)-dibenzo-thio- and -seleno-phenium-3-sulfonates (8 and 10)

Under an argon atmosphere, sodium hydride (2.6 mmol) was added to a stirred solution consisting of 294 mg (2.6 mmol) of 2-methyl-1,3-cyclopentanedione in 5 ml of dry DMF at 0 °C. After stirring for an additional 0.5 h, the mixture was cooled to −45 °C. Then, salt **8** (664 mg, 2 mmol) was added to the mixture, the stirred reaction mixture warmed to room temperature over a period of 1 h and maintained for 1 h at that temperature. To the reaction mixture, benzotrifluoride (2 mmol) was added as an internal reference for ^{19}F NMR spectroscopy. ^{19}F NMR analysis showed 2-methyl-2-(trifluoromethyl)-1,3-cyclopentanedione (**17**) to be produced in 86% yield [^{19}F NMR ($CDCl_3$) δ: −69.8 (s, CF_3) ppm for **17**]. A large amount of diethyl ether was added to the reaction mixture and insoluble precipitates were removed by filtration. The filtrate was washed with water and then aqueous NaCl solution, dried with $MgSO_4$ and filtered. Evaporation of the solvent gave an oil. This oil was found to be mainly 2-methyl-2-trifluoromethyl-1,3-cyclopentanedione (**17**) and not to contain sodium dibenzothiophenesulfonate (**18**) from the NMR analysis.

Trifluoromethylation with **10** was carried out in the same way as for **8**, using 0.88 mmol of **10**, 1.3 mmol of 2-methyl-1,3-cyclopentanedione, 1.3 mmol of sodium hydride, 4 ml of dry DMF solvent and 1 mmol of benzotrifluoride as an internal reference. The reaction time with **10** at room temperature was extended by 1.5 h, based on the time for **8**. The yield of **17** was 81%. Product **17** was found to be readily separated from sodium dibenzoselenophenesulfonate (**19**) by the same post-treatment as for **8**.

3.12. Controlled trifluoromethylation of aniline with S-(trifluoromethyl)dibenzothiophenium-3-sulfonate (8) and S-(trifluoromethyl)-7-nitrodibenzothiophenium-3-sulfonate (15): a general procedure

Under an argon atmosphere, aniline (186 mg, 2 mmol) was added to a stirred mixture of 332 mg (1 mmol) of salt **8** or **15** and 2 ml of dry DMF at room temperature. The reaction mixture was then stirred under the conditions (temperature and time) listed in Table 1. The reaction mixture at 80 °C was immediately cooled by an ice bath after the reaction. Then, 0.5 mmol of benzotrifluoride, as an internal reference for ^{19}F NMR, was added to the reaction mixture. For Runs 2 and 7 (Table 1), a small amount (as for an ^{19}F NMR sample) of the reaction mixture was diluted with dimethyl sulfoxide (DMSO-d_6) to stop the reaction. For Runs 1 and 6, since the reaction mixture was heterogeneous, DMSO was added to the reaction mixture until it became homogeneous, and then a small amount (as for an ^{19}F NMR sample) of the homogeneous solution was diluted with DMSO-d_6 to stop the reaction completely. ^{19}F NMR analysis of the sample was then carried out. The results are listed in Table 1.

*3.13. Perfluorobutylation of the sodium salt of 2-methyl-1,3-cyclopentanedione with S-(perfluoro-n-butyl)-dibenzothiophenium-3-sulfonate (**13**)*

Perfluorobutylation was carried out in a similar manner to trifluoromethylation with **10**, using 0.8 mmol of **13**, 1.04 mmol of 2-methyl-1,3-cyclopentanedione, 1.04 mmol of sodium hydride, 3.2 ml of dry DMF and 0.8 mmol of benzotrifluoride as an internal reference. The yield of 2-methyl-2-(perfluoro-n-butyl)-1,3-cyclopentanedione (**22**) was 77%. The oily product obtained was further purified by column chromatography on silica gel using a 1:5 mixture of ethyl acetate and n-hexane as an eluent.

Compound **22**: oil. ^{1}H NMR ($CDCl_3$) δ: 1.46 (3H, s, CH_3); 2.77–3.06 (4H, m, $CH_2 \times 2$) ppm. ^{19}F NMR ($CDCl_3$) δ: -81.4 (3F, m, CF_3); -113.0 (2F, m, CF_2); -118.4 (2F, m, CF_2); -126.5 (2F, m, CF_2) ppm. IR (KBr) (cm^{-1}): 1741 (CO). Mass spectrum m/z: 330 (M^+). Analysis: Calc. for $C_{10}H_7F_9O_2$: C, 36.38; H, 2.14%. Found: C, 36.44; H, 1.96%.

4. Conclusion

A new series of power-variable *S*-, *Se*- and *Te*-(trifluoromethyl)dibenzo-thio-, -seleno-, and -telluro-phenium-3-sulfonates has been developed as practically useful electrophilic trifluoromethylating agents. It should be possible to use these reagents widely for the practical production of various trifluoromethylated organic compounds[3].

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