# The Synthesis of Bis(trifluoromethyl) Sulphone and Bis(trifluoromethyl) Sulphonate by Direct Fluorination

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The reaction of elemental fluorine with dimethyl sulphone and dimethyl sulphate has been studied. The synthesis and characterization of bis(trifluoromethyl) sulphone, trifluoromethylsulphonyl fluoride, bis(trifluoromethyl) sulphate, difluoromethyl trifluoromethyl sulphate, bis(difluoromethyl) sulphate, trifluoromethoxysulphonyl fluoride, and difluoromethoxysulphonyl fluoride are described.

PREVIOUS advances in direct fluorination have led to practical syntheses of a number of oxygen-containing perfluoro-organic compounds.[1] Since the preparation of perfluoroalkyl sulphones, sulphonyl fluorides, and esters of sulphonic acids from non-fluorinated materials have been limited to electrochemical fluorinations, in which the yields are often low,[2] it was of interest to investigate the direct fluorination of dimethyl sulphone and dimethyl sulphate. For the fluorination of dimethyl sulphate a number of reaction conditions are described which show that by varying fluorine flow rates or fluorine concentrations, or by pressurizing the system with fluorine, the percentage yields of polyfluorinated and perfluorinated products can be varied significantly. One of the reasons the synthesis of bis(trifluoromethyl) sulphate was of interest was its structural similarity to dimethyl sulphate, a widely used methylating agent.

## EXPERIMENTAL

Mass spectra were measured on a Bell and Howell model 21—491 mass spectrometer operating at 70 eV. Proton n.m.r. spectra were recorded on a Varian Associates A 56/60 instrument operating at 60.0 MHz. Fluorine n.m.r. spectra were obtained using either a Varian A 56/60 instrument operating at 56.47 MHz, or a Varian HA 100 operating at 94.1 MHz. The natural abundance carbon-13 proton-noise-decoupled spectra were obtained on a Bruker WH-90 (Fourier-transform mode) spectrometer operating at a resonance frequency of 22.615 Hz. All n.m.r. spectra were obtained using neat liquids in sealed glass tubes and were referenced to external tetramethylsilane for hydrogen and external trifluoroacetic acid for fluorine. For carbon-13 spectra sealed 5-mm tubes containing the neat liquids were placed coaxially in 10-mm tubes containing $D_2O$ which served as an external lock. The carbon-13 chemical shifts were reported relative to $SiMe_4$. Positive shifts in the proton and carbon-13 spectra correspond to low-field shifts. Positive shifts in the fluorine-19 spectra refer to high-field shifts. I.r. data were recorded on a Beckman IR 20A instrument using a Pyrex cell equipped with KBr windows. A Bendix 2300 gas chromatograph equipped with a cryogenic controller and a thermal-conductivity detector was used for separations. Except for parent peaks, only peaks with intensity $\geqslant 1\%$ of the base-peak are reported in the mass-spectral data.

*Fluorination of Dimethyl Sulphone* [$(CH_3)_2SO_2$].—A sample (1.42 g, 15.1 mmol) of finely powdered dimethyl sulphone was placed in a nickel boat, which was then inserted into a 1-in (i.d.) nickel tube reactor. After flushing the reactor with helium for 3 h, a fluorine flow of 10 cm³ min⁻¹ diluted with a 20 cm³ min⁻¹ flow of helium was initiated, and maintained for 12 h. The fluorine flow was then increased to 30 cm³ min⁻¹ and the helium flow was reduced to 10 cm³ min⁻¹; this flow rate was maintained for 5 d. The reaction proceeded at room temperature. The fluorine flow was then terminated and the reactor was flushed with a 160 cm³ min⁻¹ flow of helium for 6 h. The products which condensed in a collection trap at −196 °C were fractionally distilled through slush-cooled traps at −95, −126, and −196 °C. Gas chromatographic separation at −20 °C (10 ft × 0.25 in column of 10% SE 30 on Chromosorb P) of the products collected in the trap at −126 °C yielded $(CF_3)_2SO_2$ (34%, 1.05 g) and $CF_3SO_2F$ (15%, 0.27 g). The trap at −196 °C contained $SO_2F_2$ (*ca.* 40%).

*Bis(trifluoromethyl) sulphone* [$(CF_3)_2SO_2$]. A gas-phase molecular-weight determination yielded a value of 202 (*cf.* 202 for $C_2F_6O_2S$). The i.r. spectrum exhibits bands at 1 431s, 1 253vs, 1 211s, 1 148s, 1 110s, 627s, 572w, and 501w cm⁻¹. The mass spectrum contains no parent peak, but shows peaks at $m/e$ 133 (0.4%) ($M^+ - CF_3$), 117 (1.5%, $[OSCF_3]^+$), 70 (1.2%, $[SF_2]^+$), 69 (100%, $[CF_3]^+$), 64 (2.6%, $[SO_2]^+$), 50 (2.7%, $[CF_2]^+$), 48 (4.4%, $[SO]^+$), 32 (1.3%, $S^+$), and 31 (2.1%, $[CF]^+$); m.p. −112 °C; the $^{19}F$ and $^{13}C$ n.m.r. spectra are reported in Table 2.

*Trifluoromethylsulphonyl fluoride* [$CF_3SO_2F$]. The i.r. spectra of $CF_3SO_2F$ has been partially described by Gramstad and Haszeldine;[3] the i.r. spectrum recorded in this study contains bands at 1 478s, 1 278m, 1 239vs, 1 156s, 834s, and 617m cm⁻¹; $m/e$ 83 (2.0%, $[SO_2F]^+$), 69 (100%, $[CF_3]^+$), 67 (7.3%, $[SOF]^+$), 50 (1.4%, $[CF_2]^+$, 48 (2.3%, $[SO]^+$), and 31 (1.1%, $[CF]^+$); the $^{19}F$ n.m.r. spectrum is in Table 2.

*Fluorination of Dimethyl Sulphate.*—The direct fluorination of dimethyl sulphate was attempted under a variety of reaction conditions. Three sets of conditions are described below. For reactions (*a*) and (*b*), a four-zone cryogenic reactor system, described previously,[1] was employed. Reaction (*c*) was performed in a four-zone cryogenic reactor system modified to be pressurized by inserting a Monel shut-off valve between the NaF scrubber and the collection trap. A Monel Matheson model 63–3331 gauge was employed to measure the pressure.

(*a*) A sample (2.56 g, 20.3 mmol) of dimethyl sulphate was slowly evaporated into a four-zone cryogenic reactor ($Z_1 = 40$, $Z_2 = -78$ °C) using a 160 cm³ min⁻¹ flow of helium. After 4 h zone 1 was allowed to cool. After equilibrium temperature was reached in zone 1 (−55 °C), the flow of helium was reduced to 18 cm³ min⁻¹ and a fluorine flow of 2.0 cm³ min⁻¹ was initiated. After 24 h zone 2 was warmed to −55 °C, and after another 24 h zone 2 was warmed to −35 °C. After 48 h, the fluorine flow was increased to 3.5 cm$^3$ min$^{-1}$; 8 h later, zone 3 was cooled to $-35$ °C and the helium flow reduced to 9 cm$^3$ min$^{-1}$. After 40 h zone 4 was cooled to $-35$ °C, and 48 h later the fluorine flow was terminated, and the system was flushed with a 160 cm$^3$ min$^{-1}$ flow of helium. The reactor was then warmed to ambient temperature and a 160 cm$^3$ min$^{-1}$ flow of helium was maintained for 15 h. The products trapped at $-196$ °C throughout the reaction, were fractionally distilled through slush-cooled traps at $-63$, $-126$, $-160$, and $-196$ °C. A non-condensible gas, $CF_4$, was pumped from the $-196$ °C trap prior to the low-temperature separations. The $-126$ and $-160$ °C fractions were subsequently separated by g.l.c. (10-ft × 25-in column of 10% SE-30 on Chromosorb P) at $-20$ °C and yielded $CF_3OSO_2F$ (0.341 g), $(CF_3O)_2SO_2$ (0.004 45 g), and $CF_2HOSO_2F$ (1.185 g). The $-63$ °C fraction was separated by g.l.c. at 0 °C and yielded $CF_2HOSO_2F$ (0.067 56 g), $CF_2HOSO_2OCF_3$ (0.040 90 g), and $(CF_2HO)_2SO_2$ (0.047 21 g). The $-196$ °C fraction contained $COF_2$, $SO_2F_2$, and traces of $SF_6$. A non-volatile fraction, presumed to be $(CH_3O)_2SO_2$ and partially fluorinated $(CH_3O)_2SO_2$ derivatives containing less than four fluorines, was decomposed with an ammonium hydroxide solution. The overall yield of the products was: $CF_8OSO_2F$ (10%), $(CF_3O)_2SO_2$ (0.1%), $CF_2HOSO_2F$ (41%), $CF_2HOSO_2OCF_3$ (1%), and $(CF_2HO)_2SO_2$ (4%).

(*b*) Dimethyl sulphate (2.52 g, 20 mmol) was evaporated over a 4-h period into a four-zone cryogenic reactor ($Z_1 = 15$, $Z_2 = -78$ °C) using a 160 cm$^3$ min$^{-1}$ flow of helium. Zone 1 was then allowed to cool. After equilibrium temperature was reached in zone 1 (*ca.* $-55$ °C), the flow of helium was reduced to 10 cm$^3$ min$^{-1}$, and a fluorine flow of 2.5 cm$^3$ min$^{-1}$ was initiated. After 24 h zone 2 was warmed to $-55$ °C. After 24 h, zone 3 was cooled to $-55$ °C and zone 2 allowed to warm (*ca.* $-25$ °C); 24 h later, zone 4 was cooled to $-55$ °C and zone 3 allowed to warm. At equilibrium ($Z_3 = -25$, $Z_2 = -5$, and $Z_1 = 10$ °C) the helium flow was terminated. After 24 h zone 4 was warmed to $-30$ °C and maintained at this temperature for 48 h. The fluorine flow was then terminated, and the reactor was flushed for *ca.* 6 h with a 160 cm$^3$ min$^{-1}$ flow of helium. The reactor was then allowed to warm to ambient temperature and a 160 cm$^3$ min$^{-1}$ flow of helium was maintained for 36 h. The volatile products, trapped at $-196$ °C throughout the reaction, were separated by the procedure described for reaction (*a*). The $-196$ °C fraction contained $COF_2$, $SO_2F_2$, and traces of $SF_6$. The overall yield of the products was as follows: $CF_3OSO_2F$ (22%), $(CF_3O)_2SO_2$ (2%), $CF_2HOSO_2F$ (16%), $CF_2HOSO_2OCF_3$ (12%), and $(CF_2HO)_2SO_2$ (13%).

(*c*) A sample (2.25 g, 17.9 mmol) of dimethyl sulphate was slowly evaporated into a four-zone cryogenic reactor ($Z_1 = 5$, $Z_2 = -100$ °C) using a 160 cm$^3$ min$^{-1}$ flow of helium. After 4 h, zone 2 was warmed to $-78$ °C. The fluorination conditions for the first 5 d were the same as those described in (*b*). After 5 d, zone 4 was warmed to $-30$ °C and the system was pressurized with fluorine to 2.5. After twenty-four hours, the system was depressurized and then pressurized with fluorine to 4.0 lbf in$^{-2}$. After 24 h, the reactor was depressurized and flushed for 6 h with a 160 cm$^3$ min$^{-1}$ flow of helium. The reactor was then allowed to warm to ambient temperature and a 160 cm$^3$ min$^{-1}$ flow of helium was maintained for 15 h. The volatile products, trapped at $-196$ °C throughout the reaction, were separated by the same procedure as described in (*a*). The overall yield of the products obtained was as follows: $CF_3OSO_2F$ (36%), $CF_2HOSO_2F$ (20%), $(CF_3O)_2SO_2$ (6%), $CF_2HOSO_2OCF_3$ (4%), and $(CF_2HO)_2SO_2$ (3%).

*Bis(trifluoromethyl) sulphate* [$(CF_3O)_2SO_2$]. The i.r. spectra is identical to that reported in the literature;[4] *m/e* 234 ($M^+$, 0.5%), 149 (4.3%, $[CF_3O_3S]^+$), 146.1 (1.0%, $[CF_2O_4S]^+$), 135 (1.5%, $[CF_3OCF_2]^+$), 80 (1.4%, $[SO_3]^+$), 70 (1.0%, $[SF_2]^+$), 69 (100%, $[CF_3]^+$), 64 (1.7%, $[SO_2]^+$), 48 (1.7%, $[SO]^+$), 47 (1.3%, $[COF]^+$), 44 (1.2%, $[CO_2]^+$), and 32 (1.4%, S); the m.p. of $CF_3OSO_2OCF_3$ is $-98$ °C, in agreement with ref. 5; the $^{19}F$ n.m.r. spectrum is reported in Table 2.

*Trifluoromethoxysulphonyl fluoride* [$CF_3OSO_2F$]. The i.r. spectrum is identical to that reported in the literature;[4] *m/e* 168 ($M^+$, 0.7%), 85 (1.2%, $[CF_3O]^+$), 83 (23.7%, $[SO_2F]^+$), 80 (1.1%, $[SO_2]^+$), 69 (100%, $[CF_3]^+$, 67 (3.6%, $[SOF]^+$), 64 (2.3%, $[SO_2])^+$, 48 (2.9%, $[SO]^+$), and 47 (4.4%, $[COF]^+$); m.p. $-117$ °C (lit.,[4] $-121$ °C); the $^{19}F$ and $^{13}C$ n.m.r. spectra are reported in Table 2.

*Difluoromethoxysulphonyl fluoride* [$CF_2HOSO_2F$]. The i.r. spectrum exhibits bands at 3 041w, 1 485s, 1 381m, 1 243s, 1 160s,br, 1 025vs, 920s, 836s, 642m, and 536w cm$^{-1}$; *m/e* 150 ($M^+$, 0.4%), 83 (17.1%, $[SO_2F]^+$), 67 (4.5%, $[SOF]^+$), 64 (1.9%, $[SO_2]^+$), 51 (100%, $[CF_2H]^+$,$[SF]^+$), 48 (3.2%, $[SO]^+$), 47 (4.0%, $[COF]^+$), 32 (3.0%, $S^+$), and 31 (2.0%, $[CF]^+$); m.p. between $-88$ and $-89$ °C; the $^1H$, $^{19}F$, and $^{13}C$ n.m.r. spectra are reported in Table 2. The synthesis of difluoromethoxysulphonyl fluoride by a less direct route has been previously reported.[5]

*Difluoromethyl trifluoromethyl sulphate* [$CF_3OSO_2OCF_2H$]. I.r. spectrum; 3 032vw, 2 107vw, 2 037vw, 1 485s, 1 374w, 1 231s, 1 214s, 1 156vs, 1 027s, 962s, 905m, 790m, 643m, 600m, 579m, and 537m cm$^{-1}$; *m/e* 216 ($M^+$, 0.5%), 149 (2.9%, $[CF_3O_3S]^+$), 146 (1.5%, $[CF_2O_4S]^+$), 135 (1.1%, $[CF_3OCF_2]^+$), 131 (3.1%, $[CF_2HSO_3]^+$), 81 (1.5%, $[HSO_3]^+$), 80 (2.0%, $[SO_3]^+$), 69 (41.9%, $[CF_3]^+$), 64 (1.2%, $[SO_2]^+$), 63 (2.7%), 51 (100%, $[CF_2H]^+[SF]^+$), 48 (3.1%, $[SO]^+$), 47 (2.7%, $[COF]^+$), 32 (1.2%, $S^+$), and 31 (1.4%, $[CF]^+$); m.p. $-84$ °C; the $^1H$, $^{19}F$, and $^{13}C$ n.m.r. spectra are reported in Table 2.

*Bis(difluoromethyl) sulphate* [$(CF_2HO)_2SO_2$]. I.r. spectrum; 3 035w, 1 470s, 1 377m, 1 231s, 1 162vs, 1 029s, 1 007vs, 904s, 648s, and 558m cm$^{-1}$; *m/e* 198 ($M^+$, 0.05%), 31 (1.0%, $[CF]^+$), 34 (4.4%), 51 (100%, $[CF_2]^+[SF]^+$), 64 (1.4%, $[SO_2]^+$), 81 (4.7%, $[HSO_3]^+$), 128 (4.2%, $[C_2F_2H_2O_2S]^+$), and 131 (2.1%, $[CF_2HO_3S]^+$); m.p. between $-66$ and $-67$ °C; the $^1H$ and $^{19}F$ n.m.r. spectra are reported in Table 2. Bis(difluoromethyl) sulphate has been previously prepared from the thermal decomposition of bis(fluoromethyl) sulphate.[6]

## RESULTS AND DISCUSSION

The direct fluorination of dimethyl sulphone, conducted at ambient temperature, yielded bis(trifluoromethyl) sulphone (34%) and trifluoromethylsulphonyl fluoride (15%). By contrast, the electrochemical fluorination of dimethyl sulphone performed by Haszeldine[7] produced the perfluorinated sulphone in 4.3% yield, and is the only previous synthesis reported for this compound. The fluorination procedure used here was characterized by high initial dilution (5% $F_2$) and low flow conditions (32.1 mmol in 12 h). After 12 h the fluorine flow was increased to 192.8 mmol in 24 h and the concentration to 33%. Bis(trifluoromethyl) sul-

TABLE 1

Yields in the fluorination of dimethyl sulphate *

| Compound | (*a*) | (*b*) | (*c*) |
|---|---|---|---|
| $CF_3OSO_2F$ | 10 | 22 | 36 |
| $CF_2HOSO_2F$ | 41 | 16 | 20 |
| $CF_3OSO_2OCF_3$ | 0.1 | 2 | 6 |
| $CF_2HOSO_2OCF_3$ | 1 | 12 | 4 |
| $(CF_2HO)_2SO_2$ | 4.4 | 13 | 3 |

* The letters (*a*), (*b*), and (*c*) refer to reaction conditions listed in the Experimental section.

phone is a gas at room temperature (b.p. 15.6 °C). The S–O absorption observed for $(CF_3)_2SO_2$ is essentially the same as that for $(CF_3CF_2)_2SO_2$ (S–O stretch 1 430 cm$^{-1}$).[8] Bis(trifluoromethyl) sulphone melts at −112 °C, and may prove to be an interesting low-temperature solvent.

TABLE 2

N.m.r. spectra of poly- and per-fluorinated $SO_2$-containing compounds

| Compound | $\delta_F$ [a] | $\delta_C$ [b] | $\delta_H$ [c] | $J_{FF}$ [d] | $J_{CF}$ [d] | $J_{HF}$ [d] |
|---|---|---|---|---|---|---|
| $(CF_3)_2SO_2$ | 3.12 [e] | 118.9 [f] | | | 327.4 | |
| $(CF_3O)_2SO_2$ | −19.37 [e] | | | | | |
| $CF_3OSO_2F$ | −19.05 [g] (−18.8 [h])<br>−122.21 [f,i] (−123.4 [h]) | 118.4 [f] (118.8 [10]) | | 6.9 (6.5 [h]) | 272.1 (272 [10]) | |
| $CF_2HOSO_2OCF_3$ | −19.96 [e]<br>+8.53 [j,g] | 118.5 [f]<br>115.1 [j,k] | <br>6.73 [k] | | 275.0<br>270.6 [j] | <br>68.1 |
| $(CF_2HO)_2SO_2$ | +7.92 [g] | | 6.81 [k] | | | 69.0 |
| $CF_2HOSO_2F$ | +8.27 [j,l]<br>−121.39 [i,k] | 115.2 [j,k] | 6.40 [k] | 5.3 | 276.5 | 68.2 |
| $CF_3SO_2F$ | +2.71 [g]<br>−113.79 [i,k] | | | 17.9 | | |

[a] P.p.m. from $CF_3CO_2H$, positive values are high field. [b] P.p.m. from $SiMe_4$, positive values are low field. [c] P.p.m. from $SiMe_4$ positive values are low field. [d] In Hz. [e] Singlet. [f] Quartet. [g] Doublet. [h] J. K. Ruff and R. F. Merrit, *Inorg. Chem.*, 1968, **7**, 1219. [i] Sulphonyl fluoride group. [j] Difluoromethyl group, designated only where ambiguity may arise. [k] Triplet. [l] Doublet of doublets.

Table 1 displays the yields of polyfluorinated and perfluorinated sulphates and sulphonyl fluorides isolated from three reactions in which different fluorine flow rates, concentrations, and pressures were employed. From these data it is apparent that the yields of perfluorinated products can be varied significantly. Reaction (*a*) was characterized by relatively low fluorine concentrations (11—39%) and flow rates (120—210 mmol h$^{-1}$). This reaction yielded primarily polyfluorinated materials. The high yield of $CF_2HOSO_2F$ may, in part, be a consequence of the helium flow maintained throughout the reaction. It is possible that this compound (vapour pressure at −30 °C, *ca.* 24 Torr) was swept out of the reactor by the helium flow before it had undergone sufficient reaction. By increasing the fluorine concentration [25—100%, reaction (*b*)], the yield of perfluorinated products was greatly increased.

In reaction (*c*) we pressurized the final stages of a low-temperature direct fluorination, which had not been done in previous studies. The higher yields of the perfluorinated sulphate and sulphonyl fluoride suggest that by pressurizing the system the fluorine is better able to diffuse through and fluorinate partially-fluorinated materials.

The polyfluorinated and perfluorinated compounds characterized in this study are colourless liquids or gases. The asymmetric $SO_2$ stretching frequencies in the polyfluorinated and perfluorinated sulphates [S–O stretch at 1 493 cm$^{-1}$ $(CF_3O)_2SO_2$; 1 485 cm$^{-1}$ $CF_3OSO_2OCF_2H$; and 1 470 cm$^{-1}$ $(CF_2HO)_2SO_2$] occur at higher frequencies than observed for dimethyl sulphate (S–O stretch 1 412 cm$^{-1}$).[9] The $^{19}F$, $^{13}C$, and $^{1}H$ n.m.r. spectra of the poly- and per-fluorosulphates and sulphonyl fluorides are summarized in Table 2. The $^{19}F$ and $^{1}H$ spectra contain resonances in the expected regions. The $^{13}C$ chemical shifts of the trifluoromethyl carbons in $(CF_3O)_2SO_2$, $CF_3OSO_2F$, and $(CF_3)_2SO_2$ fall within the narrow spectral range previously observed for trifluoromethyl carbons.[10] A surprisingly small $^{13}C$ upfield shift (*ca.* 3 p.p.m.) is observed for the replacement of a fluorine by a hydrogen in the perfluoro-sulphonyl fluoride and -sulphate.

One might consider the preservation of sulphates and sulphones bonded to carbon during direct fluorination to be quite surprising. However, with the recently reported preservation of metal–carbon bonds [11] this might be predictable. This new sulphate and sulphone chemistry does suggest that the moieties might be preserved as pendant groups on hydrocarbon polymer surfaces during direct fluorination. Such chemistry, therefore, might have impact in the areas of electrochemical membranes, battery separators, and polymer-supported catalysis.

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