Chemical Transformation of Bis((perfluoroalkyl)sulfonyl)methanes and 1,1,3,3-Tetraoxopolyfluoro-1,3-dithiaycloalkanes

Shizheng Zhu,[1] Guoling Xu,[1] Chaoyue Qin,[1] Xu Yong,[1] Chu Qianli,[1] and Darryl D. DesMarteau[2]

[1]Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shaghai 200032, China

[2]Chemistry Department, Clemson University, Box 341905, Clemson, SC, 29634-1905

ABSTRACT: *Halogenation of the potassium or silver salts of bis((trifluoromethyl)sulfonyl)methane $(CF_3SO_2)_2CH_2$ and its cyclo analogues $(CF_2)_nSO_2CH_2SO_2CF_2$ with N-fluoro-bis((trifluoromethyl)sulfonyl)imine $(CF_3SO_2)_2NF$, chlorine or bromine gave good yields of the corresponding α-halo disulfones $(CF_3SO_2)_2CHX$ and $(CF_2)_nSO_2CHXSO_2CF_2$ (X: F, Cl, Br; n = 1,2). Some chemical transformations of these fluorinated α-halo-disulfones are described.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 147–152, 1999

INTRODUCTION

Compounds containing two geminal sulfonyl groups are of interest because of their unusual properties [1]. Studies have developed mainly in two directions: the first being investigation of their thermodynamic or kinetic acidity and the formation, stability, and reactivity of the corresponding carbanions; the second being a search for their new and improved syntheses. Bis((perfluoroalkyl)sulfonyl)methanes $(R_1SO_2)_2CH_2$ have been known for a long time [2,3] and have been shown to be very strong hydrocarbon acids [3]. Recently, we have reported the synthesis of the fluorinated cyclic disulfones $(CF_2)_nSO_2CH_2SO_2CF_2$ (**1**) (n = 1,2,3) [4]. As expected, compounds **1** are highly acidic with $pk_a \leq 1$ in H_2O. The methylene carbon is easily functionalized to give both mono and disubstituted derivatives. A single α-substitution gives a new acid whose acidity is affected by the nature of the substituent.

RESULTS AND DISCUSSION

1,1,3,3-Tetraoxopolyfluoro-1,3-dithacycloalkanes

$(CF_2)_nSO_2CH_2SO_2CF_2$ (n = 1, **1a**; n = 2, **1b**) (**1**) have been prepared by the reaction of α,ω-bis(fluorosulfonyl)perfluoroalkanes $FO_2S(CF_2)_nSO_2F$ with CH_3MgCl in THF. Compounds **1** are readily neutralized by the action of potassium or silver carbonate to give the corresponding salts.
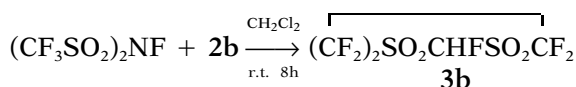
$$1 + M_2CO_3 \rightarrow \underset{\textbf{2}}{(CF_2)_nSO_2CHMSO_2CF_2} \; (M: K, Ag)$$
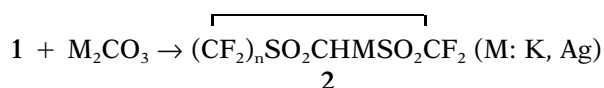
$n = 1$, M = K, **2a**; $n = 1$, M = Ag **2c**;
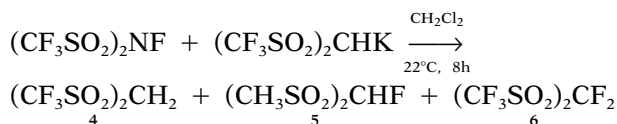$n = 2$, M = K, **2b**; $n = 2$, M = Ag **2d**;

This reaction occurs rapidly and quantitatively at 22°C in acetone solution. N-fluoro-bis((trifluoromethyl)sulfonyl)imine $(CF_3SO_2)_2NF$ is known as a strong electrophilic fluorination reagent [5] and has been widely used to prepare many monofluorine substituted compounds. It reacted smoothly with **2b** to give α-fluoro-1,1,3,3-tetraoxopolyfluoro-1,3-dithacycloalkanes.

$$(CF_3SO_2)_2NF + \textbf{2b} \xrightarrow[\text{r.t. 8h}]{\text{CH}_2\text{Cl}_2} \underset{\textbf{3b}}{(CF_2)_2SO_2CHFSO_2CF_2}$$

The ^{19}F NMR spectrum of **3b** is very different from that of $(CF_2)_nSO_2CHMSO_2CF_2$ for which the ^{19}F NMR is an apparent first-order spectrum with two resonances for the CF$_2$–C and CF$_2$–S groups in the ratio of 1:2 at $\delta = 126.0$ and -121.6. For compound **3b**, the spectrum consists of two second-order AB patterns, and the observed bands can be analyzed as a double AB spectrum due to the nonequivalent axial and equatorial fluorines of each CF$_2$ group in the molecule **3b**. The assignment of this spectrum is based upon the assumption that equatorial (B) fluorines are generally more highly shielded than axial fluorines (A) [6–7]. For CF$_2$S, $\Delta\gamma_{AB} = 1716$ Hz ($\delta = 20.3$), and the coupling constant $^2J_{AB} = 264$ Hz. For the CF$_2$C, $\Delta\gamma_{AB} = 1163$ Hz ($\delta = 13.8$), and $^2J_{AB} = 288$ Hz. A large solvent dependence for the ^{19}F NMR spectrum of **3b** was observed. For example, in CDCl$_3$, it is a multiplet (d-t) at $\delta = 168.5$ ($^2J_{HF} = 45$ Hz, $^4J_{FF} = 9$ Hz); in acetone-d$_6$, the 2-F is a triplet at $\delta = -170.1$ ($^4J_{FF} = 9$ Hz), indicating a fast exchange of the acidic hydrogen with the more polar solvent.

Koshar [3] has reported the chloride and the bromide of bis((trifluoromethyl)sulfonyl)methane $(CF_3SO_2)_2CHX$ (X: Br, Cl), but no corresponding fluoride has been prepared up to the present. We used $(CF_3SO_2)_2NF$ to react with $(CF_3SO_2)_2CHK$ in CH$_2$Cl$_2$ at 22°C, and three products were obtained:

$$(CF_3SO_2)_2NF + (CF_3SO_2)_2CHK \xrightarrow[\text{22°C, 8h}]{\text{CH}_2\text{Cl}_2}$$

$$\underset{\textbf{4}}{(CF_3SO_2)_2CH_2} + \underset{\textbf{5}}{(CH_3SO_2)_2CHF} + \underset{\textbf{6}}{(CF_3SO_2)_2CF_2}$$

The observed products can be explained as follows:

$$\textbf{5} + (CF_3SO_2)_2CHK \rightarrow \textbf{4} + (CF_3SO_2)_2CFK \xrightarrow{(CF_3SO_2)_2NF} \textbf{6}$$
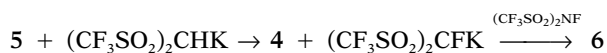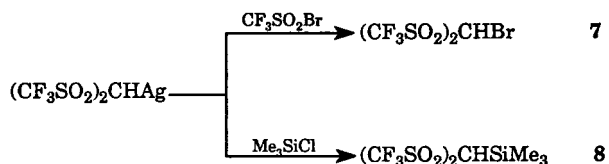
Compound **5** is more acidic than **4** and the mixture

of **4–6** is obtained even with a substantial excess of $(CF_3SO_2)_2NF$.

Both **5** and **6** are liquids and can be separated and purified by column chromatography. They were fully characterized by spectroscopic methods and elemental analyses. In the IR and ^{19}F NMR spectra, it is apparent that the fluorine substitution shifts the $\nu_{antisym}$ (SO$_2$) absorption to higher wave numbers and the CF$_3$ groups shift downfield. The values $\nu_{antisym}$ (SO$_2$) 1398 cm^{-1}, 1411 cm^{-1}, and 1429 cm^{-1} and the δ CF$_3$ are -76.5, -73.4, and -69.4 for compounds **4**, **5**, and **6**, respectively.
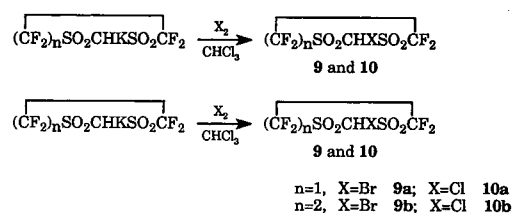
Treatment of $(CF_3SO_2)_2CHAg$ with CF_3SO_2Br formed the bromide $(CF_3SO_2)_2CHBr$ **7**. In this reaction, the carbanion did not attack the sulfonyl sufur atom but abstracted the bromine atom of CF_3SO_2Br.

Refluxing $(CF_3SO_2)_2CHAg$ with excess chlorotrimethylsilane afforded the silylated compound $(CF_3SO_2)_2CHSiMe_3$ **8**.

$$(CF_3SO_2)_2CHAg \begin{cases} \xrightarrow{CF_3SO_2Br} (CF_3SO_2)_2CHBr \quad\quad \textbf{7} \\ \\ \xrightarrow{Me_3SiCl} (CF_3SO_2)_2CHSiMe_3 \quad \textbf{8} \end{cases}$$

Products **7** and **8** are thermally stable liquids with b.p. 52°C/4 torr and 70°C/0.1 torr, respectively.

The bromides and chlorides, **9** and **10**, can also be prepared by direct treatment of the potassium salts with bromine or chlorine gas.

$$(CF_2)_nSO_2CHKSO_2CF_2 \xrightarrow[\text{CHCl}_3]{X_2} \underset{\textbf{9 and 10}}{(CF_2)_nSO_2CHXSO_2CF_2}$$

$$(CF_2)_nSO_2CHKSO_2CF_2 \xrightarrow[\text{CHCl}_3]{X_2} \underset{\textbf{9 and 10}}{(CF_2)_nSO_2CHXSO_2CF_2}$$

$n=1$, X=Br **9a**; X=Cl **10a**
$n=2$, X=Br **9b**; X=Cl **10b**

These reactions occur rapidly at room temperature in CHCl$_3$ or CCl$_4$ and usually give good yields. As mentioned earlier, the ^{19}F NMR spectrum of each 2-fluoro-substituted compound **3** is a second-order AB spectrum for the ring CF$_2$ groups with a strong solvent dependence. Similarly, in the case of the bromide **9b**, the observed spectrum depends on the solvent used; for example, in $(CD_3)_2CO$, it is an apparent first-order spectrum. In the less polar solvent CDCl$_3$, it is a double AB pattern for CF$_2$S, $\Delta\gamma_{AB} = 1741$ Hz ($\delta = 20.7$) and the coupling constant $^2J_{AB} = 264$ Hz; for the CF$_2$C, $\Delta\gamma_{AB} = 1138$ Hz ($\delta = 13.5$) and $^2J_{AB} = 289$ Hz.

Under similar conditions, the *gem*-dibromo di-

sulfone $(CF_2)_nSO_2CBr_2SO_2CF_2$ **11** was also prepared. It was readily decomposed by the action of light, but it is thermally stable. When heated to 120°C (m.p. 91–94°C), it showed little decomposition. The α-mononohaldisulfones **9** and **10** behave similarly. The homolytic dissociation of the carbon-bromine bond of compounds **9a** and **9b** occurred readily under irradiation or under the influence of free radical catalysts. For example, irradiation of **9b** in toluene afforded benzyl bromide and **1b** in high yields.

When this photoreaction was carried out in allyl ether, the product was the 2,3-substituted tetrahydrofuran derivative **12**.
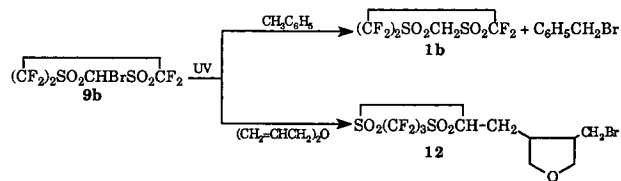

Attempts to extend this reaction to fluoroalkenes failed, both under irradiation or by using a free radical catalyst, such as AIBN and BPO. Compound **9b** did not add to $CF_2=CCl_2$ or to $CF_2=CFCl$.

Under the same conditions, $(CF_3SO_2)_2CHF$ did not react with $(CH_2=CHCH_2)_2O$. Similar to the perfluoroalkyl iodides [8], the bromine atom in compound **9** is also readily extracted. This can be demonstrated by the following reaction:
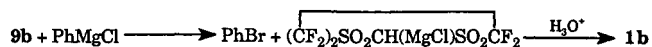
As with the usual allyl halides, these monohalides can readily be transformed into the corresponding Grignard reagents:
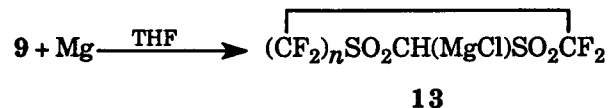
Compared to the ordinary Grignard reagents, RMgX, however, **13** is unreactive. For example, when it was stirred with PhCOCl or CF_3COCl for 12 hours, no reaction occurred, and only a small amount of **1** was detected in the reaction mixture.

Heating of $CF_2SO_2CHMgClSO_2CF_2$ with excess of $PhCH_2Br$ gave $SO_2(CF_2)_2SO_2CH-CH_2C_6H_5$ **14** in 75% yield. This 2-benzyl-substituted product can also be obtained in 65% yield by the reaction of **2b** with benzyl bromide.

In summary, a variety of bis(perfluoroalkanesulfonyl)methyl halides $R_fSO_2CHXSO_2R_f$ (X: F, Cl, Br) have been synthesized. Some photoreactions and reactions of organometallic derivatives of these fluorinated α-halo disulfones have been described.

EXPERIMENTAL

Melting points were taken on a Mel-Temp melting-point apparatus. All the boiling and melting points

TABLE 1 Fluorinated α-Halodisulfones Prepared

Compounds	M.p. or B.p. (°C)	Yield (%)	Element Analysis (found/calcd)
$(CF_2)_2SO_2CHFSO_2CF_2$ **3b**	145–146	81	C:15.18/15.48 F:37.02/36.77
$(CF_3SO_2)_2CHF$ **5**	40–2/4 torr	45	C:12.29/12.09 F:44.71/44.63
$(CF_3SO_2)_2CF_2$ **6**	61–4/8 torr	31	C: 11.52/11.39 F: 41.88/42.09
$(CF_2)_2SO_2CHBrSO_2CF_2$ **9b**	101–108	82	C: 12.69/12.94 F: 30.25/30.73
$CF_2SO_2CHBrSO_2CF_2$ **9a**	99	85	C: 11.30/11.21 F: 23.41/23.68
$(CF_2)_2SO_2CHClSO_2CF_2$ **10b**	135	85	C: 14.35/14.70 F: 35.11/34.92
$(CF_2)_2SO_2CBr_2SO_2CF_2$ **11**	91–94	78	C: 10.35/10.67 F: 24.98/25.37

are uncorrected. Infrared spectra were obtained using a Perkin-Elmer 1430 or IR-440 spectrometer. ^{19}F NMR and ^{1}H NMR were recorded on either a Varian-90 or JEOL FX-90Q spectrometer, CFCl$_3$ or TMS being used as an internal standard. MS spectra were obtained using a Hewlett-Packard 5985B GC/MS spectrometer or a Finnigan 4021 GC/MS instrument. All solvents were dried before use.

Fluorination of the Disulfone

A typical procedure was carried out as follows: A mixture of potassium salt (CF$_2$)$_2$SO$_2$CHKSO$_2$CF$_2$ (3.3 g 10 mmol), which was obtained by neutralization of **1b** (2.92 g, 10 mmol) with K$_2$CO$_3$ (0.7 g, 5 mmol) in acetone, plus (CF$_3$SO$_2$)$_2$NF (3.0 g, 10 mmol) and CH$_2$Cl$_2$ (30 mL) was stirred at room temperature for 12 hours. After removal of the (CF$_3$SO$_2$)$_2$NK by filtration, the filtrate was evaporated to dryness, and the crude product (2.5 g) was recrystallized from CH$_3$CN and CHCl$_3$ to give pure products **3b**.

Similar treatment of (CF$_3$SO$_2$)$_2$CHK (3.2 g, 10 mmol) with (CF$_3$SO$_2$)$_2$NF (3.0 g, 10 mmol) afforded (CF$_3$SO$_2$)$_2$CH$_2$ (0.5 g), (CF$_3$SO$_2$)$_2$CHF (1.4 g), and (CF$_3$SO$_2$)$_2$CF$_2$ (0.9 g).

(CF$_2$)$_2$SO$_2$CHFSO$_2$CF$_2$ **3b**

IR (υ_{max}, cm^{-1}) 2965, 2911 (m, C-H), 1408, 1342 (s, SO$_2$), 1220, 1120 (s, C-F). $\delta_{H,ppm}$ (CDCl$_3$) 6.25 (d-t, $^2J_{HF}$ = 45 Hz, $^4J_{HF}$ = 6 Hz).

$\delta_{F,ppm}$ (CDCl$_3$) -105.8 (2 X CF$_2^a$$-S, AB^2J_{FF}$ = 264 Hz, $^4J_{FF}$ = 6 Hz), -126.2 (2 X CF$_2^e$$-$S, AB), -118.0 (CF$_2^a$$-C, AB^2J_{FF}$ = 288 Hz), -131.8 (CF$_2^e$-C, AB), -168.0 (CHF, d). MS (m/z, %) 311 (M$^+$H, 100), 292 (MH$^+$-F, 34.6), 131 (C$_3$F$_5^+$, 30.4), 100 (C$_2$F$_4$, $^+$, 96.8). Elemental analysis for C$_4$HF$_7$O$_4$S$_2$: found: C, 15.18; F, 37.02; calcd: C, 15.48; F, 36.77.

(CF$_3$SO$_2$)$_2$CHF **5**

IR (υ_{max}, cm^{-1}) 2951 (m, C-H), 1411 (vs, SO$_2$), 1221, 1105 (s, C-F). $\delta_{H,ppm}$ (CDCl$_3$) 7.50 ($^2J_{HF}$ = 44 Hz). $\delta_{F,ppm}$ (CDCl$_3$) -73.5 (d, CF$_3$), -170.2 (d, CHF). MS (m/z, %) 299 (M$^+$H, 14.2), 281 (MH$^+$-F, 100), 133 (CF$_3$SO$_2^+$, 9.66), 69 (CF$_3$, 35.4). Elemental analysis for C$_3$HF$_7$O$_4$S$_2$: found: C, 12.29; F, 44.71; calcd: C, 1209; F, 44.63.

(CF$_3$SO$_2$)$_2$CF$_2$ **6**

IR (υ_{max}, cm^{-1}) 149 (vs, SO$_2$), 1230 (s, SO$_2$), 1110 (s, CF), $\delta_{F,ppm}$ (CDCl$_3$) -69.4 (CF$_3$, s), -94.4 (CF$_2$, s). MS (m/z, %) 317 (M$^+$H, 0.9), 301 (MH$^+$-O, 3.2), 281 (M$^+$-F-O, 100.0), 133 (CF$_3$SO$_2^+$, 13.1), 117 (CF$_3$SO$^+$, 5.0).

Elemental analysis for C$_4$F$_8$O$_4$S$_2$: found: C, 11.52; F, 41.88; calcd: C, 11.39; F, 42.09.

Reaction of (CF$_3$SO$_2$)$_2$CHAg with CF$_3$SO$_2$Br

CF$_3$SO$_2$Br (1.07 g, 5 mmol) was injected into a 25 mL flask containing a mixture of (CF$_3$SO$_2$)CHAg (1.93 g, 5 mmol) and CHCl$_3$ (15 mL). After the mixture had been stirred for 12 hours at room temperature, the solvent was evaporated, and the residue was distilled under reduced pressure to give the product (CF$_3$SO$_2$)$_2$CHBr **7** (2.2g, 62%) b.p. 52°C/4 torr (lit. 94°C/1196 Pa)[3] δ_H(CDCl$_3$): 6.13 (s, CH), δ_F(CDCl$_3$): -72.6 (s, CF$_3$).

Reaction of (CF$_3$SO$_2$)$_2$CHAg with Me$_3$SiCl

A mixture of (CF$_3$SO$_2$)$_2$CHAg (1.93 g, 5 mmol) and Me$_3$SiCl (15 mL) was stirred for 5 hours at 50°C. The excess Me$_3$SiCl was removed by evaporation, and the residue was distilled in vacuum to give the product (CF$_3$SO$_2$)$_2$CHSiMe$_3$ **8** (1.0 g, 57%) b.p. 70–71°C/13.3 Pa.

(CF$_3$SO$_2$)$_2$CHSiMe$_3$ **8**

IR (υ_{max}, cm^{-1}) 3076, 2989, 2924 (s, CH), 1398, 1326, 1213 (s, SO$_2$), 1113 (s, CF), $\delta_{H,ppm}$ (CD$_3$COCD$_3$) 5.05 (s, CH), 0.1 (s, CH$_3$), $\delta_{F,ppm}$ (CD$_3$COCD$_3$) -76.86 (s, CF$_3$). MS (m/z, %) 353 (M$^+$H, 4.8), 352 (M$^+$, 10.2), 357 (M$^+$-CH$_3$, 7.5), 133 (CF$_3$SO$_2^+$, 12.1), 69 (CF$_3^+$, 100.0). Elemental analysis for C$_6$H$_{10}$F$_6$O$_4$S$_2$Si: found: C, 20.57; H, 2.92; F, 32.60; calcd: C, 20.45; H, 2.84; F, 32.39.

Preparation of the Bromide and Chloride

(CF$_2$)$_n$SO$_2$CHXSO$_2$CF$_2$ (X: Br, Cl)

Typical procedure: Bromine (2.0 g, 12.5 mmol) was added dropwise to a 50 mL flask containing a mixture of **2b** (3.3 g, 10 mmol) and CCl$_4$ (30 mL). After the mixture had been stirred for 4 hours at room temperature, the solvent and excess bromine were removed under reduced pressure, and the residue was recrystallized from CHCl$_3$ and CH$_3$CN (1:1) to give **9b** (2.9 g).

Similarly, compounds **9a**, **10a**, and **11** were prepared.

(CF$_2$)$_2$SO$_2$CHBrSO$_2$CF$_2$ **9b**

IR (υ_{max}, cm^{-1}) 2981, 2953 (m, CH), 1401, 1218 (s, SO$_2$), 1200, 1150 (s, CF), $\delta_{H,ppm}$ (CDCl$_3$) 6.50 (s, CHBr), $\delta_{F,ppm}$ (CDCl$_3$) -106.3 (2 X CF$_2^a$S, AB $^2J_{FF}$ = 264 Hz), -127.0 (2 X CF$_2^e$S, AB), -118.8 (CF$_2^a$C, AB $^2J_{FF}$ = 289 Hz), -132.3 (CF$_2^e$C, AB $^2J_{FF}$ = 289 Hz), $\delta_{F,ppm}$ (CD$_3$COCD$_3$) -121.2 (2 X CF$_2$S, m), -125.7 (CF$_2$S, m). MS (m/z, %) 373/371 (M$^+$H, 8.2/8.8), 372/370 (M$^+$, 2.7/3.6), 291 (MH$^+$-Br, 43.2), 150 (C$_3$F$_5^+$,

72.3), 100 ($C_2F_4^+$, 100.0). Elemental analysis for $C_4HF_6O_4S_2Br$: found: C, 12.69; F, 30.25; calcd: C, 12.94, F, 30.73.

$(CF_2)_2SO_2CHClSO_2CF_2$ 10b

IR (v_{max}, cm^{-1}) 2983, 2950 (m, CH), 1403, 1220 (vs, SO$_2$), 1200–1105 (vs, CF); $\delta_{H,ppm}$ (CDCl$_3$) 6.63 (CHCl, s); $\delta_{F,ppm}$ (CDCl$_3$) −106.0 (2 X CF_2^aS, AB $^2J_{FF}$ = 258 Hz, −126.5 (2 X CF_2^eS, AB $^2J_{FF}$ = 258 Hz), −118.3 (CF_2^aC, AB $^2J_{FF}$ = 284 Hz), −132.0 (CF_2^eC, AB $^2J_{FF}$ = 284 Hz). MS (m/z, %) 331/229 (M$^+$H, 7.3/7.8), 313/211 (MH$^+$-O, 1.6/1.8), 328/326 (M$^+$, 3.4/3.8), 100 ($C_2F_4^+$, 100.0). Elemental analysis for $C_4HF_6O_4S_2Cl$: found: C, 14.35; F, 35.11; calcd: C, 14.70; F, 34.92.

$CF_2SO_2CHBrSO_2CF_2$ 10a

IR (v_{max}, cm-1) 2980, 2925 (m, CH), 1408, 1355 (s, SO$_2$), 1220–1105 (s, CF); $\delta_{H,ppm}$ (CDCl$_3$) 6.37 (s, CHBr); $\delta_{F,ppm}$ (CDCl$_3$) − 117.3 (2 X CF_2^a, AB $^2J_{FF}$ = 226 Hz), −119.9 (2 X CF_2^e, AB $^2J_{FF}$ = 226 Hz). MS (m/z, %) 323/321 (M$^+$H, 8.7/9.0), 322/320 (M$^+$, 2.4/2.1), 306/304 (M$^+$-O, 1.3/1.6), 259/257 (M$^+$H-SO$_2$, 1.8/2.0), 242 (MH$^+$-Br, 48.3), 100 ($C_2F_4^+$, 100.0). Elemental analysis for $C_3HF_4O_4S_2Br$: found: C, 11.30; F, 23.41; calcd: C, 11.21; F, 23.68.

$(CF_2)_2SO_2CBr_2SO_2CF_2$ 11

IR (v_{max}, cm^{-1}) 1413, 1289 (s, SO$_2$), 756, 641 (s, C-Br), 1215, 1192, 1174, 1110 (s, CF); $\delta_{F,ppm}$ (CD$_3$COCD$_3$) −110.5 (2 X CF$_2$S, m), −124.1 (CF$_2$C, m). MS (m/z, %) 453/451/449 (M$^+$H, 46.3/81.4/39.9), 373/371 (MH$^+$-Br, 15.9/20.3), 263 (MH$^+$-O-CBr$_2$, 100.0), 174/172/170 (CBr$_2^+$, 5.6/12.5/5.6). Elemental analysis for $C_4F_6O_4S_2Br_2$: found: C, 10.35; F, 24.98; calcd: C, 10.67; F, 25.37.

Reaction of $(CF_2)_2SO_2CHBrSO_2CF_2$ 9a with Allyl Ether

A mixture of **9a** (3.7 g, 10 mmol) and allyl ether (10 mL) contained in a quartz tube equipped with a reflux condenser, dry tubing, and a stirring bar was irradiated with an 800 W low-pressure mercury lamp for 4 hours. The excess allyl ether was removed at reduced pressure, and the residue was recrystallized from THF/CHCl$_3$ to give product **12** (3.4 g, 72%).

SO$_2$(CF$_2$)$_3$SO$_2$CH-CH$_2$ ⟋⟍ CH$_2$Br **12**
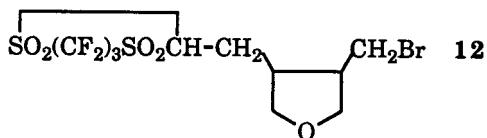
IR (v_{max}, cm^{-1}) 2865 (m, CH), 1393, 1380 (s, SO$_2$), 1218, 1200, 1109, 1153 (s, CF), 1110 (C–O). $\delta_{H,ppm}$ (CDCl$_3$) 5.40 (t, SO$_2$CHSO$_2$), 4.05–3.75 (m, 2 X OCH$_2$, cyclo CH, 4H), 2.50 (m, CH$_2$Br), 1.71 (m, C-CH$_2$-C). $\delta_{F,ppm}$ (CDCl$_3$) −109.7 (2 X CF_2^aS, AB $^2J_{FF}$ = 269 Hz), −129.9 (2 X CF_2^eS, AB), −118.7 (CF_2^aC, AB J_{FF} = 288 Hz), −132.1 (CF_2^eC, AB). MS (m/z, %) 471/469 (M$^+$H, 14.7/14.1), 389 (M$^+$-Br, 100.0), 359 (M$^+$-Br-CH$_2$O, 2.4). Elemental analysis for $C_{10}H_{11}F_6O_5S_2Br$: found: C, 25.71; H, 2.64; F, 24.18; calcd.: C, 25.59; H, 2.35; F, 24.31.

Preparation of $SO_2(CF_2)_2SO_2CCH_2Ph$ 14

Benzyl bromide (17 g, 10 mmol) was added dropwise to a 50 mL flask containing a solution of $SO_2(CF_2)_2SO_2CHMgCl$ and THF (30 mL) that was prepared by treatment of $SO_2(CF_2)_2SO_2CHCl$ (2.8 g, 10 mmol) with Mg (0.124 g, 10 mmol) in 30 mL of dry THF at 60°C. After the addition, this reaction mixture was refluxed for 8 hours. The ^{19}F NMR spectrum showed the reaction to be completed. The reaction mixture was poured into ice water (50 mL), and the solid was filtered off and dried, giving the crude product (2.2 g, 71%). Recrystallization from CH$_3$CN/CHCl$_3$ gives pure product.

$SO_2(CF_2)_2SO_2CHCH_2Ph$ 14

IR (v_{max}, cm^{-1}) 2941 (m, CH), 1599, 1495 (m, C$_6$H$_5$), 1377, 1353 (s, SO$_2$), 1202–1135 (s, CF). $\delta_{H,ppm}$ (CDCl$_3$) 7.57 (s, Ph), 4.88 (t, CH), 3.60 (d, J = 8 Hz). $\delta_{F,ppm}$ (CDCl$_3$) − 119.34 (s, CF_2^eS), −117.94 (s, CF_2^aS). MS (m/z, %) 333 (M$^+$H, 4.3), 332 (M$^+$, 24.7), 167 (M$^+$-C$_3$F$_6$SO$_2$-H), 141 (M$^+$-C$_3$F$_6$-CH$_2$C$_6$H$_5$), 103 (M$^+$-C$_3$F$_6$O$_4$S$_2$H, 100.0). Elemental analysis for $C_{10}H_8F_4O_4S_2$: found: C, 36.50; H, 2.63; F, 22.71; calcd: C, 36.14; H, 2.41; F, 22.89.

REFERENCES

[1] Neplynev, V. M.; Bazarova, I. M.; Lozinskii, M. O. Russ Chem Rev (Eng Transl) 1986, 55, 883.
[2] Gramstad, T.; Haszeldine, R. W. J Chem Soc 1957, 4069.
[3] Koshar, R. J.; Mitsch, R. A. J Org Chem 1973, 38, 3358.
[4] Zhu, S. Z.; Pennington, W. T.; DesMarteau, D. D. Inorg Chem 1995, 34, 792.
[5] (a) Singh, S.; DesMarteau, D. D.; Zuberi, S.; Witz, M.; Huang, H. N. J Am Chem Soc 1987, 109, 7194; (b) DesMarteau, D. D.; Witz, M. J. J Fluorine Chem 1991, 52, 7.
[6] Lee, J.; Orrell, K. G. Trans Faraday Soc 1967, 63, 21.
[7] Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. High Resolution NMR Spectroscopy; Pergamon Press: Oxford, UK, 1965, Vol. 2, p 921.
[8] Banks, R. E. Fluorocarbons and Their Derivatives; Oldbourne Press: London, 1964; p 59.