PS-100 spectrometer, and the samples contained Freon-11 and Me_4Si as internal standards.

(1) **(1-Bromo-2,2,2-trifluoroethyl)sulfur Pentafluoride.** In a typical reaction a 10-mL stainless-steel Hoke cylinder was charged with 10 mmol of $SF_5CH{=}CF_2$ and 11.5 mmol of Br_2 and then placed in a 110 °C oven for 24 h. The cylinder was cooled to room temperature and the volatile material condensed onto Hg contained in a 50-mL Pyrex reactor to remove unreacted Br_2. After being shaken for 10 min, the remaining mixture was fractionated by using −45, −80, −95, and −196 °C cold traps. The −45 °C trap was empty, and the −80 and −95 °C traps contained impure product. The −196 °C trap contained 1.5 mmol of a material identified as $FCH(Br)CF_3$. The −80 and −95 °C traps were combined, and final purification accomplished by gas chromatography, yielding 6.17 mmol (61.7%) of $SF_5CH(Br)CF_3$. Anal. Calcd for C_2HBrF_8S: C, 8.31; H, 0.35; F, 52.59; mol wt 289.0. Found: C, 7.81; H, 0.39; F, 52.26; mol wt 287.1.

The vapor pressure curve of $SF_5CH(Br)CF_3$ is represented by the equation $\log P(\text{mm}) = 7.69 - 1671.1/T$, giving a boiling point of 74.0 °C with a $H(\text{vap}) = 7.65$ kcal/mol and a $S(\text{vap}) = 22.0$ eu. The infrared spectrum consists of bands at 3028 (w), 1318 (w), 1262 (s), 1220 (m), 1185 (ms), 1133 (ms), 973 (w), 906 (s), 881 (vs), 799 (ms), 763 (w), 724 (mw), 695 (mw), 671 (m), 610 (m), 575 (mw), 544 (vw), and 534 (w) cm^{-1}. The ^{19}F NMR showed a typical AB_4 spectrum ($J(AB_4) = 142.2$ Hz) for the SF_5 group [$\delta(SF(ax)$ 71.7, δ $(SF_4(eq))$ 61.7], and the CF_3 resonance (δ −69.0) was a quintet ($J(SF_4{-}CF_3) = 12.5$ Hz) of doublets ($J(H{-}CF_3) = 6.5$ Hz). The ^1H NMR contained a complex resonance at 5.52 ppm downfield from Me_4Si.

(2) **(Trifluoroacetyl)sulfur Pentafluoride.** In a typical preparation a 100-mL Pyrex reactor fitted with a Teflon stopcock is charged with 5.0 mmol $SF_5CH(Br)CF_3$ followed by 10.5 mmol $S_2O_6F_2$. The mixture was slowly warmed to room temperature in an empty dewar flask cooled to −196 °C. The volatile materials were removed slowly while holding the reactor at 0 °C to retain FSO_3H and lower volatile bromine fluorosulfates which may have formed. The resulting gaseous mixture was separated by fractional condensation using traps cooled to −95, −118, −128, and −196 °C. The −95 °C trap contained 4.5 mmol of $S_2O_5F_2$ while the −118 and −128 °C traps contained $CF_3C(O)SF_5$ with traces of $S_2O_5F_2$, and the −196 °C trap contained 0.1 mmol of a mixture of $CF_3C(O)F$, SiF_4, and SO_2F_2. Refractionation of the −118 and −128 °C traps through another −95 °C trap resulted in of $CF_3C(O)SF_5$: 4.1 mmol (82% yield); mol wt 226.3, theory 224.1.

The infrared spectrum of $SF_5C(O)CF_3$ has absorptions at 1845 (mw), 1822 (m), 1248 (s), 1210 (s), 985 (w), 880 (vs), 861 (vs), 736 (m), 670 (pqr, w), 612 (m), 570 (w), and 465 (w) cm^{-1}. The gas-phase Raman spectrum contained adsorptions (relative intensity) at 1843.8 (1.2), 1820.5 (1.7), 1247.1 (1.5), 1205.9 (0.2), 1016.6 (1.0), 868.8 (1.8), 857.8 (0.4), 815.0 (1.6), 733.7 (35.3), 666.8 (100), 613.5 (4.9), 597.8 (4.8), 570.3 (6.0), 464.3 (6.0), 398.8 (8.1), 366.0 (5.6) 333.9 (0.2), 266.4 (60.1), and 226.6 (24.1) Δcm^{-1}. The UV spectrum indicates an intense band below 200 nm and a second band from 230 to 340 nm with a $\lambda_{max} = 289$ nm and $\epsilon = 39.7$ mol^{-1} cm^{-1}. The ^{19}F NMR spectrum contains a CF_3 group (δ −71.8) and an SF_5 group [$\delta(SF(ax))$ 61.5, δ $(SF_4(eq))$ 45.4]. The integration of these resonances gave an $SF(ax)/SF_4(eq)/CF_3$ ratio of 1:4.2:3.2. The CF_3 group was coupled to the equatorial sulfur fluorines, giving a quintet ($J = 10.1$ Hz), while the AB_4 pattern for the SF_5 had a $J = 144.5$ Hz.

Chemical analysis of the $CF_3C(O)SF_5$ was accomplished by analysis of the products formed from exhaustive fluorination. Thus, 0.58 mmol of $CF_3C(O)SF_5$ was condensed into a prefluorinated, 10-mL Hoke cylinder followed by 1.46 mmol of F_2. After warming to room temperature, the cylinder was placed in an oven heated to 160 °C for 24 h. The cylinder was cooled to −196 °C and the excess fluorine removed under a static vacuum. The condensed material (1.77 mmol) contained only CF_4, COF_2, and SF_6 as identified from a high-pressure infrared spectrum of the mixture.[9-11] Fractionation of the mixture by using −135, −155, and −196 °C traps resulted in the isolation of $COF_2{-}SF_6$ mixtures (1.2 mmol) in the −155 and −196 °C traps. The CF_4, which pumps through a −196 °C trap under dynamic vacuum, was determined as 0.57 mmol by difference. The mixture of COF_2 and SF_6 was condensed into a 20-mL Pyrex reactor containing 2 mL of a KOH solution. After being shaken for 0.5 h at room temperature, the reactor was cooled to −20 °C, and the volatile gases were transferred into another reactor containing P_2O_5 to remove traces of water vapor. The volatile gas was identified as 0.60 mmol of SF_6 by its infrared spectrum. The COF_2 that reacted with the KOH was determined as 0.60 mmol by difference. The analysis corresponds to the following (numerical values in mmHg):

$$35CF_3C(O)SF_5 + F_2 \text{ (excess)} \rightarrow 34CF_4 + 36COF_2 + 36SF_6 \quad (3)$$

Registry No. 1, 82390-50-9; 2, 82390-51-0; $SF_5CH{=}CF_2$, 58636-78-5; Br_2, 7726-95-6; $S_2O_6F_2$, 13709-32-5.

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(9) Chambers, A. A.; McKean, D. C. *Spectrochim. Acta* **1966**, *22*, 521.

(10) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1973**, *2*, 140.

(11) Classsen, H. H.; Goodman, D. L.; Holloway, J. H.; Selig, H. *J. Chem. Phys.* **1970**, *56*, 341.

Peroxytrifluoroacetic Acid. A Convenient Reagent for the Preparation of Sulfoxides and Sulfones

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In the course of another investigation,[2] we discovered that peroxytrifluoroacetic acid[3] is an especially convenient reagent for the oxidation of sulfides to sulfoxides and sulfones. While it has the chemical selectivity advantages characteristic of other electrophilic oxidants,[5,6] it reacts more rapidly at low temperature than other peroxy acids,[5] and the byproduct carboxylic acid, trifluoroacetic acid (bp 72 °C), is easily removed from the reaction mixture by flash evaporation.

Since a stoichiometric amount of oxidant can be used, in general, no purification of sulfones is necessary. If higher yields of sulfones are desired, excess peroxytrifluoroacetic acid may be employed. For example, the yield of di-*n*-butyl sulfone is 99% when excess peracid is used. However, **caution** must be exercised to assure that all peroxides are destroyed before evaporating trifluoroacetic acid. Peroxytrifluoroacetic acid may be destroyed by the addition of a small amount of platinum on asbestos or platinum on carbon, although complete decomposition of the peroxide may take several hours.

Sulfoxides retain a small amount of trifluoroacetic acid after flash evaporation which can be removed by dissolving the sulfoxide in an organic solvent and washing with 10% $NaHCO_3$. After thorough drying and removal of solvent, no further purification is required.

The use of a strong acid, trifluoroacetic acid, as the solvent allows the selective oxidation of sulfides possessing

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(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This investigation was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining.

(2) Venier, C. G.; Squires, T. G.; Chen, Y.-Y.; Shei, J. C.; Metzler, R. M.; Smith, B. F. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1981**, *26* (1), 20.

(3) Prepared by the mixing of hydrogen peroxide with trifluoroacetic acid.[4]

(4) Emmons, W. D.; Ferris, A. F. *J. Am. Chem. Soc.* **1953**, *75*, 4623.

(5) Drabowicz, J.; Mikolajczyk, M. *Org. Prep. Proced. Int.* **1982**, *14*, 45.

(6) Truce, W. E.; Klinger, T. C.; Brand, W. W. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; Chapter 10.

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Table I. Oxidation of Sulfides to Sulfoxides and Sulfones with Peroxytrifluoroacetic Acid[a]

	sulfoxides (**1b**–**10b**)				sulfones (**1c**–**10c**)			
		mp (bp, mmHg), °C				mp (bp, mmHg), °C		
sulfide	% yield	obsd	lit.	lit. ref[a]	% yield	obsd	lit.	lit. ref[a]
di-*n*-butyl (**1a**)	83	30–33	32–33	IV, **1**, 1561	80[b]	45	44–45	IV, **1**, 1561
di-*n*-octyl (**2a**)	98	68–70	71–72	IV, **1**, 1768	89	74–76	76–77	IV, **1**, 1768
bis(2-ethylhexyl) (**3a**)	81	12–15		‡	88	(130–132 0.05 mm)		‡
diphenyl (**4a**)	80	69–71	71	IV, **6**, 1489	99	123–124	128–130	IV, **6**, 1490
phenyl benzyl (**5a**)	84	122–123	124	IV, **6**, 2646	99	146–147	148–149	IV, **6**, 2647
phenyl phenylethyl (**6a**)	93	(138, 0.05 mm)		‡	96	53–56	56–58	IV, **6**, 3085
benzothiophene (**7a**)					58	141–142[c]	142–143	III/IV, **17**, 485
phenyl allyl (**8a**)	80	(107–110, 0.5 mm)	(103–104, 0.36 mm)	IV, **6**, 1480	77[b]	(122–124, 0.7 mm)	(110–113, 0.5 mm)	IV, **6**, 1480
1,2-bis(2-pyridyl)-3,6-dithiaoctane (**9a**)	89[d]	102–104		‡	81[e]	145 dec		‡
methionine (**10a**)	61	235 dec	240 dec	III, 4, 1650	81	245 dec	250 dec	III, 4, 1650

[a] All references are the edition, volume, and page of *Beilstein*. Compounds marked with a double dagger have not been previously reported. Satisfactory analytical data (±0.4% for C, H, N, S) were reported for all new compounds listed in this table. [b] CF_3CO_2H removed by a water wash of the benzene solution. [c] Recrystallized from methanol. [d] Di-sulfoxide. [e] Disulfone.

amine functionality (**9a** and **10a**). Sulfides having double bonds (**7a** and **8a**) can be oxidized if stoichiometric amounts of the oxidant are used.[7]

Peroxytrifluoroacetic acid is a quick, convenient, and selective reagent for the oxidation of sulfides to either sulfoxides or sulfones.

Experimental Section

Preparation of Sulfoxides from Sulfides. General Procedure. In a 25-mL, three-necked, round-bottomed flask, outfitted with a magnetic stirrer, thermometer, and addition funnel, was placed trifluoroacetic acid (5 mL) and the sulfide (1.5 g). Peroxytrifluoroacetic acid (1 equiv), from a stock solution prepared by mixing 8.6 mL of 30% hydrogen peroxide and trifluoroacetic acid to a final volume of 25 mL to give a 4 M solution of the peracid, was added dropwise to the stirred, cooled (0 °C, ice–salt bath) sulfide mixture. The reaction was kept at 0 °C until the peroxide was discharged (starch–iodide paper) and the starting material was consumed (TLC, silica gel, dichloromethane or chloroform; 15 min to 3 h). Solvent was removed on a rotary evaporator, and the residue was taken up in benzene (30 mL),[8,9] washed with 10% sodium bicarbonate (2 × 10 mL), dried over anhydrous magnesium sulfate, and stripped of solvent to give the sulfoxide in high purity as evidenced by TLC, GC, HPLC, melting point, IR, and/or ^1H NMR. Typical sulfoxide S–O stretches at 1030–1050 cm^{-1} were observed for products **1b**–**6b** and **8b**–**10b**.

Preparation of Sulfones from Sulfides. General Procedure. In a 25-mL, three-necked, round-bottomed flask, outfitted with a magnetic stirrer, thermometer, and addition funnel, were placed trifluoroacetic acid (5 mL) and the sulfide (1.5 g). Peroxytrifluoroacetic acid (2 equiv; prepared as above) was added dropwise to the stirred, cooled (0 °C, ice–salt bath) sulfide mixture. The reaction temperature was raised to 30 °C and maintained until the peroxide was discharged (starch–iodide paper; 30 min to 5 h). Solvent was removed by rotary evaporation, benzene (25 mL) was added, and the solvent was again removed on the evaporator. This procedure was repeated three additional times to completely remove residual trifluoroacetic acid. In most cases[8,9] the product needed no further purification as evidenced by TLC, GC, HPLC, melting point, IR, and/or ^1H NMR. The typical sulfone S–O stretches at 1125–1160 and 1270–1320 cm^{-1} were observed for products **1c**–**10c**.

Registry No. 1a, 544-40-1; **1b**, 2168-93-6; **1c**, 598-04-9; **2a**, 2690-08-6; **2b**, 1986-89-6; **2c**, 7726-20-7; **3a**, 16679-04-2; **3b**, 82374-34-3; **3d**, 82374-35-4; **4a**, 139-66-2; **4b**, 945-51-7; **4c**, 127-63-9; **5a**, 831-91-4; **5b**, 833-82-9; **5c**, 3112-88-7; **6a**, 13865-49-1; **6b**, 34917-41-4; **6c**, 27846-25-9; **7a**, 95-15-8; **7c**, 825-44-5; **8a**, 5296-64-0; **8b**, 19093-37-9; **8c**, 16212-05-8; **9a**, 82374-36-5; **9b**, 82374-37-6; **9c**, 82374-38-7; **10a**, 63-68-3; **10b**, 3226-65-1; **10c**, 7314-32-1; peroxytrifluoroacetic acid, 359-48-8; trifluoroacetic acid, 76-05-1.

Supplementary Material Available: Table II listing infrared S–O bond stretching frequencies and ^1H NMR resonances for **1b**–**6b**, **8b**–**10b**, and **1c**–**10c** (1 page). Ordering information is given on any current masthead page.

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(7) Durst, T. In "Comprehensive Organic Chemistry"; Jones, D. N., Ed.; Pergamon Press: New York, 1979; Chapter 11.7.

(8) Compounds **9b** and **9c**, which are present as their trifluoroacetate salts, were dissolved in chloroform, washed with 5% sodium hydroxide to liberate the free amines, and then reisolated.

(9) Methionine sulfoxide (**10b**) and methionine sulfone (**10c**) were precipitated from water by the addition of acetonitrile.

Kinetics and Mechanism of the Reaction of Carbon Disulfide with Piperidine in Ethanol

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Introduction

During the study of the aminolysis reactions of bis(ethoxythiocarbonyl) sulfide and other related compounds in ethanolic media, it was found that carbon disulfide (one of the products of the reactions) and the substrate could compete in their reactions toward the amine. In order to obtain the overall scheme, it was thought necessary to study in detail the mechanism of the reactions of carbon disulfide with amines in ethanol.

The reverse reaction of carbon disulfide with amines, i.e., decomposition of dithiocarbamates (eq 1) has been

$$CS_2 + R^1R^2NH \rightleftharpoons R^1R^2NCS_2^- + H^+ \qquad (1)$$

subject to study by several authors.[1–4] Nevertheless, the

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(1) D. M. Miller and R. A. Latimer, *Can. J. Chem.*, **40**, 246 (1962).

(2) S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *Anal. Chem.*, **41**, 1441 (1969).

(3) S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *J. Phys. Chem.*, **74**, 860 (1970).