1,3-dioxan-5-ylhydrazono)-2,2-dimethyl-1,3-dioxane-4,6-dione. Samples of the compound prepared by our method decomposed with gas evolution at various temperatures 10–25 °C above the reported melting point of 143 °C dec.[26] The IR spectrum was identical with that reported.

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Registry No. 1a, 82430-99-7; **1b**, 82431-00-3; **1c**, 82431-01-4; **2a**, 82431-67-2; **2b**, 82431-68-3; **2c**, 82431-69-4; **3a**, 82431-02-5; **3b**, 82431-03-6; **3c**, 82431-04-7; **3d**, 82431-05-8; **3e**, 82431-06-9; **3f**, 82431-07-0; **4a**, 21315-43-5; **4b**, 82431-08-1; **4c**, 52600-63-2; 4-(diethylamino)-2-butanone, 3299-38-5; [(dimethylamino)methyl]ferrocene, 1271-86-9; 1-[(dimethylamino)methyl]-2-naphthol, 5419-02-3; gramine, 87-52-5; *N*-methylgramine, 52972-61-9; isopropylidene methylmalonate, 3709-18-0; isopropylidene ethylmalonate, 17216-65-8; isopropylidene phenylmalonate, 15231-78-4; isopropylidene benzylmalonate, 3709-27-1; isopropylidene acetamidomalonate, 7270-66-8; isopropylidene benzylidenemalonate, 1214-54-6; α-methyl-δ-oxocaproic acid, 54248-02-1; α-methyl-δ-oxocaproic acid semicarbazone, 82431-09-2; α-ethyl-δ-oxocaproic acid, 58045-80-0; α-ethyl-δ-oxocaproic acid semicarbazone, 82431-10-5; α-phenyl-δ-oxocaproic acid, 5662-73-7; isopropylidene phenylmalonate diethylammonium, 82431-11-6; β-ferrocenyl-α-methylpropionic acid, 12093-96-8; β-ferracenyl-α-ethylpropionic acid, 36619-43-9; β-ferracenyl-α-phenylpropionic acid, 1272-82-8; 3-(ethoxymethyl)indole, 78440-77-4; 3-(piperidinomethyl)indole, 5355-42-0; *N*-acetyltryptophan, 1218-34-4; benzyl[(*N*-methylindol-3-yl)methyl]malonic acid, 82431-12-7; isopropylidene phenyldiazomalonate, 82431-13-8.

(Trifluoroacetyl)sulfur Pentafluoride

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The synthesis of $SF_5C(O)$ derivatives has resulted in only one compound, $SF_5C(O)F$, reported[1] as a product from the photolysis of S_2F_{10} and $FC(O)C(O)F$. Our efforts in the synthesis of SF_5 derivatives has centered on developing potential precursors to $SF_5C(O)$ derivatives. We report herein a successful attempt to prepare these derivatives by proceeding through an intermediate, $SF_5CH(Br)CF_3$, isolated from the reaction of Br_2 with a previously reported[2] olefin, $SF_5CH{=}CF_2$. This olefin resists the addition of SF_5Cl or SF_5Br, and the photolytic addition of Br_2 leads to extensive cleavage of the SF_5 group, giving S_2F_{10}. However, the thermal reaction, which results in less cleavage, was found to give BrF addition rather than Br_2 addition (eq 1). The reaction is undirectional and consistently resulted in 55–60% yields of the BrF addition product when repeated in the same cylinder.

$$SF_5CH{=}CF_2 + Br_2 \xrightarrow{110\ ^\circ C} SF_5CH(Br)CF_3 + FCH(Br)CF_3 \quad (1)$$

(Trifluoroacetyl)sulfur pentafluoride can be obtained in high yield through the reaction of $SF_5CH(Br)CF_3$ with a slight excess of bis(fluorosulfuryl) peroxide ($S_2O_6F_2$, over a 1:2 ratio; eq 2). The low-volatility product FSO_3H, reported as a product in $S_2O_6F_2$ hydrogen abstraction reactions,[3-5] was not monitored, and the identification of bromine or bromine fluorosulfates was precluded by the workup procedure. The $SF_5C(O)CF_3$ is a low-melting (−112 to −111 °C) white solid, giving a colorless liquid having a boiling point of 15.6 °C and a vapor pressure curve of log $P(\mathrm{mm}) = 7.698 - 1391.1/T$. The heat of vaporization for $SF_5C(O)CF_3$ is 6.37 kcal/mol and the Trouton constant of 22.0 eu indicates that no appreciable intermolecular association is present. In comparison to $CF_3C(O)CF_3$, having a boiling point of −27.4 °C, the boiling point of $SF_5C(O)CF_3$ appears to be abnormally high. However, this variation is consistent when compared to $CF_3C(O)F$ (bp −59 °C) and $SF_5C(O)F$ (estimated[1] bp −10 °C).

$$SF_5CH(Br)CF_3 + S_2O_6F_2 \rightarrow SF_5C(O)CF_3 + S_2O_5F_2 \quad (2)$$

Vorob'ev and co-workers[6] proposed $SF_5C(O)CF_3$ as an intermediate from the reaction of $CsSF_5$ and $CF_3C(O)Cl$ although only $CF_3C(O)F$ and SF_4 were isolated. We have found that $SF_5C(O)CF_3$ is a stable compound and does not decompose at room temperature in dry Pyrex glass during a 24-h period. Trace amounts of moisture cause extensive hydrolysis to $CF_3C(O)F$, SOF_2, and SiF_4, which is comparable to the hydrolytic sensitivity reported[1] for $SF_5C(O)F$. Thermal decomposition to $CF_3C(O)F$ and SF_4 is evident at 80 °C in dry Pyrex, but approximately 35% of the material was recovered after 16 h. The decomposition at 23 °C in prefluorinated stainless-steel vessels was much more rapid (65% after 1 h), while KF caused essentially complete decomposition in Pyrex glass vessels on warming a sample from −196 °C to room temperature.

The preparation of $SF_5C(O)CF_3$ with other oxidizing agents has been unsuccessful. We have found that $SF_5CH(Br)CF_3$ is resistant to oxidation by aqueous acidified permanganate (100 °C, 1 h), permanganate–acetone (23 °C, 24 h; 100 °C, 1 h), $m\text{-}ClC_6H_4CO_3H$ (23 °C, 48 h), NBS–aqueous diglyme (23 °C, 3 h), and 50% H_2O_2 (23 °C, 4 h; 95 °C, 16 h). In each case the $SF_5CH(Br)CF_3$ was quantitatively recovered and in most cases with decomposition of the oxidizing agent.

The synthesis of $SF_5C(O)CF_3$ allows a direct comparison of the chemistry of SF_5 carbonyl compounds with the synthetically useful $CF_3C(O)CF_3$. Our initial screening reactions indicate that typical addition reactions to the carbonyl function result in cleavage of the SF_5 group and subsequent formation of a $CF_3C(O)$ product. The reaction of HCN with $SF_5C(O)CF_3$, both with and without base, resulted in decomposition of the ketone, giving $CF_3C(O)F$, SF_4, SOF_2, and SiF_4. Attempts to add Me_2NH gave $CF_3C(O)NMe_2$, while CH_3OH led to the isolation of $CF_3CO_2CH_3$.

Experimental Section

Bis(fluorosulfuryl) peroxide ($S_2O_6F_2$)[7] and $SF_5CH{=}CF_2$[2] were prepared by the literature method, and Br_2 (J. T. Baker) and F_2 (Matheson Gas Products) were used as received. Gases and volatile liquids were handled in conventional Pyrex glass or stainless-steel vacuum lines, and quantities were determined by PVT measurements. Infrared spectra were taken on a Perkin-Elmer Model 567 and a Beckman Model IR 12 spectrometer. The Raman spectrum was recorded on a Jarrell-Ash Model 500 laser Raman spectrometer, and the UV spectrum was taken on a Cary 118 spectrometer. The NMR spectra[8] were taken on a JEOL

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(1) Czerepinski, R.; Cady, G. H. *J. Am. Chem. Soc.* **1968**, *90*, 3954.

(2) De Marco, R. A.; Fox, W. B. *J. Fluorine Chem.* **1978**, *12*, 137.

(3) Kierchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 2886.

(4) Krespan, C. G. *J. Fluorine Chem.* **1972**, *2*, 173.

(5) Merrill, C. I. 6th International Symposium on Fluorine Chemistry, Durham, England, July 1971.

(6) Vorob'ev, M. D.; Filatov, A. S.; Englin, M. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1973**, *43*, 2371.

(7) Shreeve, J. M.; Cady, G. S. *Inorg. Synth.* **1963**, *1*, 124.

(8) NMR chemical shifts follow the IUPAC convention of positive values being downfield and negative values being upfield from the standard.

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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 $\log P(\mathrm{mm}) = 7.69 - 1671.1/T$, giving a boiling point of 74.0 °C with a $H(\mathrm{vap}) = 7.65$ kcal/mol and a $S(\mathrm{vap}) = 22.0$ 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] Claassen, 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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[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.