Table I
Powder Spectra for $NOSO_3CF_3$[a]
d Spacings from Lines in X-ray Powder Photograph

Sample prepared by—							
Method I		Method II		Method I		Method II	
d, A	Intens	*d*, A	Intens	*d*, A	Intens	*d*, A	Intens
		5.74	L			3.12	L
5.59	L	5.52	L			3.06	L
5.25	H	5.20	H	3.08	M	3.01	M
		5.05	L	2.97	L	2.97	L
		4.85	L			2.93	L
4.58	H	4.55	H	2.87	L	2.90	L
		4.25	L			2.76	L
4.19	M	4.19	M			2.70	L
3.84	H	3.84	H			2.66	L
		3.80	H			2.62	L
		3.67	L			2.58	L
3.61	L	3.64	L			2.51	L
		3.56	L			2.49	L
3.48	L	3.47	L			2.45	L
		3.40	L			2.44	L
3.34	L	3.35	L			2.41	L

[a] H, high; M, medium; L, low.

Model E 612 Raman spectrograph equipped with E 613 and E 614 cameras. A Toronto arc was used for excitation and spectra were recorded on Kodak spectroscopic plates, Type 11a-o. A solid sample of $NOSO_3CF_3$ gave a spectrum of four lines (cm^{-1}): 2230 s, 1224 b, 982 m, and 715 w. The most intense line (2230 cm^{-1}) was due to nitrosyl stretching and was in the range expected for a high degree of ionic character (NO^-) for the nitrosyl group.[9]

Trichloro(trifluoromethanesulfonato)titanium(IV).—In one experiment excess $TiCl_4$ (2.2809 g, 12.00 mmoles) was added to CF_3SO_3H (0.8597 g, 5.73 mmoles) contained in the 30-cc Pyrex glass reactor described previously. The vessel was allowed to warm from −183 to 25° whereupon a reaction took place with the evolution of a gas later shown to be HCl by infrared analysis. The only other volatile substance present was $TiCl_4$. On the basis of the original weight of CF_3SO_3H, the weight of the product corresponded closely to that expected for production of $TiCl_3(SO_3CF_3)$. Similar results were observed in two experiments: calcd wt of product if $TiCl_3(SO_3CF_3)$, 1.7372, and 1.7024 g; found, 1.7400 and 1.7000 g.

Dichlorobis(trifluoromethanesulfonato)titanium(IV).—Excess CF_3SO_3H (1.2355 g, 8.23 mmoles) was added to $TiCl_4$ (0.1730 g, 0.91 mmole) in the same manner as described above. A reaction took place on warming the vessel from −183 to 25° with the evolution of HCl. The reactants were stirred together overnight at 25°, and the product was then pumped to constant weight; calcd wt of product if $TiCl_2(SO_3CF_3)_2$, 0.3802 g; found, 0.3824 g.

Thermal Decomposition.—When a 1.6612-g sample of $TiCl_3(SO_3CF_3)$ was heated under vacuum, it began to evolve $TiCl_4$ when its temperature reached about 60°. The sample was held at 76° for 8 hr while pumping to constant weight. The $TiCl_4$ was collected in a trap held at −183° and later identified by its melting point. A pure sample of $TiCl_4$ and the unknown both melted near −23°. Apparently the decomposition followed the equation

$$2TiCl_3(SO_3CF_3) = TiCl_4 + TiCl_2(SO_3CF_3)_2$$

(calcd wt of product if $TiCl_2(SO_3CF_3)_2$, 1.1406 g; found, 1.1428).

Analysis.—Both $TiCl_3(SO_3CF_3)$ and $TiCl_2(SO_3CF_3)_2$ are lemon-yellow, very hygroscopic compounds. Analysis for titanium and chlorine was accomplished by conventional wet methods. In each case the compound was hydrolyzed with water in an evacuated bulb and washed into a beaker with 2 *N* HNO_3. NH_4OH (15 *M*) was then added to precipitate the hydrous oxide of titanium, and the solution was boiled to expel ammonia. The precipitate was separated by filtration, ignited, and weighed as TiO_2. The filtrate was diluted to the mark in a volumetric flask and after acidification, chloride was determined on aliquots of this solution by the Volhard method. *Anal.* Calcd for $TiCl_3(SO_3CF_3)$: Ti, 15.79; Cl, 35.08. Found: Ti, 16.1; Cl, 35.0. Calcd for $TiCl_2(SO_3CF_3)_2$: Ti, 11.49; Cl, 17.01. Found: Ti, 11.7; Cl, 16.8.

Melting Point.—A sample of $TiCl_2(SO_3CF_3)_2$ turned to a dark orange liquid containing bubbles in the vicinity of 222°.

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[9] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

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Reactions of Bromine(I) Fluorosulfate with Simple Inorganic Molecules and Polyfluoroolefins. A Novel Route to Perfluoro-2,3-butanedione

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Bromine fluorosulfate acts as a fluorosulfating agent with sulfur dioxide to give trisulfuryl fluoride, $S_3O_8F_2$. With phosphorus trifluoride, it is an oxygenating agent to give phosphoryl fluoride. Addition across double bonds of polyfluoroolefins occurs essentially quantitatively. The preparations of the compounds 2-bromo-3-fluorosulfatooctafluorobutane, 3-bromoheptafluoro-2-butanone, and 3-fluorosulfatoheptafluoro-2-butanone as intermediates in the synthesis of the diketone perfluoro-2,3-butanedione are discussed.

Bromine(I) fluorosulfate[1] is an easily prepared, high-boiling liquid which is stable in Pyrex under anhydrous conditions for several months. Gilbreath and Cady[2] have examined the reactions of $BrOSO_2F$ with C_2F_4 and

[1] J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 352 (1960).

[2] W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2**, 496 (1963).

SF_4. In comparing these reactions with those of $FOSO_2F$ with the same compounds, it was seen both fluorosulfates add across the double bond in tetrafluoroethylene to give perfluoroethyl fluorosulfate and 2-bromotetrafluoroethyl fluorosulfate, respectively. However, analogous reactions are not obtained with SF_4. Fluorine fluorosulfate unpairs the unshared electron pair on the sulfur to give pentafluorosulfur fluorosulfate in 25% yield at 70°, while bromine fluorosulfate at 80° gives only SO_2F_2, $S_2O_5F_2$, SF_6, and Br_2 and none of the addition compound.

Successful addition of bromine fluorosulfate across olefinic double bonds coupled with the defluorosulfurylation process developed by Lustig and Ruff[3] suggests a synthesis which should be of general applicability to vicinal perfluorodiketones. These workers synthesized the acid fluoride, $CF_3CF(OSO_2F)C(O)F$, by the reaction of $CF_3CF(OSO_2F)CF_2(OSO_2F)$ with KF at 60° for 16 hr. They report the preparation of several other carbonyl compounds with adjacent fluorosulfate groups by analogous reactions and the unsuccessful conversion of these to the corresponding dicarbonyl compounds by a second defluorosulfurylation in the presence of KF or a stronger Lewis base such as cesium fluoride. Only degradation products such as fluorocarbons, carbon dioxide, carbon monoxide, and oxygen and nearly quantitative yields of sulfuryl fluoride were obtained.

In the present work, in an attempt to obtain a sulfuryl derivative analogous to that obtained by the addition of $S_2O_6F_2$ to SO_2 to give $S_3O_8F_2$, $BrOSO_2F$ was allowed to react with SO_2. Simple addition does not occur, but essentially stoichiometric amounts of $S_3O_8F_2$ and bromine are obtained. However, with PF_3 oxygenation occurs to give OPF_3 and $S_2O_5F_2$.

While addition of bromine fluorosulfate to vinyl fluoride gives an unstable, colorless, volatile liquid, chlorotrifluoroethene or *cis,trans*-perfluoro-2-butene reacts readily and essentially stoichiometrically to give stable liquids. The unsymmetric chloroolefin apparently yields both addition isomers which were not successfully separated. *cis,trans*-Perfluoro-2-butene gives 2-bromo-3-fluorosulfatooctafluorobutane which can be subsequently defluorosulfurylated.[3] Reaction of the resulting bromoketone with peroxodisulfuryl difluoride gives rise to a fluorosulfatoketone[4] which is then defluorosulfurylated to produce a vicinal perfluorodiketone, perfluoro-2,3-butanedione. The reaction scheme is summarized in the four reactions

$$BrOSO_2F + CF_3CF{=}CFCF_3 \longrightarrow CF_3CFBrCF(OSO_2F)CF_3 \quad (1)$$

$$CF_3CFBrCF(OSO_2F)CF_3 \xrightarrow[70°,\ 12\ hr]{CsF} CF_3CFBrCOCF_3 + SO_2F_2 \quad (2)$$

$$CF_3CFBrCOCF_3 + S_2O_6F_2 \longrightarrow CF_3CF(OSO_2F)COCF_3 + BrOSO_2F \quad (3)$$

$$CF_3CF(OSO_2F)COCF_3 \xrightarrow[70°,\ 18\ hr]{CsF} CF_3COCOCF_3 + SO_2F_2 \quad (4)$$

Experimental Section

Reagents.—Bromine fluorosulfate was prepared by the method of Roberts and Cady.[1] *cis,trans*-Perfluoro-2-butene and chlorotrifluoroethene were obtained from the Matheson Co., Inc., and phosphorus trifluoride, from K & K Laboratories, Inc. All other materials were of reagent grade.

General Methods.—Infrared spectra were obtained using either a Perkin-Elmer 137 Infracord or a Beckman IR5A infrared spectrophotometer. All were gas phase contained in a 50-mm Pyrex cell with sodium chloride windows. A Varian Model 4311B high-resolution nuclear magnetic resonance spectrometer was used to determine the nmr spectra at 40 Mc. Mass spectra were recorded using a Consolidated Engineering Corp. Type 21-103 mass spectrometer. Regnault's method was used to obtain vapor density. Liquid density was obtained from a single-capillary pycnometer. The method of Kellogg and Cady[5] was used for vapor pressure measurements. Because of the hygroscopic properties of $BrOSO_2F$, all reactions were carried out under vacuum conditions.

In general, the reactions were initiated by the slow addition of the volatile reactant to the bromine fluorosulfate at room temperature and addition was continued until the color of the $BrOSO_2F$ had disappeared, leaving a clear, colorless liquid in the 150-ml Pyrex reaction vessel.

The reaction products were separated using fractional codistillation and/or gas chromatography as will be indicated later.

Reaction with SO_2.—A slight excess of SO_2 was slowly added to a vessel containing a few tenths of a milliliter of $BrOSO_2F$. An increase of pressure was observed, and the color of the $BrOSO_2F$ gave way to a red-brown vapor and liquid bromine. An infrared spectrum of the gas in the bulb indicated only the presence of trisulfuryl fluoride. The red-brown gas condensed to a red and yellow solid at −183°. The reaction which occurs is

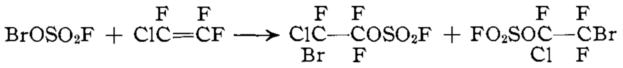
$$SO_2 + 2BrOSO_2F \longrightarrow S_3O_8F_2 + Br_2$$

Reaction with PF_3.—Upon addition of a slight excess of PF_3 to a few tenths of a milliliter of $BrOSO_2F$, the pressure slowly rose and a red-brown gas filled the bulb. From infrared spectra, the products of the reaction were identified as OPF_3 and $S_2O_5F_2$ formed according to the reaction

$$PF_3 + 2BrOSO_2F \longrightarrow OPF_3 + Br_2 + S_2O_5F_2$$

Reaction with Vinyl Fluoride.—Vinyl fluoride and bromine fluorosulfate readily combine on contact to give a colorless, volatile liquid. Although the experimental molecular weight was in good agreement with that calculated for the addition compound, the liquid gradually darkened on standing. The compound could be distilled from the apparent decomposition products, but, on standing again at room temperature, the darkening process was repeated. A similar darkening effect was observed when the product of the reaction of $S_2O_6F_2$ and vinyl fluoride was allowed to stand at ambient temperature.[6]

Reaction with Chlorotrifluoroethene.—Chlorotrifluoreoethene was slowly added to $BrOSO_2F$ to form a clear, colorless liquid. Purification was effected by trap-to-trap distillation and by fractional codistillation using a granular magnesium column. A single peak was obtained and it was assumed that one isomer had preferentially been formed. However, analysis of the mass spectrum of this material indicated that the two possible addition isomers were present



$$BrOSO_2F + Cl\overset{F}{C}{=}\overset{F}{C}F \longrightarrow Cl\underset{Br}{\overset{F}{C}}{-}\underset{F}{\overset{F}{C}}OSO_2F + FO_2SO\underset{Cl}{\overset{F}{C}}{-}\underset{F}{\overset{F}{C}}Br$$

Separation of these isomers was attempted using a column of silicone SF-96 (Wilkens Instrument and Research, Inc.) on firebrick in an Aerograph Model A90P gas chromatograph. Three compounds were indicated in the mixture. The first,

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(3) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **3**, 287 (1964).

(4) J. J. Delfino and J. M. Shreeve, *ibid.*, **5**, 308 (1966).

(5) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3086 (1948).

(6) C. T. Ratcliffe and J. M. Shreeve, *Inorg. Chem.*, **3**, 631 (1964).

present in very small amounts, was not identified. Mass spectra of the second and third materials showed that the separation had not been successful and that both fractions were isomeric mixtures. No other separation was attempted. There was little difference in the infrared spectra of the two fractions. Molecular weight determinations gave 296 ± 2 compared to 296 as the calculated value. It can be concluded that nonspecific addition occurs across the double bond. The nmr spectra are complex but indicate at least two slightly chemically different sulfur–fluorine resonances at -50.4 and at -50.6 ppm (relative to CCl_3F). In the carbon–fluorine region, the spectrum is complex and indicates considerable overlap.

Reaction with *cis,trans*-Perfluoro-2-butene.—This reaction (1) goes very smoothly at ambient temperature although considerable heat is generated at the liquid–gas interface. The compound may be purified by prolonged pumping at $-20°$ to remove perfluorobutene which is apparently very soluble in the reaction product. Final purification was obtained by fractional codistillation.

Properties of 2-Bromo-3-fluorosulfatooctafluorobutane.—The experimental molecular weight was 379 ± 5; that calculated for $C_4F_8BrOSO_2F$ is 379. The density was obtained at several temperatures with an interpolated value at 25° of 2.036 g/ml. An equation, $d_{g/ml} = 2.094 - 0.0023t$, defines the density over the temperature range of 1.4–34.2°. Since the compound forms a glass, it was not possible to determine its melting point. The vapor pressure was measured over the temperature range 313–372°. A boiling point of 375 ± 1°K is obtained from a Clausius–Clapeyron plot of the data. The heat of vaporization is 10.4 kcal/mole. *Anal.* Calcd for $C_4F_8BrOSO_2F$: S, 8.45; C, 12.68. Found: S, 8.80; C, 12.78. The infrared spectrum, taken at 15 mm pressure, consists of bands at 1500 (s) (S–O), 1250 (vs) (S–O, C–F), 1195 (m), 1137 (w), 1110 (s), 1059–1041 (m) (doublet), 949–940 (m) (doublet), 902 (w) (S–F), 884 (s), 746 (w), and 722 (m) cm^{-1}. At an ionizing potential of 70 v, the most prominent species in the mass spectrum with their relative abundances include: CF_3^+, 69, 100; $C_2F_3^+$, $^{81}Br^+$, 81, 7.9; $^{79}Br^+$, 79, 6.6; $C_2F_3{}^{79}Br^+$, 160, 4.6; $C_3F_5^+$, 131, 4.4; $C_3F_3^+$, $C^{81}Br^+$, 93, 4.1; $C_2F_3{}^{81}Br^+$, $C_4F_6^+$, 162, 4.1; $C_3F_2^+$, 74, 4.1; SO_2F^+, 83, 3.1; $C_4F_8{}^{79}Br^+$, 279, 2.7; $C_4F_8{}^{81}Br^+$, 281, 2.6; $C_2F_4{}^{81}Br^+$, 181, 2.3; $C_2F_2^+$, 62, 2.2; SO_2^+, 64, 2.0. Peaks also present in very small abundance include: $C_4F_8{}^{81}BrSO_3^+$, 361; $C_4F_8{}^{79}Br(SO_3)^+$, 359; $C_3F_6{}^{81}BrSO_3^+$, 311; and $C_3F_6{}^{79}BrSO_3^+$, 309.

With trichlorofluoromethane as the internal reference, the nuclear magnetic resonance spectrum consisted of a singlet sulfur–fluorine resonance at -50.7 ppm, a carbon–fluorine resonance of the CF_3 groups at 75.5 ppm, and carbon–fluorine resonances of the methylene groups at 127 and 139 ppm. The spectrum attributed to carbon–fluorine resonances is very complex.

Preparation of 3-Bromoheptafluoro-2-butanone.—Reaction 2 is exactly analogous to the one carried out by Lustig and Ruff.[3] It proceeds quantitatively at 70° in 12 hr. Purification was achieved by retaining the product mixture in a $-96°$ cold trap and by pumping the SO_2F_2 into a $-183°$ cold trap. No further purification was found to be necessary. *Anal.* Calcd for C_4F_7BrO: F, 48.0; C, 17.3; Br, 28.8. Found: F, 46.4; C, 16.5; Br, 26.2. The average molecular weight is 279 compared to a calculated value of 277.

The infrared spectrum consists of strong bands at 1282, 1240, 1210, and 1190 (C–F) cm^{-1} and moderate bands at 1789 (C=O), 1147, 908, 842, 709, and 690 cm^{-1}. Analysis of the nuclear magnetic resonance spectrum (CCl_3F internal standard) assigns a doublet at 84.7 ppm to the CF_3 adjacent to the secondary fluorine ($J = 16.4$ cps), a doublet at 89.1 ppm to the CF_3 removed from the secondary fluorine ($J = 8.8$ cps), and a complex resonance at 153 ppm to $\gg$CF. The assignments of the CF_3 resonances were made on the basis of the relative magnitudes of the coupling constants.

Preparation of 3-Fluorosulfatoheptafluoro-2-butanone.—Reaction 3 was run in a 1-l. Pyrex vessel by adding peroxodisulfuryl difluoride to, say, 30 mm of 3-bromoheptafluoro-2-butanone until the former was present in excess. Sufficient $S_2O_6F_2$ was added to convert the bromine produced to the less volatile bromine(I) fluorosulfate in an attempt to increase the ease of product separation. The product mixture was separated by fractional codistillation but it was not possible to free the 3-fluorosulfatoheptafluoro-2-butanone from unreacted starting material. Separation was also attempted without success, using a 20-ft, 0.25-in. column consisting of Kel-F No. 90 on Chromosorb-P. Therefore, the impure 3-fluorosulfatoheptafluoro-2-butanone was used in reaction 4.

Preparation of Perfluoro-2,3-butanedione.—Reaction 4 was carried out in a 50-ml Pyrex vessel equipped with a Teflon needle-valve stopcock. To a few grams of anhydrous cesium fluoride was added 120–200 mm of the impure compound. A reaction time of 16 hr was found to be sufficient to achieve all possible conversion as indicated by no change in the infrared spectrum of the reaction mixture. The products were separated by fractional codistillation and, in this manner, perfluoro-2,3-butanedione was obtained pure. It is difficult to estimate the yield since the starting material was highly impure, but from comparison of infrared spectra the conversion to the diketone appears to be about 90%. There was no 3-fluorosulfatoheptafluoro-2-butanone present in the products; however, carbonyl fluoride, a decomposition product, is formed which tends to detract from the possibility of quantitative yield.

The perfluoro-2,3-butanedione was identified by comparison of the infrared spectrum with that reported in the literature.[7] Molecular weight determination gives a value of 192 compared with a calculated value of 196.

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[7] L. O. Moore and J. W. Clark, *J. Org. Chem.*, **30**, 2472 (1965).