2 refer to the scrambling of a sulfur and an oxygen atom on a dimethylgermanium group. The equilibrium constants, $K = [(CH_3)_2Ge(S\text{-})_2][(CH_3)_2Ge(O\text{-})_2]/[(CH_3)_2Ge(O\text{-})(S\text{-})]^2$, calculated on the basis of such scrambling are 0.87 ± 0.05 for eq 1 and 0.59 ± 0.03 for eq 2 at 120°. These may be compared with the scrambling[10] of methoxyl and methylthio groups on the dimethylgermanium moiety in terms of the deviation of the free energy from the random value. For the latter case, this deviation corresponds to +0.9 kcal, whereas for the equilibrium constants of 0.87 and 0.59 the respective values are +0.5 and +0.3 kcal. The sign of the deviation is the same in all three cases and the size is not much different.

In the three cases (ref 5 and 6 and the data reported here) where equilibrium constants have been obtained for the stepwise substitution of a bridging moiety in hexatomic rings, the equilibrium constants of the general type of eq 4 and 5 are close to random, and an argument (such as the one given in the preceding paragraph) which ignores cyclization can be used for accounting for the deviations from randomness. At first glance, one would expect the wide range of observed values of the ring–chain[13] equilibrium constants for hexatomic rings would lead to correspondingly large deviations from randomness in the scrambling of bridging atoms in this sized ring. This apparent problem is resolved by requiring that there be a linear change, with increasing substitution of one bridging group by another, in the free energy (exclusive of the entropy contribution due to simple scrambling) of formation of the rings.

A statistical-mechanical study[13] has shown that the primary contribution to the differences between the ring–chain constants is the torsional freedom within the rings. Likewise, the torsional freedom must also play a key role in establishing the values of the equilibrium constants of the type of eq 4 and 5 of this paper. This means that the stepwise replacement of pairs of adjacent bonds by either weaker or stronger bonds must lead to a nearly fixed incremental change in the over-all torsional energy of the ring in order to have these equilibrium constants be approximately random. Presumably such behavior results from the strong coupling of the torsional vibrations within any hexatomic ring.

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Derivatives of Bis(trifluoromethyl)ketene Which Contain Fluorosulfato, Difluoramino, Fluorimino, and/or Fluoroxy Groups

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Abstract: Addition reactions across the carbon–carbon double bond in bis(trifluoromethyl)ketene with peroxodisulfuryl difluoride, tetrafluorohydrazine, difluoraminofluorosulfate, and fluorine fluorosulfate yield $(CF_3)_2C(OSO_2F)C(O)OSO_2F$, $(CF_3)_2C(NF_2)CFO$, $(CF_3)_2C(NF_2)C(O)OSO_2F$, $(CF_3)_2C(OSO_2F)CFO$, and $(CF_3)_2CFC(O)OSO_2F$, respectively. While in the presence of CsF only, $(CF_3)_2C(NF_2)CFO$ is converted to $(CF_3)_2C{=}NF$. With CsF and F_2, the former and $(CF_3)_2C{=}C{=}O$ give rise to $(CF_3)_2C(NF_2)CF_2OF$ and $(CF_3)_2CFCF_2OF$, respectively. These new compounds have been characterized and structures confirmed by nmr, mass, and infrared spectra.

Numerous investigations dealing with the interaction of bis(trifluoromethyl)ketene ($(CF_3)_2C{=}C{=}O$) and organic materials have been reported; *e.g.*, cycloaddition to both the C=C and C=O groups occurs with vinyl benzoate at 100°, and simple alkenes also add to form cyclobutanones and linear adducts.[1] Knunyants and coworkers have published extensively on the reaction chemistry of $(CF_3)_2C{=}C{=}O$.[2–11] However, the reactions of $(CF_3)_2C{=}C{=}O$ with typical inorganic fluorine-containing free-radical sources had not been

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Table I

Compound	Reaction conditions	Mol wt	Anal, %
$(CF_3)_2C(OSO_2F)C(O)OSO_2F$	$(CF_3)_2C{=}C{=}O + S_2O_6F_2$, 25°	376 ± 8 (376)[a]	S, 16.84 (17.02); F, 38.92 (40.42)
$(CF_3)_2C(NF_2)CFO$	$(CF_3)_2C{=}C{=}O + N_2F_4$, 20°, uv	248.2 (249)	F, 69.01 (68.71)
$(CF_3)_2C(NF_2)C(O)OSO_2F$	$(CF_3)_2C{=}C{=}O + NF_2OSO_2F$, 95°	326.4 (329)	S, 9.53 (9.72); F, 51.97 (51.98); C, 14.88 (14.59); N, 4.58 (4.25)
$(CF_3)_2C(OSO_2F)CFO$	$(CF_3)_2C{=}C{=}O + FOSO_2F$, −25°	296 (296)	
$(CF_3)_2CFC(O)OSO_2F$	$(CF_3)_2C{=}C{=}O + FOSO_2F$, −25°		
$(CF_3)_2C{=}NF$ (0.23 mmole)	$(CF_3)_2C(NF_2)CFO$ (0.25 mmole) + $CsF + F_2$ (0 mmole), 25°	182.8 (193)	
$(CF_3)_2C(NF_2)CF_2OF$ (0.248 mmole)	$(CF_3)_2C(NF_2)CFO$ (0.25 mmole) + $CsF + F_2$ (1.9 mmoles), −78 to −20°	285.1 (287)	Ox. equiv, 1.87 (2.0)
$(CF_3)_2CFCF_2OF$ (2.84 mmoles)	$(CF_3)_2C{=}C{=}O$ (3 mmoles) + $CsF + F_2$ (13.5 mmoles), −78 to −15°	248 (254)	Ox. equiv, 1.89 (2.0)

[a] Numbers in parentheses are calculated values.

examined. Subsequent fluorination of these addition compounds could lead to new fluoroxy molecules.

Compounds similar to some of those discussed in this paper were reported by Lustig, Ruff, and coworkers while this work was underway.[12–15] Addition of NF_2OSO_2F to perfluoroalkene double bonds, *e.g.*, C_2F_4, C_3F_6, followed by defluorosulfurylation, gives 2-difluoroaminoacyl fluorides ($CF_2(NF_2)CFO$, $CF_3CF(NF_2)CFO$). The latter are readily converted *via* CsF-catalyzed fluorination to fluoroxydifluoraminoalkanes.[14,15] Ruff reported a general method for the preparation of 2-haloiminoperfluoropropanes ($(CF_3)_2C{=}NX$) by the catalytic halogenation of $(CF_3)_2C{=}NH$.[13] The highest yield (70%) of the fluorimine was obtained in the presence of potassium fluoride and equimolar amounts of fluorine and the imine. We have found that the new compound $(CF_3)_2C(NF_2)CFO$ may be converted at room temperature in the presence of CsF to $(CF_3)_2C{=}NF$ in yields as high as 96%.

The reactivity of the carbon–carbon double bond in $(CF_3)_2C{=}C{=}O$ has been examined with $S_2O_6F_2$, $FOSO_2F$, NF_2OSO_2F, and N_2F_4. Addition compounds are obtained in all cases. For NF_2OSO_2F and N_2F_4, the 2-fluoramino isomers seem to be strongly favored over the 1-fluoramino compounds. When these fluoramino addition compounds are catalytically fluorinated, identical fluoroxy compounds result. Bis(trifluoromethyl)ketene also may be easily fluorinated to give a rather unstable hypofluorite, $(CF_3)_2CFCF_2OF$, which slowly decomposes to C_3F_8 and COF_2.

Experimental Section

Materials. $S_2O_6F_2$,[16] $FOSO_2F$,[17] and NF_2OSO_2F[18] were prepared and purified by the literature methods. Bis(trifluoromethyl)ketene was obtained from E. I. du Pont de Nemours and Co. and was purified by gas chromatography by using a Kel-F Haloport column [Kel-F No. 3 oil (3-M Co.) on Haloport F (F & M Scientific Corp.) (1:4)]. Tetrafluorohydrazine was purchased from Air Products, Inc. Fluorine was obtained from the Allied Chemical Co. and was purified by passing through a sodium fluoride scrubber to remove HF and a trap held at −183°.

Apparatus. A standard Pyrex vacuum system with Teflon stopcocks (Fischer & Porter Co.) was employed for material transfer because some compounds dissolved Kel-F stopcock grease. Since the reaction of $S_2O_6F_2$ and $(CF_3)_2C{=}C{=}O$ required a grease-free system, Pyrex storage tubes with Teflon stopcocks which contained the reactants and a Pyrex reaction vessel were sealed directly to the vacuum line precluding greased joints. The ultraviolet irradiation apparatus was 1-l. round-bottom Pyrex bulb equipped with a 2-mm vacuum stopcock and a quartz insert (20 cm long and 2.5-cm id) which was sealed into the bulb with a ₮ 45/50 ground-glass joint. The lamp (Hanau, Q-81) was inserted so that the arc was near the center of the bulb.

Molecular Weight. Molecular weights were determined by the method of Regnault and are listed in Table I. A calibrated bulb with a volume of 254.4 ml was used for the determinations. The bulb was fitted with a Teflon 1.25-mm stopcock with a Pyrex 10/30 ₮ inner joint. Pressures were measured with a mercury manometer.

Elemental Analysis. 2-Difluoramino-2-trifluoromethylpropanoyl fluorosulfate was analyzed by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, N. Y. Since most of the compounds attacked Pyrex glass slowly at room temperature or decomposed if stored in Pyrex at room temperature for a week or more, they were analyzed in this laboratory. Fluorine was determined by a null point potentiometric method,[19,20] after the compound was fused with sodium metal. Sulfur was determined as $BaSO_4$ after basic hydrolysis of $(CF_3)_2C(OSO_2F)C(O)OSO_2F$. Elemental analysis results are given in Table I.

Safety Precautions. It should be noted that the new hypofluorites are potentially hazardous and proper precautions of shielding and working with small quantities should be observed.

Reaction with $S_2O_6F_2$. After the system was flamed out under vacuum, 2 mmoles of $(CF_3)_2C{=}C{=}O$ was transferred into the reaction vessel, and $S_2O_6F_2$ was added slowly to the reaction vessel in about 0.1-mmole amounts. On occasions when $S_2O_6F_2$ was added too rapidly flashes of light were observed. Addition of $S_2O_6F_2$ was continued until the pressure in the reaction vessel had dropped to about 5 torr (roughly the vapor pressure of the product at room temperature). Colorless droplets of $(CF_3)_2C(OSO_2F)C(O)OSO_2F$ appeared on the inside walls of the reaction vessel. After completion of the reaction, $(CF_3)_2C{=}C{=}O + S_2O_6F_2 \rightarrow (CF_2)_2C(OSO_2F)\text{-}C(O)OSO_2F$, SiF_4 and traces of $(CF_3)_2C{=}C{=}O$ were removed by pumping on the mixture held at −20°. Further purification was accomplished by passing a stream of dry helium through the liquid. Yields were in excess of 90%.

Reaction with $FOSO_2F$. $(CF_3)_2C{=}C{=}O$ (1 mmole) and dry nitrogen (10 mmoles) were added to a 1-l. reaction vessel which was held at about −25° in an ethyl alcohol–water slush bath. A total of 1.2 mmoles of $FOSO_2F$ was added slowly to react according to $(CF_3)_2C{=}C{=}O + FOSO_2F \rightarrow (CF_3)_2CFC(O)OSO_2F$ (87%) + $(CF_3)_2C(OSO_2F)CFO$ (13%). These percentages were obtained from nmr data. After 3 hr N_2, SiF_4, and excess $FOSO_2F$ were pumped off at −25°. Nearly quantitative reaction occurred. Satisfactory separation of the isomers was not realized.

Reaction with NF_2OSO_2F. A 2-l. Pyrex bulb with a break-seal and 4-mm quick opening Teflon stopcock was heated to 200–250° under dynamic vacuum. Failure to flame out the vacuum system and reaction vessel decreased the yield of the addition product and

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Table II. ^{19}F Nmr Spectra (Chemical Shifts in Parts per Million)

Compound	OF	SF	NF_2	CFO	CF_3	CF_2	CF
$(CF_3)_2C(OSO_2F)C(O)OSO_2F$	. . .	−48.1 septet, 1.0[a] −46.8 singlet, 1.0	. . .	. . .	72.0 doublet, 6.3	. . .	. . .
$(CF_3)_2C(OSO_2F)CFO$	. . .	−47.1 complex	. . .	−33.7 complex	73.1 2 doublets	. . .	. . .
$(CF_3)_2CFC(O)OSO_2F$	. . .	−46.0 singlet	. . .	. . .	76.3 doublet	. . .	182.7 septet
$(CF_3)_2C(NF_2)C(O)OSO_2F$	. . .	−48.6 singlet, 1.0	−35.5 1.9	. . .	63.8 triplet, 6.1	. . .	. . .
$(CF_3)_2C(NF_2)CFO$	. . .	. . .	−34.1 1.8	−41.5 septet, 1.0	66.1 quintet, 6.1	. . .	. . .
$(CF_3)_2C(NF_2)CF_2OF$	−151.4 singlet, 1.0	. . .	−35.4 2.3	. . .	66.7 6.0	82.8 2.0	. . .
$(CF_3)_2CFCF_2OF$	−144.6 singlet	. . .	. . .	. . .	75.8 br quartet	90.2 14 lines	179.2 complex

[a] Hyperfine splitting and relative peak area.

increased the yield of nitrogen oxides. When the system was at ambient temperature, 2.6 mmoles of $(CF_3)_2C{=}C{=}O$ and 3.2 mmoles of NF_2OSO_2F were transferred into the vessel and the stopcock was sealed off. The reaction vessel was heated slowly in an oven over a period of 1 hr until the temperature reached 95°. Heating was continued at this temperature for 7–8 hr. The products were removed from the reaction vessel through the break-seal. The volatile products, CO_2, SO_2F_2, and SiF_4, were pumped off at −70°, and further purification was accomplished by using a Kel-F Haloport column. Typical yields of purified $(CF_3)_2C(NF_2)C(O)OSO_2F$ ranged between 80 and 94% (2.1–2.5 mmoles). No positive evidence for $(CF_3)_2C(OSO_2F)C(O)NF_2$ was found.

Reaction with N_2F_4. A mixture of $(CF_3)_2C{=}C{=}O$ (0.97 mmole) and N_2F_4 (2.1 mmoles) was transferred into a vessel equipped with a quartz insert and was subjected to ultraviolet radiation. Tap water (about 20°) was allowed to flow continuously around the lamp and over the reaction vessel. When the ultraviolet lamp was new, irradiation for about an hour was sufficient. Prolonged irradiation resulted in decomposition of the product and increased the yield of nitrogen oxides. In this reaction the major product was $(CF_3)_2C(NF_2)CFO$ and only minor amounts of the isomer, $(CF_3)_2CFC(O)NF_2$, apparently were obtained. This was not positively identified. $(CF_3)_2C(NF_2)CFO$ was purified by pumping off the volatile products, NF_3, N_2F_4, COF_2, CO_2, SiF_4, and lower fluorocarbons, at −78°. Further purification was made by using a Kel-F Haloport column which permitted efficient separation of $(CF_3)_2C(NF_2)CFO$ from NO_2. Typical yields of purified $(CF_3)_2C(NF_2)CFO$ ranged between 0.58 and 0.88 mmole (59–91%). Lower yields are attributed to the presence of moisture in the system or to inadequate cooling during irradiation.

General Procedure for Fluoroxy Compounds.[14,15] A 1.5–3.5-g sample of cesium fluoride was ground to a fine powder with a mortar and pestle and dried in a vacuum oven for 18 hr. The dried cesium fluoride was transferred into a 100-ml Monel Hoke cylinder or 750-ml nickel vessel prepared by silver soldering together two nickel crucibles which contained 12 stainless steel balls (3/8-in. diameter). The reactor was evacuated, filled with fluorine to 1 atm, and then heated to 200° in the oven for 6 hr. Fluorine was pumped out through a soda lime trap. To ensure the presence of finely ground catalyst, the reactor was shaken manually for 0.5 hr. A 0.25-mmole sample of $(CF_3)_2C(NF_2)CFO$ was condensed into the reactor at −183° and then approximately 2 mmoles of purified fluorine, diluted with nitrogen (360 torr of F_2 + 320 torr of N_2), was added. The reactor was placed in a slush bath (−78°) which was allowed to warm slowly to −20° over a period of 6–8 hr. When the temperature of the slush bath reached −20°, the products were transferred into a trap maintained at −183°, and nitrogen and unreacted fluorine were pumped off through a soda lime trap. A similar procedure was employed for fluorination of $(CF_3)_2C{=}C{=}O$ except the reactions were carried out with larger quantities. (Typically 3 mmoles gave about 2.8 mmoles of hypofluorite.)

In most runs no further purification was necessary for either compound. Whenever traces of impurities due to the presence of starting materials or decomposition products were observed, the compounds were purified by fractional codistillation or trap-to-trap distillation. In the case of $(CF_3)_2CFCF_2OF$, a trap at −78° retained the hypofluorite, and the impurities, C_3F_8, COF_2, and starting material, were found in the trap at −183°.

When $(CF_3)_2C(NF_2)CFO$ (0.25 mmole) was allowed to remain at room temperature in the presence of only CsF, 2-fluoriminoperfluoropropane (0.23 mmole) and carbonyl fluoride (0.21 mmole) were obtained. The fluorimine was purified by using a Kel-F Haloport column.

A summary of the experimental data is given in Table I.

Infrared Spectra. Infrared spectra of new materials were recorded with a Beckman Model IR 5A spectrophotometer (sodium chloride prism, 5000–625-cm^{-1} range, 3-min scan) or a Perkin-Elmer Model 137 infrared spectrophotometer (sodium chloride prism, 4000–667-cm^{-1} range, 12-min scan). The gaseous samples were contained in a 5-cm glass cell with NaCl windows. The following are the frequencies (cm^{-1}) for $(CF_3)_2C(OSO_2F)C(O)OSO_2F$: 1836 (s), 1485 (vs), 1290 (vs), 1250 (vs), 1163 (w), 1087 (s), 991 (s), 965 (vs), 873 (s), 842 (s), 805 (w), 773 (m); for a mixture of $(CF_3)_2CFC(O)OSO_2F$ and $(CF_3)_2C(OSO_2F)CFO$: 1872 (ms), 1845 (s), 1492 (vs), 1312 (vs), 1265 (vs) broad, 1192 (ms), 1130 (m), 1095 (m), 990 (vs), 965 (vs), 862 (s), 845 (vs), 808 (m), 778 (m), 748 (w), 708 (w); for $(CF_3)_2C(NF_2)C(O)OSO_2F$: 1824 (s), 1490 (vs), 1280 (vs), 1240 (vs), 1150 (m), 1065 (m), 1010 (s), 980 (vs), 952 (s), 910 (s), 860 (vs), 844 (s), 814 (w), 800 (w), 775 (s), 745 (w); for $(CF_3)_2C(NF_2)CFO$: 1868 (vs), 1260 (s), 1175 (w), 1068 (w), 1008 (vs), 947 (s), 910 (s), 745 (w), 708 (s); for $(CF_3)_2C(NF_2)CF_2OF$: 1280 (s), 1220 (s), 1175 (m), 1130 (w), 1062 (m), 1010 (vs), 953 (vs), 918 (s), 883 (ms), 805 (ms), 735 (s) broad; for $(CF_3)_2CFCF_2OF$: 1282 (vs) broad, 1195 (sh), 1165 (s), 1125 (s), 985 (vs) broad, 882 (s), 808 (s), 750 (s), 727 (s); and for $(CF_3)_2C{=}NF$: 1639 (m), 1350 (vs), 1250 (vs), 1213 (vs), 1181 (sh), 1023 (vs), 940 (sh), 733 (m).

^{19}F Nmr Spectra. ^{19}F nmr spectra were recorded at room temperature with a Varian Model V 4310 spectrometer operating at 40 Mc, a Varian Model DP-60 spectrometer at 56.4 Mc, a Varian Model 4311 B at 40 Mc, or a Varian HA 100 at 91.4 Mc (at −60°). In all cases CCl_3F was used as an external reference and resonances are given in ppm. The chemical shifts and assignments are given in Table II.

Oxidizing Equivalent. The oxidizing equivalents of fluoroxy compounds were determined by permitting the weighed sample to react with aqueous acidic iodide solution and titrating the liberated iodine with standard sodium thiosulfate. These are given in Table I.

Mass Spectra. Mass spectral cracking patterns were recorded with a Consolidated Engineering Corp. Type 21–103 mass spectrometer. The ionizing potential was 70 v at ambient temperature. The principal peaks in the spectra of the compounds are given (species, mass number, relative intensity). $(CF_3)_2C(OSO_2F)C(O)OSO_2F$: CO^+, N_2^+, 28, 17; CF^+, 31, 20; O_2^+, SO_2^{2+}, 32, 12; CO_2^+, 44, 23; SiF^+, 47, 9; SO^+, 48, 28; SO_2^+, 64, 38; SiF_2^+, 66, 8; FSO^+, 67, 15; CF_3^+, 69, 100; CO_2S^+, 76, 3; FSO_2^+, 83, 57; SiF_3^+, 85, 34; $C_2F_3O^+$, 97, 23; SiF_4^+, 104, 18; $C_2O_3SF^+$, 123, 7; $C_3F_5O^+$, 147, 20; $C_4F_5O^+$, 159, 43; $C_3F_3O_3S^+$, 173, 13; $C_4F_7O_3S^+$, 249, 6; $C_4F_7O_4S^+$, 277, 1; $C_4F_8O_7S_2^+$, 376, 1 (molecule ion); $(CF_3)_2C(NF_2)C(O)OSO_2F$: CO^+, N_2^+, 28, 9; CF^+, 31, 31; O_2^+, SO_2^{2+}, 32, 3; NF^+, 33, 19; C_2F^+, 43, 4; CO_2^+, 44, 17; SiF^+, 47, 2; SO^+, 48, 32; CF_2^+, 50, 8; NF_2^+, 52, 0.6; $C_2F_2^+$, 62, 1; CF_2N^+, SO_2^+, 64, 8;

FSO^+, 67, 0.5; CF_3^+, 69, 100; $C_3F_2^+$, 74, 1; CO_2S^+, 76, 3; SO_3^+, 80, 7; $C_2F_3^+$, 81, 3; FSO_2^+, 83, 2; SiF_3^+, 85, 11; $C_3F_3^+$, 93, 4; $C_2F_4^+$, 100, 5; CFO_3S^+, 111, 2; $C_2FNO_4S^+$, 153, 0.9; $C_4F_6^+$, 162, 35; $C_4F_7^+$, 181, 13; $C_3F_7N^+$, 183, 0.6; $C_3F_8N^+$, 202, 0.2; $C_4F_8NO^+$, 230, 0.7; and for $(CF_3)_2C(NF_2)CFO$: CO^+, N_2^+, 28, 0.8; NO^+, 30, 0.9; CF^+, 31, 0.9; O_2^+, 32, 0.5; NF^+, 33, 0.8; CO_2^+, 44, 1; NO_2^+, 46, 2; NF_2^+, 52, 1; CNF_2^+, 64, 0.4; CF_3^+, 100, 69; $^{13}CF_3^+$, 70, 1; $C_2NF_2^+$, 76, 1; $C_2F_3^+$, 81, 0.6; SiF_3^+, 85, 0.3; $C_3F_3^+$, 93, 0.5; $C_2F_3N^+$, 95, 0.5; $C_2F_4^+$, 100, 1; $C_3F_5^+$, 131, 0.3; $C_3F_6^+$, 150, 0.5; $C_3F_7^+$, 169, 0.7; $C_4F_7^+$, 181, 0.6; $C_3F_8N^+$, 202, 0.5.

Results and Discussion

Infrared spectra of these new compounds have many bands in common and some assignments are possible. Absorbances in the 1872–1824-cm^{-1} region are attributed to C=O stretch. The asymmetric and symmetric S=O stretching frequencies of the OSO_2F group are assigned to bands in the 1492–1485- and the 1265–1240-cm^{-1} regions, respectively.[12] These compounds have typical C–F bands located between 1350 and 1065 cm^{-1}.[21] N–F vibrations result in bands from 1023 to 910 cm^{-1}.[15] The bands assigned to S–O–X stretch in numerous fluorosulfate derivatives are found in the vicinity of 790 cm^{-1}.[17] Bands assigned to S–F stretch occur between 873 and 842 cm^{-1}.[12] The bands at 882 and 883 cm^{-1} in the fluoroxy compounds are attributed to O–F stretch.[17,22] In $(CF_3)_2C{=}NF$, an absorption at 1639 cm^{-1} is assigned to C=N.

As is typical of fluorosulfate-containing compounds,[12,23] all ^{19}F S–F nmr resonances occur from −46.0 to −48.6 ppm. The broadened NF_2 bands occur from −34.1 to −35.5 with the =NF resonance at −46.2 ppm. CF_3, CF_2, and CF resonances fall from 66.1 to 76.3, 82.8 to 90.2, and 179.2 to 182.7 ppm, respectively. Hyperfine splitting has been useful in many cases in making correct assignments. In $(CF_3)_2C(OSO_2F)C(O)OSO_2F$, the septet ($J$ = 3.6 cps) at −48.1 is assigned to FO_2SOC since this fluorine would be expected to interact more strongly with the six equivalent methyl fluorines than the fluorine of $FO_2SOC{=}O$ which is assigned to the singlet at −46.8. The doublet (J = 3.6 cps) at +72.0 is assigned to CF_3. In the mixture of isomers, $(CF_3)_2C(OSO_2F)CFO$ and $(CF_3)_2CFC(O)OSO_2F$, the relative amounts (13:87) were determined by measuring the areas of the two OSO_2F peaks in the nmr spectrum. Again bands were assigned based on the hyperfine splitting. In the former, the CF_3 groups are split by CFO to a doublet (J = 8 cps) and split again by the OSO_2F (J = 3.2 cps) to a quartet of equally intense peaks. Although in theory the CFO fluorine should be split into 14 peaks, roughly 10 of these are clearly discernible from the background. However, from these it is possible to determine J_{CFO-SF} = 5.4 cps and to confirm the value of J_{CFO-CF_3} = 8 cps. Because of the rather small, nearly equivalent values for J_{SF-CFO} (3.2 cps) and J_{SF-CF_3} (5.6 cps), the SF region is very complex, but 14 lines are observed and the coupling constants are confirmed. The spectrum of $(CF_3)_2CFC(O)OSO_2F$ is much simpler where six methyl fluorines couple with CF to give a septet (J_{CF-CF_3} = 7.3 cps), CF splits the CF_3 resonance into a doublet (J_{CF_3-CF} = 7.5 cps), and the SF resonance is a singlet. Similarly for $(CF_3)_2C(NF_2)C(O)OSO_2F$, where the two fluorines of NF_2 couple with the six equivalent CF_3 fluorines ($J_{CF_3-NF_2}$ = 16 cps, 1:2:1), while the NF_2 fluorine resonance is typically broadened with no fine structure. As above, no interaction occurs with the fluorosulfate fluorine. In the $(CF_3)_2C(NF_2)CFO$ spectrum, the septet at −41.5 (J = 9 cps) is assigned to CFO where the fine structure is a result of interaction with the methyl fluorines. Further splitting, apparently from CFO–NF_2 coupling, occurs but J is very small. While NF_2 is a broadened resonance at −34.1, the CF_3 resonance appears to be an ill-defined quintet.

It is surprising to note that the OF group in neither of the fluoroxy compounds couples with the remainder of the molecule. In the case of $(CF_3)_2C(NF_2)CF_2OF$, this may be due to the lack of resolution (which precludes the reporting of J values), but for $(CF_3)_2CFCF_2OF$ such is not the case (Varian HA-100). The latter spectrum was determined at −60° since it has been observed that the molecule, although apparently reasonably stable under ambient laboratory conditions, decomposes rather rapidly in the magnetic field. On heating in glass, the decomposition occurs essentially quantitatively to give COF_2 and C_3F_8. The remainder of the spectrum for $(CF_3)_2CFCF_2OF$ seems reasonable. Coupling between CF_3 and CF gives rise to a septet (J_{CF-CF_3} = 7 cps) at 179.2, but further not completely resolved splitting also is observed ($J \cong 3$ cps). Resonance at +75.8 ppm assigned to CF_3 is a broadened quartet which arises from overlap of CF_3–CF_2 ($J_{CF_3-CF_2}$ = 9 cps) and CF_3–CF (J_{CF_3-CF} = 7 cps) interactions. At +90.2 ppm is a 14-peak multiplet which fits in fairly well with CF_2–CF_3 ($J_{CF_2-CF_3}$ = 9 cps) and CF_3–CF ($J_{CF_3-CF} \cong 3$ cps) interactions. Assigning the resonance at +82.8 to CF_2 in $(CF_3)_2C(NF_2)CF_2OF$ is not out of line since, in $CF_3CF(NF_2)CF_2OF$, Lustig[15] has assigned a resonance at +86.1 to CF_2 while, in $CF_2(NF_2)CF_2OF$, the CF_2 adjacent to OF is at +92.5. Our value of +82.8 ppm is in keeping with the trend that as fluorines on CF_2 are replaced by CF_3 groups, the resonance position of the adjacent CF_2 is shifted downfield. Chemical shifts and coupling constants for $(CF_3)_2C{=}NF$ are essentially the same as those reported by Ruff.[13]

In the reactions of N_2F_4 and NF_2OSO_2F with $(CF_3)_2C{=}C{=}O$, little, if any, of the fluoramides, $(CF_3)_2CFC(O)NF_2$ and $(CF_3)_2C(OSO_2F)C(O)NF_2$, was observed during the work-up of the product mixture. However, in the latter case the presence of $(CF_3)_2C{=}O$, SO_2F_2, and CO_2 as minor components suggests that this isomer might have formed but decomposed during the reaction. However, no nitrogen-containing species, other than nitrogen oxides, were isolated. In the case of the former, C_3F_8 as well as nitrogen oxides and NF_3 were often observed as minor products. Possibly this isomer was unstable under the conditions used. The nmr spectrum taken on an unpurified sample gave no indication of two types of NF_2 or OSO_2F groups which should be evident if even small amounts of $(CF_3)_2C(OSO_2F)C(O)NF_2$ were present.

The action of CsF on $(CF_3)_2C(NF_2)CFO$ to abstract COF_2 provides a novel route to $(CF_3)_2C{=}NF$ in greater than 90% yield. Not even after heating the residual CsF to 200° for several hours is an equivalent amount of COF_2 recovered. However, this was not carried out

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under conditions of dynamic vacuum. The CsF-catalyzed fluorination of $(CF_3)_2C(NF_2)CFO$ and $(CF_3)_2C{=}C{=}O$ occurs readily below −20° to give nearly quantitative conversion to the respective fluoroxy compounds. With $(CF_3)_2C(NF_2)C(O)OSO_2F$, fluorination occurs more slowly and is encouraged by slightly higher temperatures (20°). In this case, $(CF_3)_2C(NF_2)CF_2OF$ and decomposition products are obtained. Under no conditions tried was it possible to retain the fluorosulfate moiety in the molecule.[24]

These fluoroxy compounds are not sensitive to glass or moisture but do attack mercury with vigor. Advantage of their action on acidic iodide solution was taken to determine the number of oxidizing equivalents. The experimental value of about 1.9 agrees fairly well with a theoretical two-electron change.

As is often typical of fluorosulfate-containing compounds of this type, small amounts of moisture tend to produce a cloudy solution and Kel-F stopcock grease is readily dissolved. It is advantageous to work in glass systems with Teflon stopcocks and without standard taper joints.

The mass spectral data are consistent with the proposed structures, although a molecule ion was obtained only in the case of $(CF_3)_2C(OSO_2F)C(O)OSO_2F$. For every molecule CF_3^+ was the predominant species.

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The Preparation and Some Properties of the Lanthanide Oxidecarbides, Ln_4O_3C

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Abstract: A series of lanthanide oxidecarbides (Ln = La, Nd, Gd, Ho, Er) of fcc symmetry has been prepared by reducing the sesquioxide with appropriate mixtures of graphite and the corresponding lanthanide metal. The neodymium analog, which was studied extensively, was found to have the approximate stoichiometry Nd_4O_3C. The X-ray powder diffraction pattern of this phase is indexable on cubic symmetry and has a lattice parameter, $a_0 = 5.1407 \pm 0.0001$ Å. The X-ray intensities are consistent with a NaCl-type lattice. Vapor-phase chromatographic analysis of the hydrolysis products suggests the presence of C^{4-} ions in the structure. Data presented indicate that this is a carbon-stabilized monoxide phase which is common to the lanthanide series.

Attempts to prepare oxidecarbides of the heavier analogs of $Nd_2O_2C_2$[1] by reduction of the sesquioxide either by graphite or by a lanthanide metal–graphite mixture produced a cubic phase which is shown in this study to be an oxidecarbide. This phase contains significantly less carbon than the formerly reported $Ln_2O_2C_2$ phase and has been prepared in pure form by many different techniques. Five lanthanide elements (La, Nd, Gd, Ho, Er) have been shown to exhibit this phase, and it probably exists throughout the entire series.

Two other oxidecarbides exhibiting similar cubic-type structures have been reported: a zirconium oxidecarbide phase[2] produced by plasma furnace reduction of zirconium dioxide with graphite, and the previously reported uranium monoxide now said to be an oxidecarbide.[3] The uranium phase is reported to exhibit a wide range of oxygen/carbon ratios, and the zirconium ($ZrC_{1-\epsilon}O_\epsilon$) phase is a simple solid solution derived from the cubic ZrC. The value of the lattice parameter of the zirconium species lies between those of the ZrC and ZrO, and a thermodynamic treatment of uranium oxidecarbide was based on a binary mixture of UO and UC. In fact, both compounds have been interpreted by use of a model of a carbon atom-substituted fcc NaCl-type monoxide lattice.

Several monoxides of lanthanide elements prepared by a variety of methods have been reported. Most methods effect reduction of the sesquioxide by carbon or by the corresponding metal. Achard, *et al.*, reported the europium, samarium, and ytterbium monoxides prepared by reducing the sesquioxides with carbon.[4–7] Other reports have appeared describing lower oxides, LaO, CeO, NdO, SmO, Sm_2O, YbO, and YO.[8,9] In many instances, the particular phase is described by only one report. When two or more reports have appeared on any phase, the published lattice parameters are often found to vary considerably, and only

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