at present, no means to decide which mechanism is dominant in the tetranuclear complex under investigation.

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Registry No. $[Cr\{(OH)_2Cr(en)_2\}_3](S_2O_6)_3$, 73079-34-2; $[Cr\{(OH)_2Cr(en)_2\}_3]I_6$, 69786-52-3.

Supplementary Material Available: A listing of nonvanishing matrix elements (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Kansas State University,
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Synthesis of 1,1-Bis(fluorooxy)perhaloalkanes by Reaction of Fluorinated Carboxylic Acids with Fluorine in the Presence of Cesium Fluoride

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The reaction of CF_3CO_2H, $C_2F_5CO_2H$, n-$C_3F_7CO_2H$, and $ClCF_2CO_2H$ with F_2 in the presence of CsF at -111 °C forms the corresponding 1,1-bis(fluorooxy)perhaloalkanes in high yield. The reaction occurs in two steps in which the acidic proton is first fluorinated to form $RC(O)OF{\cdot}CsF$ or $RC(O)OF$, followed by a fast fluorination of the carbonyl oxygen forming $RCF(OF)_2$. The fluorination of $(CF_2CO_2H)_2$ forms $[CF_2CF(OF)_2]_2$, but the compound could not be characterized due to its explosiveness above -20 °C. The new compounds $RCF(OF)_2$ ($R = C_2F_5$, n-C_3F_7, $ClCF_2$) are characterized by IR, NMR, and physical properties. Additional characterization of the previously known $CF_3CF(OF)_2$ is also given.

Introduction

Compounds containing oxygen–fluorine bonds are among the most reactive compounds in chemistry.[1-3] The O–F bond is relatively weak, and this, coupled with high bond energies of oxygen and fluorine to many elements, accounts for their reactivity. During a 10-year period from 1955 to 1965, the search for high energy oxidizers for use in advanced chemical propellants spawned considerable research in this area.[4] One area of this endeavor involved the synthesis of compounds containing more than one O–F group per molecule. However, few such compounds were actually isolated and fully characterized.

In 1967, the first bis(fluorooxy) compound (other than OF_2 and O_2F_2) $CF_2(OF)_2$ was reported by several groups.[5-7] This was followed by the other new geminal compounds $CF_3CF(OF)_2$, $(CF_3)_2C(OF)_2$,[8] and $SeF_4(OF)_2$[9] and by several nongeminal compounds $FO(CF_2)_3OF$,[10] $FO(CF_2)_4OF$, $FO(CF_2)_5OF$,[11] and $FOCF_2OOCF_2OF$.[12] No other fully characterized examples have appeared in the chemical literature. Five of these examples are best prepared by the CsF-catalyzed fluorination of carbon–oxygen double bonds, but the only geminal compound that can be prepared in this way is $CF_2(OF)_2$. As such, it has been the only geminal derivative available for further chemical studies.

We were interested in carrying out some reactions of $CF_3CF(OF)_2$. The reported method of synthesis from $NaOC(CF_3)_2OH$ and fluorine was of very low yield and always gave both $CF_3CF(OF)_2$ an $(CF_3)_2C(OF)_2$. The latter is especially prone to explosive decomposition making this method undesirable from several points of view. We therefore looked for a better preparative method. The low-temperature fluorination of CF_3CO_2H in the presence of CsF proved very effective. This reaction and its extension to several other carboxylic acids are described in this paper.[13]

Table I. Reactions of RCO_2H with F_2 in the Presence of CsF

R	molar ratio of $RCO_2H:F_2$	reacn condn temp, °C	reacn condn time, h	% yield of $RCF(OF)_2$[a]
CF_3	1.0:2.2	−78	6.0	84[b]
CF_3	1.0:2.2	−111	6.0	87[b]
CF_3	1.0:5.0	−78	6.0	85[b]
CF_3	1.0:5.0	−111	6.0	100
CF_3	1.0:5.0	−111	3.0	100
CF_3CF_2	1.0:5.0	−111	3.0	96
$CF_3CF_2CF_2$	1.0:5.0	−111	3.0	92
$ClCF_2$	1.0:5.0	−111 to −20	10.0	
		−20 to −8.5	30.0	100

[a] Based on RCO_2H and determined by GLC analysis. [b] Some byproducts were found.

Experimental Section

General Data. All compounds were handled in a Pyrex or stainless-steel vacuum system equipped with glass–Teflon or stainless-steel valves. Pressures were measured with a precision Heise Bourdon tube gauge in the metal system and a Wallace and Tiernan differential pressure gauge in the glass system. Amounts of volatile compounds were determined by *PVT* measurements by assuming ideal gas behavior. Molecular weights were determined by vapor density measurements. Temperatures were measured with a digital readout copper–constantan thermocouple.

Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrometer by using a 10-cm glass cell fitted with silver chloride windows. NMR spectra were taken at low temperature on a Varian

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XL-100-15 spectrometer by using trichlorofluoromethane as a solvent and internal reference.

Caution! All of the geminal bis(fluorooxy)alkanes described in this work are strong oxidizers and explosive and must be handled with care. We recommend a maximum sample size of 2–3 mmol and that the compounds be manipulated at low temperatures, so that their vapor pressure does not exceed 30 torr.

Reagents. Fluorine (Air Products and Chemicals, Inc.) was used after passing through a NaF scrubber. CsF from commercial sources was dried by heating to ca. 500 °C and then treated with 2 atm F_2 at 22 °C for 20 h. Carboxylic acids from commercial sources were purified by distillation before use.

Reaction of Carboxylic Acids with Fluorine in the Presence of CsF. Reactions were carried out in 75-mL stainless-steel reactors fitted with stainless-steel valves. Carboxylic acid (ca. 2.5 mmol) shown in Table I was condensed onto the dry CsF (10 g) as follows. Liquid acids were vacuum transferred into the reactor cooled to −195 °C, and the amount was calculated by difference in weight of the acid container. In the case of solid acids, dry air was admitted to the reaction tube and a weighed amount of acid was added onto the CsF. The reactor was then cooled to −195 °C and evacuated. After addition of the acids, fluorine was added by partial condensation, and the amount was measured by the presure change from a known volume. The amounts of acid and F_2 are shown in Table I. The mixture was then allowed to warm and was kept at an appropriate temperature for the times indicated. The mixture was then cooled to −195 °C, and excess F_2 was pumped out. The reaction vessel was then slowly warmed up to 22 °C while pumping through a trap at −195 °C. The compounds condensed at −195 °C were then fractioned through traps at temperatures low enough to stop the O–F compound but not the decomposition products.

$CF_3CF(OF)_2$: see ref 8 and 13.

$CF_3CF_2CF(OF)_2$: bp ~0 °C; vapor pressure at −28.5 °C = 126 mmHg, trapped at −120 °C; melting point not determined, glass at −195 °C; mol wt 223.0, calcd 220.02; IR 1347 (m), 1278 (w), 1244 (vs), 1237 (vs), 1200 (sh), 1135 (w), 1118 (m), 988 (s), 925 (w), 885 (m), 815 (w), 737 (m), 660 (w), 538 (w) cm^{-1}; NMR at −20 °C $CF_3{}^ACF_2{}^BCF^C(OF^D)_2$ $\phi_A{}^*$ 82.4 (d-t-t), $\phi_B{}^*$ 123.1 (t-d-q), $\phi_C{}^*$ 109.0 (t-q-t), $\phi_D{}^*$ −154.3 (d-t-q) [$J_{AB} = 1.5$, $J_{AC} = 8.0$, $J_{AD} = 1.0$, $J_{BC} = 2.0$, $J_{BD} = 8.0$, $J_{CD} = 23.5$ Hz].

$CF_3CF_2CF_2CF(OF)_2$: bp ~40 °C; vapor pressure at −15 °C = 66 mmHg, trapped at −111 °C, melting point not determined, glass at −195 °C; mol wt 267.0, calcd 270.03; IR 1346 (m), 1290 (sh) 1230 (vs), 1142 (s), 1085 (w), 1035 (w), 1000 (w) C_3F_8?, 950 (m), 918 (sh), 900 (w), 870 (s), 840 (w), 783 (w), 732 (s), 685 (w), 650 (w), 600 (m), 530 (m) cm^{-1}; NMR at −20 °C $CF_3{}^ACF_2{}^BCF_2{}^CCF^D(OF^E)_2$ $\phi_A{}^*$ 81.4 (t), $\phi_B{}^*$ 127.0 (d-t-t), $\phi_C{}^*$ 119.6 (t-q-t), $\phi_D{}^*$ 108.1 (t-t), $\phi_E{}^*$ −153.8 (d-t-t) [$J_{AC} = 10.0$, $J_{BC} = 2.5$, $J_{BD} = 12.0$, $J_{BE} = 3.0$, $J_{CE} \simeq 11.0$, $J_{DE} \simeq 23.0$, $J_{AB} \simeq J_{AD} \simeq J_{AE} \simeq J_{CD} \simeq$ O Hz].

$ClCF_2CF(OF)_2$: melting point not determined, glass at −195 °C; very explosive, boiling point and vapor pressure difficult to determine; mol wt 180.0 measured at low pressure (10 torr), calcd 186.47; IR 1270 (m), 1208 (s) CF_3Cl?, 1172 (vs), 1135 (m), 1105 (s) and 1097 (s) CF_3Cl?, 1042 (vw), 967 (vs), 914 (m), 881 (m), 857 (m), 781 (m), 750 (w-br), 686 (w) cm^{-1}; NMR at −70 °C $ClCF_2{}^ACF^B(OF^C)_2$ $\phi_A{}^*$ 65.9 (t-d), $\phi_B{}^*$ 109.7 (t-t), $\phi_C{}^*$ −150.1 (d-t) [$J_{AB} = 4.5$, $J_{AC} = 10.0$, $J_{BC} = 28.0$ Hz].

Decomposition of $R_fCF(OF)_2$ ($R_f = CF_3$, C_2F_5, and n-C_3F_7). Pure $R_fCF(OF)_2$ (0.5 mmol) was placed in a 5-mL glass tube equipped with a glass–Teflon valve and heated at 53 °C for 8 h in a water bath. After O_2 was removed at −195 °C, the contents of the bulb were then condensed into an NMR sample tube with a measured amount of internal standard $CFCl_3$. The amount of recovered $R_fCF(OF)_2$ was calculated by ^{19}F NMR integration. The results are given in Table II.

Results and Discussion

The reactions of several halogenated carboxylic acids with fluorine over CsF proceed in excellent yield according to eq 1. The reaction conditions are summarized in Table I, and

$$RCO_2H + 2F_2 \xrightarrow[\text{low } T]{CsF} RCF(OF)_2 + CsF{\cdot}HF \qquad (1)$$

$$R = CF_3,\ C_2F_5,\ n\text{-}C_3F_7,\ ClCF_2$$

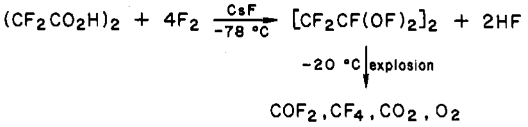
the effects of variation of temperature and fluorine ratio are shown for CF_3CO_2H. The reaction temperature is very important. At higher temperatures some additional products and decomposition products were observed. At too low a temperature, the reactions will not proceed. It appears that for the reaction to proceed, the temperature must be high enough for intermediate products to have some volatility or mobility. With R = CF_3, C_2F_5, and n-C_3F_7, reactions proceed to completion at −111 °C by using excess fluorine. With a greater than 2:1 excess of F_2, essentially no byproducts are formed. When R = $ClCF_2$, only 1 molar equiv of F_2 is used up at −111 °C. At −20 to −8.5 °C for 40 h, a second mole of F_2 is consumed.

Table II. Relative Stability of $R_fCF(OF)_2$ at 53 °C[a]

R_f	% recovered $R_fCF(OF)_2$[b]	products
CF_3	98	CF_4, COF_2, O_2
CF_3CF_2	35	C_2F_6, COF_2, O_2
$CF_3CF_2CF_2$	22	C_3F_8, COF_2, O_2

[a] In Pyrex glass for 8 h. [b] Determined by ^{19}F NMR analysis.

Other carboxylic acids were observed to react under these conditions, but the desired products could not be isolated. With HCF_2CO_2H, explosions occurred at −195 °C forming CF_4 in large amounts. With $FSO_2CF_2CO_2H$, ~1 molar equiv of F_2 was absorbed from −150 to −78 °C. Further reaction at temperatures of up to −10 °C resulted in some additional reaction, but SO_2F_2 was the main volatile product. With anhydrous oxalic acid, 1 mol of F_2 was absorbed at −111 °C. At −78 °C another 0.5 was absorbed. The only volatile product, however, was CO_2. With perfluorosuccinic acid, a 15:1 fluorine to acid reaction at −78 °C resulted in the reaction of 4 mol of F_2 after 5 days. A similar reaction carried out at −111 °C with 5:1 mole ratio resulted in an explosion. When an attempt was made to remove the compound by pumping it through a −195 °C trap as the reactor warmed slowly from −78 °C, no volatiles were observed up to ~−20 °C, at which temperature, an energetic explosion occurred. We believe these observations are consistent with reaction 2. The sequence of



$$\begin{tikzcd}(CF_2CO_2H)_2 + 4F_2 \arrow[r, "CsF", "-78\,^\circ C"'] & \left[CF_2CF(OF)_2\right]_2 + 2HF \arrow[d, "-20\,^\circ C"', "explosion"] \\ & COF_2, CF_4, CO_2, O_2\end{tikzcd} \qquad (2)$$

reactions leading to the 1,1-bis(fluorooxy)alkanes is of interest. The decision to carry out the reactions in the first place was based on the premise that $CF_3C(O)OF$[14] could be fluorinated to form $CF_3CF(OF)_2$ in the presence of CsF. However, the prospects of using one explosive compound to prepare another explosive one were not inviting. It was concluded that if $CF_3C(O)OF$ could be generated in situ in the presence of CsF and F_2, the desired product would be obtained. Some previous studies on the preparation of CF_3OOF[15] and SF_5OOF[16] suggested that the reaction of an aicidic proton with F_2/CsF occurs readily at low temperature. We believe the reactions occur in the sequence of (3) and (4).

$$RCO_2H + F_2 \xrightarrow{CsF} [RCO_2F] + HF \qquad (3)$$

$$[RCO_2F] + F_2 \xrightarrow{CsF} RCF(OF)_2 \qquad (4)$$

Attempts to isolate the intermediate RCO_2F in the case of R = CF_3 were not successful. Reaction of CF_3CO_2H and F_2 (1:1) at −111 °C for 2 h consumed most of the fluorine and a 40% yield of $CF_3CF(OF)_2$ was pumped out at −111 °C.

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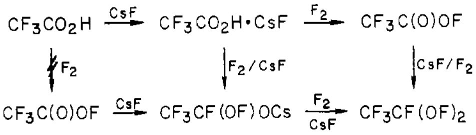
Warming to 22 °C while pumping on the reactor resulted in a 5% yield of unknown volatile compounds but no CF_3CO_2H. Addition of an additional molar equivalent of F_2 to the residue and treating in the same way resulted in another 45% of $CF_3CF(OF)_2$. The total gases formed corresponded to the original amount of CF_3CO_2H. If CF_3CO_2H is condensed onto CsF at −195 °C and then warmed to 22 °C, it cannot be removed under vacuum. If CF_3CO_2Cs is allowed to react with F_2 under these conditions, $CF_3CF(OF)_2$ is formed in good but not as high a yield as when the acid is used. Fluorine and CF_3CO_2H at −111 °C without CsF show little or no reaction. These observations taken together suggest the following possibilities, with the HF product omitted:



The second reaction with fluorine is probably very fast compared to the first, otherwise one would expect to see some CF_3CO_2F or other intermediate products. Whether or not free $CF_3C(O)OF$ is actually an intermediate is uncertain. The reaction of a known sample $CF_3C(O)OF$ with CsF/F_2 has not been carried out, but it should react readily at low temperature. A related compound has been shown to react in this way,[17] and the facile nature of this reaction with a variety of carbonyl compounds is well established (eq 5–7).[3]

$$FC(O)OF + F_2 \xrightarrow{CsF} CF_2(OF)_2 \qquad (5)$$

$$RC(O)F + F_2 \xrightarrow{CsF} RCF_2OF \qquad (6)$$

$$RC(O)R' + F_2 \xrightarrow{CsF} RR'CFOF \qquad (7)$$

R and R′ = fluoroalkyl

The characterization of the isolated 1,1-bis(fluorooxy)-fluoroalkanes by IR and ^{19}F NMR spectroscopy was very straightforward. The low-field chemical shifts of the OF groups combined with the expected multiplicity and relative areas of the observed resonances provide unambiguous proof of structure.[3,18] The IR spectra contain absorptions in the 850–900 cm^{-1} region which can be assigned to $\nu(OF)$ and 900–1000 cm^{-1} due to $\nu(CO)$. In each case, minor impurities due to decomposition products were observed in the IR spectra.

The thermal stabilities of the $R_fCF(OF)_2$ compounds were compared at 53 °C as summarized in Table II. Their controlled thermolysis is nearly quantitative according to eq 8.

$$RCF(OF)_2 \rightarrow RF + COF_2 + {}^1/_2O_2 \qquad (8)$$

This is in agreement with the rapid decomposition of $CF_3CF(OF)_2$ determined in metal. In glass, however, earlier work suggested much greater glass attack than we have observed.[8]

Under our conditions, the stability decreases with increasing number of carbons with the greatest change from 2 to 3 carbons. $ClCF_2CF(OF)_2$ was too explosive to check in this way. In one instance with this compound, a 1-mmol sample detonated in the vacuum line while being transferred to an NMR tube. The damage was rather impressive considering the small sample size. For the four compounds R = $ClCF_2$, CF_3, C_2F_5, and n-C_3F_7, the greatest tendency toward explosive decomposition was at higher pressures in the gas phase. Workers at 3M Company found no evidence for decomposition of pure $CF_3CF(OF)_2$ up to 200 °C in metal.[8] This is surprising as the compound exploded on several occasions during handling in glass at 22 °C. A 2-mmol sample in an ~20 mL glass tube at 22 °C explodes when the tube is suddenly broken. In another instance, a 2-mmol sample exploded near 22 °C while it was being allowed to vaporize in the hood after removing the tube from liquid nitrogen and opening the glass–Teflon valve. Quite clearly, these energetic compounds are unpredictable. Their apparent stability depends on a variety of factors, and all geminal bis(fluorooxy) compounds should be considered explosive under all conditions.

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Registry No. $CF_3CF_2CF(OF)_2$, 72985-54-7; $CF_3CF_2CF_2CF(OF)_2$, 72985-55-8; $ClCF_2CF(OF)_2$, 72985-56-9; F_2, 7782-41-4; CF_3CO_2H, 76-05-1; $CF_3CF_2CO_2H$, 422-64-0; $CF_3CF_2CF_2CO_2H$, 375-22-4; $ClCF_2CO_2H$, 76-04-0; $CF_3CF(OF)_2$, 16329-92-3.

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Synthesis and Properties of 2-(Pentafluorothio)-3,3-difluorooxaziridine

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The synthesis and properties of the novel perfluorooxaziridine $F_5S\overline{NCF_2O}$, is achieved by dehydrofluorination of $F_5SN(H)CF_2OOCF_3$ with NaF. The peroxide is prepared by the addition of CF_3OOH to the azaalkene $SF_5N{=}CF_2$. The new oxaziridine is only the second example of a perfluorinated compound of this type, and its reaction chemistry is suprisingly different from that of $CF_3\overline{NCF_2O}$. The latter is reactive to fluoride only at nitrogen, whereas $SF_5\overline{NCF_2O}$ undergoes attack at both nitrogen and carbon.

Introduction

We recently reported the synthesis of the first perfluorooxaziridine, $CF_3\overline{NCF_2O}$.[1] This novel compound is the only perfluorinated, two-heteroatom, three-membered heterocycle known. It exhibits an interesting reaction chemistry which is quite analogous to $CF_2\overline{CFCF_2O}$.[2-4] Nucleophiles attack the nitrogen exclusively forming a variety of compounds of the type $CF_3N(Nu)C(O)F$. As an indication of its utility in

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