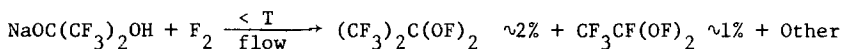
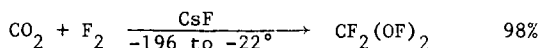


A FACILE SYNTHESIS OF 1,1-BIS(FLUOROXY)PERFLUOROETHANE

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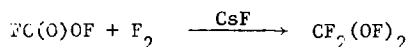
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Geminal bis(fluoroxy)perfluoroalkanes were first described in 1967, but no new well characterized examples have been reported since then. In principle, a variety of such compounds should be capable of existence if a method can be found for their synthesis. The three known examples $\text{CF}_2(\text{OF})_2$,²⁻⁴ $\text{CF}_3\text{CF}(\text{OF})_2$ ⁵ and $(\text{CF}_3)_2\text{C}(\text{OF})_2$ ⁵ were obtained in the highest yields by the following reactions.



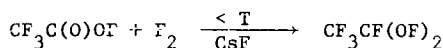
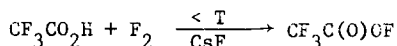
Clearly, $\text{CF}_2(\text{OF})_2$ is the only available compound for further synthetic work and some interesting reactions are known.⁶

We were interested in carrying out reactions with $\text{CF}_3\text{CF}(\text{OF})_2$ and therefore looked for a new method for its synthesis. From a report that $\text{CF}_2(\text{OF})_2$ could be obtained in high yield by the CsF catalyzed fluorination of $\text{FC}(\text{O})\text{OF}$,⁷ an alternate synthesis became obvious.



Fluorination of $\text{R}_f\text{C}(\text{O})\text{OF}$ in the presence of CsF should lead to high yields of $\text{R}_f\text{CF}(\text{OF})_2$. Unfortunately, acyl hypofluorites are themselves difficult to prepare and they are rather explosive.⁶ However, it would only be necessary to have $\text{R}_f\text{C}(\text{O})\text{OF}$ formed as an intermediate at low temperature in the presence of CsF and F_2 for the alternate synthesis to occur.

Previous work by us had shown that acidic hydrogens react very readily with fluorine at low temperature in the presence of CsF.^{8,9} Therefore the following route seemed reasonable.



Reaction of $\text{CF}_3\text{CO}_2\text{H}$ with excess fluorine in the presence of CsF at -111° gives $\text{CF}_3\text{CF}(\text{OF})_2$ in essentially quantitative yield. This preparation makes this unusual compound readily available for the first time and it is very probable that this reaction will succeed with a variety of carboxylic acids. This work is in progress and preliminary evidence for $\text{CF}_3\text{CF}_2\text{CF}(\text{OF})_2$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}(\text{OF})_2$ has been found.

Experimental

All reactions were carried out in glass and stainless steel vacuum systems as previously described.⁸ Cesium fluoride (10 g) was dried by heating, placed in a 75 ml ss reactor and treated with 2 atm of F_2 at 22°. The vessel was evacuated and CF_3CO_2H (3 mmol) was condensed onto the CsF at -196°. F_2 (15 mmol) was added and the vessel was held at -111° for 6 hr. Excess fluorine was then removed at -196° by pumping and the product was collected by pumping through a trap at -196° as the reactor warmed in the air. No purification of the product was required.

^{19}F nmr in $CFCl_3$ at -20° showed only 3 multiplets. $CF_3^A CF^B (OF^C)_2$: ϕ_A^* 77.2,t; ϕ_B^* 112.6,t; ϕ_C^* -150.0,d-q; $J_{AB} \leq 0.5$, $J_{AC} = 10.2$, $J_{BC} = 28.5$ Hz. Mol. wt. 168.8, calcd. 170.01. These data along with the ir spectra agree very closely with the values of Thompson and Prager.⁵

Caution! Extreme care must be used in working with $CF_3CF(OF)_2$ and related compounds. These materials may explode with considerable force under appropriate conditions. They must be considered explosive under all conditions in the absence of appropriate testing.

Acknowledgment

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