Notes

An Improved Synthesis of 2,2-Bis(fluoroxy)perfluoropropane

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Introduction

Recently $CF_2(OF)_2$ has been found to form 1,3-dioxolanes by low temperature reaction with alkenes.[1] This direct and versatile reaction has renewed interest in the synthesis and reactivity of geminal bis(fluoroxy) compounds.

1,1-Bis(fluoroxy)perhaloalkanes can be prepared in high yields by fluorination of the corresponding perhalo carboxylic acid in presence of CsF.[2,3] For nonterminal geminal bis(fluoroxy) compounds no general methods of synthesis have appeared in the chemical literature. The only example known is the formation of $(CF_3)_2C(OF)_2$ by fluorination of solid $NaOC(CF_3)_2OH$ with dilute fluorine at −20 °C,[4] but the yield is only 2% and the resultant mixture of different fluoroxy compounds is difficult to separate. Herein a new preparative method for 2,2-bis(fluoroxy)perfluoropropane based on hexafluoroacetone is described. The method can probably be extended to other ketones, but these were not investigated. The reactivity of 2,2-bis(fluoroxy)-perfluoropropane and other geminal bis(fluoroxy) compounds with alkenes is under investigation and will be the subject of future publications.

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 MKS BARATRON Type 223B pressure transducer. Amounts of volatile compounds were determined by *PVT* measurements by assuming ideal gas behavior. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR by using a 10 cm glass cell fitted with silver chloride windows. NMR spectra were taken on a Bruker AC 200 (188 MHz) spectrometer by using carbon tetrachloride as a solvent, trichlorofluoromethane as internal reference, and a capillary containing acetone-d_6 as an external lock. ***Caution!*** The 2,2-bis(fluoroxy)perfluoropropane described in this work is a strong oxidizer, is explosive, and must be handled with care. We recommend a maximum sample size of 2−3 mmol and recommend that the compound be manipulated at low temperature, so its vapor pressure does not exceed 20 Torr.

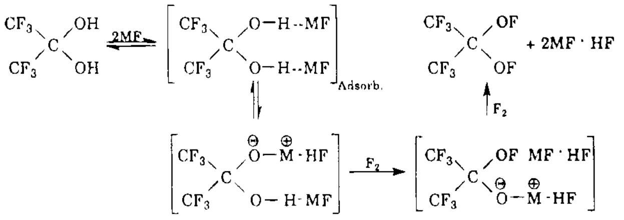
Reagents. Fluorine (Air Products and Chemicals, Inc.) was used after passing through a NaF scrubber. Hexafluoroacetone was obtained from a commercial source and was used as received. Hexafluoroacetone hydrate was prepared following the literature method.[5] Potassium fluoride and cesium fluoride were dried by heating in the air for 1-2 h with a Bunsen burner using a ceramic crucible and ground to a powder under anhydrous conditions. Before use in reactions KF and CsF were treated with F_2 (1 atm, 22 °C) for 1 h.

Table 1. Reaction of $(CF_3)_2C(OH)_2$ with F_2 in the Presence of MF

MF	[hydrate], mmol	[fluorine], mmol	temp, °C	time, h	% $(CF_3)_2C(OF)_2$[a]
CsF	1.0	3.7	−110	4.0	65[b]
CsF	1.0	10.0	−110	4.5	75
KF	2.5	10.0	−110	4.0	90[b]
KF	2.5	20.0	−85	10.0	93

[a] % of total products in −196 °C trap by ^{19}F NMR. [b] Some unreacted hydrate was observed in the trap cooled to −70 °C.

Scheme 1



Reaction of Hexafluoroacetone Hydrate with Fluorine in the Presence of CsF or KF. Reactions were carried out in a 75 mL stainless steel reactor fitted with stainless steel valve and containing 6.0 g of preactivated metal fluoride. The $(CF_3)_2C(OH)_2$ is a low melting solid with about 15 Torr vapor pressure at room temperature which allows it to be transferred under vacuum into the reactor containing the dry metal fluoride cooled to −196 °C. The amount (1−2 mmol) transferred was determined by weighing. After adding the hydrate to the reactor, the cylinder was heated to 50 °C and shaken vigorously to mix the melted hydrate with the metal fluoride. The reactor was cooled to −196 °C, and fluorine was added by partial condensation. The reactor was placed in a cold bath and allowed to warm to an appropriate temperature. Representative reactions are summarized in Table 1. After an appropriate reaction time the reactor was cooled to −196 °C and excess fluorine was removed under dynamic vacuum. The reaction vessel was allowed to warm slowly in the ambient air up to 22 °C while pumping through a trap cooled to −196 °C. The compounds collected in the trap were passed through a trap cooled to −70 °C into a trap cooled to −196 °C under dynamic vacuum to remove any unreacted hydrate. A representative sample of the reaction products in the −196 °C trap was used to estimate the percentage of $(CF_3)_2C(OF)_2$ by ^{19}F NMR (see Results and Discussion). Due to the instability of $(CF_3)_2C(OF)_2$ the yield of this product could not be determined accurately. The percentage of $(CF_3)_2C(OF)_2$ in the −196 °C trap approximated the calculated yield. Pure (ca. 98%) $(CF_3)_2C(OF)_2$ was obtained by passing the contents of the −196 °C trap through traps cooled to −122 and −196 °C in vacuo with the desired product collecting in the former trap.

IR and ^{19}F NMR data of $(CF_3)_2C(OF)_2$ are in agreement with the literature values.[4]

IR: 1287 (vs), 1262 (vs), 1223 (vs), 1125 (s), 1077 (s), 1021 (s), 888 (m), 741 (m) cm^{-1}. ^{19}F NMR: $\delta(CF_3) = -70.2$ (t), $\delta(OF) = 148.1$ (sept), $^4J_{F-F} = 14$ Hz.

Results and Discussion

The fluorination of $(CF_3)_2C(OH)_2$ in the presence of CsF or KF gives 2,2-bis(fluoroxy)perfluoropropane in good yield according to Scheme 1. A similar mechanism has been proposed for fluorination of CF_3OOH to CF_3OOF in presence of CsF[6] and for the synthesis of 1,1-bis(fluoroxy) compounds

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(1) (a) Navarrini, W.; Fontana, S. (Ausimont SpA), EP-B499157, 1992; *Chem. Abstr.* **1992**, *117*, 236286h. (b) Navarrini, W.; Bragante, L.; Fontana, S.; Tortelli, V.; Zedda, A. *J. Fluorine Chem.* **1995**, *71*, 111.
(2) Sekiya, A.; DesMarteau, D. D. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 203.
(3) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1980**, *19*, 1328.
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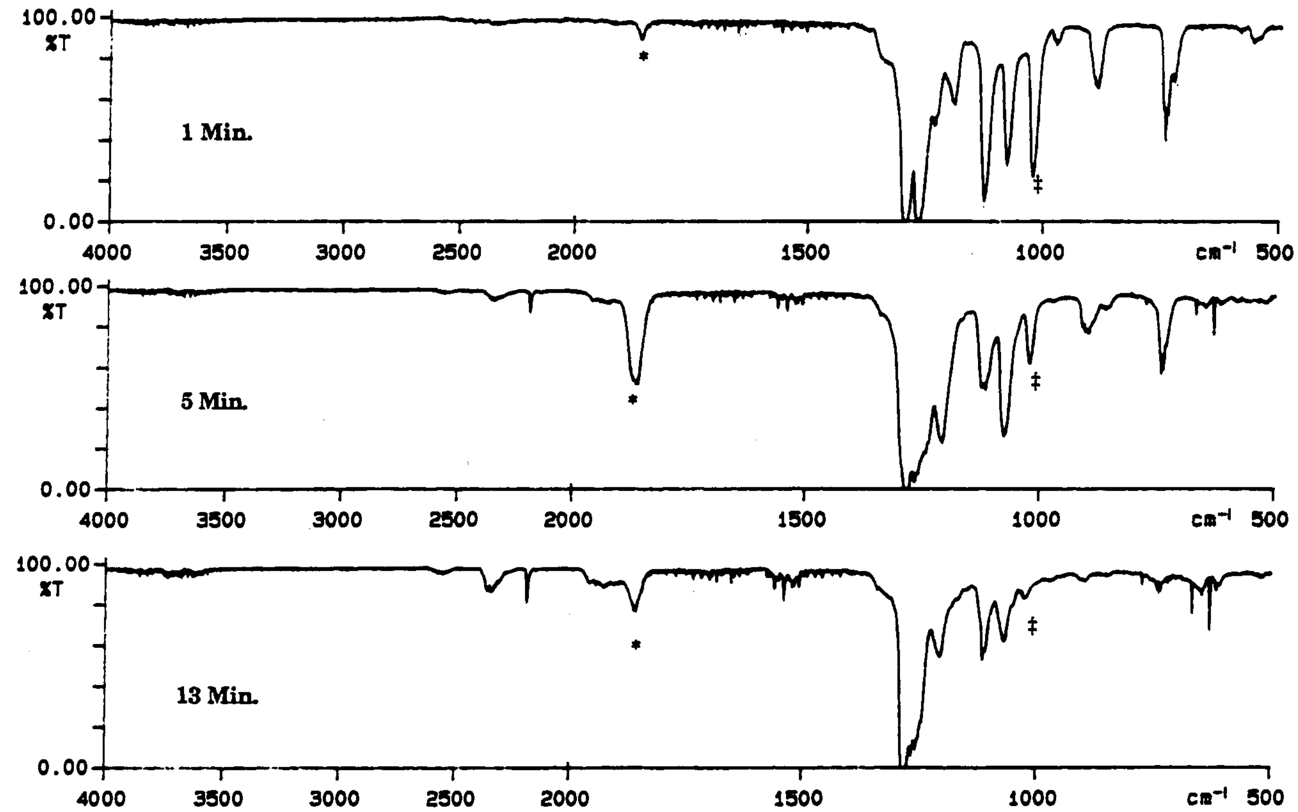


Figure 1. FT/IR of $(CF_3)_2C(OF)_2$ at 1, 5, and 13 min showing growth and disappearance of $CF_3C(O)OF$ as $(CF_3)_2C(OF)_2$ decomposes to CF_4 and CO_2. The presence of $CF_3C(O)OF$ is indicated by ν (C═O) at 1861 cm^{-1} (*) and the disappearance of $(CF_3)_2C(OF)_2$ by the decreasing ν (OF) at 1021 cm^{-1} (‡). After 1 h the spectrum indicates only CF_4 and CO_2 are present.

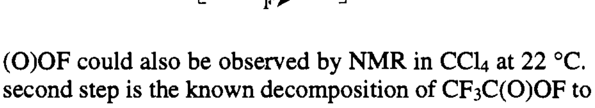
starting from perfluorocarboxylic acids in the presence of CsF.[3] Mixing of MF with the hydrate is a key factor in the reaction. A good yield of $(CF_3)_2C(OF)_2$ can be achieved with a thorough mixing of the hydrate and the MF. This can be achieved by heating the hydrate/MF mixture at 50−60 °C (above the melting point of the hydrate) with vigorous shaking. The formation of a complex between MF and the hydrate is indicated by the fact that the initial vapor pressure of the monohydrate is ~15 Torr at 22 °C, but after mixing with MF the vapor pressure is <0.1 Torr. The hydrate can only be removed slowly under dynamic vacuum at 22 °C.

If the mixture of MF and $(CF_3)_2C(OH)_2$ is heated to 70−100 °C, the yield of $(CF_3)_2C(OF)_2$ decreases. This may be due to the disassociation of the loss of H_2O from the hydrate to form $(CF_3)_2CO$ and/or the formation of alkoxide salt by loss of HF, and/or an increase in the amount of free hydrate. Also a major side reaction becomes important at ca. 80 °C as shown in eq 1.[7] Fluorination of the hydrate without MF gives $(CF_3)_2CFOF$[8]

$$(CF_3)_2C(OH)_2 + CsF \rightarrow CF_3H + CF_3C(O)OH\cdot CsF \quad (1)$$

and catalytic fluorination of $(CF_3)_2C{=}O$ with MF also gives $(CF_3)_2CFOF$ in high yield.[9] Fluorination of the dilithium salt of the hydrate is reported to give bis(trifluoromethyl)dioxirane in good yield.[10] Reaction of $CF_3CO_2H.CsF$ with fluorine at −78 °C gives $CF_3CF(OF)_2$ in high yield.[3] We observed significant amounts of all three products in reactions where the MF hydrate mixture was heated to 70−100 °C and substantial amounts of $(CF_3)_2CFOF$ when the hydrate was added to the metal fluoride and not heated and mixed thoroughly. We also observed increased amounts of $(CF_3)_2CFOF$ when the metal fluoride contained HF, presumably due to the inability of MF·HF to form a complex with the hydrate. Although it was expected that CsF would give better yields of $(CF_3)_2C(OF)_2$, KF proved to be more effective. In the absence of a more complete study on the nature of the interaction between $(CF_3)_2C(OH)_2$ and MF, we have no explanation for this apparent dichotomy.

2,2-Bis(fluoroxy) perfluoropropane decomposes quickly in Pyrex at 22 °C and the final products of decomposition are CF_4 and CO_2. This decomposition could be monitored by FT-IR spectroscopy (see Figure 1). A peak at 1861 cm^{-1}, detected after a short time, became strong in 10 min and disappeared almost completely in 1 h, indicating the existence of an intermediate in the decomposition. According to the established pattern of decomposition of the fluoroxy compounds,[11] the first step is the formation of tetrafluoromethane and trifluoroacetyl hypofluorite as the intermediate (eq 2). The intermediate $CF_3C(O)OF$ could also be observed by NMR in CCl_4 at 22 °C. The second step is the known decomposition of $CF_3C(O)OF$ to CO_2



(2)

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(7) CF_3H was readily identified by NMR (^{19}F −79.0, d; ^1H 5.6, q; J_{HF} = 79.0 Hz) and IR (ν(CH) = 3034 cm^{-1}). A 1 mmol sample of $(CF_3)_2C(OH)_2$ heated with 6.0 g of CsF from 60 to 100 °C over 1.5 h gave CF_3H in 75% yield as the only volatile product.

(8) Prager, J. H.; Thompson, P. G. *J. Am. Chem. Soc.* **1965**, *87*, 230.

(9) Lustig, M.; Pitochelli, A. R.; Ruff, J. K. *J. Am. Chem. Soc.* **1967**, *89*, 2841.

(10) Talbott, R. J.; Thompson, P. J. U.S. Patent 3632606, 1972; *Chem. Abstr.* **1972**, *76*, P 99638.

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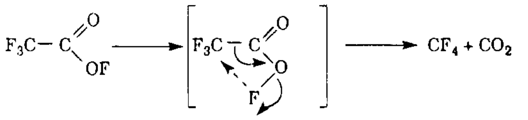
and CF_4 (eq 3).[12] The stability of 2,2-bis(fluoroxy)perfluoropropane is improved in solutions of perhalocarbons at low temperature: it can be stored at −30 °C in CCl_4 solution (0.1 mmol/mL) for several days with little change.



(3)

Finally, all the byproducts observed under varying conditions by ^{19}F NMR can be explained. The formation of $CF_3C(O)OF$, $(CF_3)_2CFOF$, $CF_3CF(OF)_2$, $(CF_3)_2CO_2$, CF_4, CF_3H, and CO_2, can arise as described above. The presence of small amounts of $CF_2(OF)_2$ and an additional source of $CF_3CF(OF)_2$ arise from the catalytic fluorination of CO_2 and $CF_3C(O)OF$, respectively, which must have formed before the excess fluorine is removed. Small amounts of COF_2 were observed, but not CF_3OF, indicating the COF_2 is formed most probably by the known decomposition of $CF_3CF(OF)_2$ at higher temperature after the fluorine has been removed.

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(12) Stewart, R. D.; Cady, G. H. *J. Am. Chem. Soc.* **1955**, *77*, 6110. The IR and ^{19}F NMR of $CF_3C(O)OF$ do not appear to be known: IR 1861 cm^{-1} (C=O); ^{19}F NMR δ +171.2 (1F, q), −70.5 (3F, d), $^4J_{FF} = 6.0$ Hz.