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Perfluoroalkyl hypobromites: synthesis and reactivity with some fluoroalkenes

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Abstract

The first perfluoroalkyl hypobromites have been prepared by the reaction of bromine(I) fluorosulfate with perfluorinated tertiary alkoxides of general formula $R_fC(CF_3)_2ONa$ where $R_f = CF_3$ or CF_3CF_2. These hypobromites are of lower thermal stability but they behave similarly to analogous hypochlorites and decompose rapidly above −20 °C to give $CF_3C(O)CF_3$ and either CF_3Br or CF_3CF_2Br. New polyfluoroethers generated from the reaction of perfluoroalkyl hypobromites with fluoroalkenes have been characterized by ^{19}F and ^1H NMR spectroscopy, IR spectroscopy and MS.

Keywords: Perfluoroalkyl hypobromites; Synthesis; Fluoroalkenes; NMR spectroscopy; Mass spectrometry; IR spectroscopy

1. Introduction

Halogen fluorosulfates are extremely potent oxidizers and have been effectively used to generate other *O*-halogen derivatives by metathesis reactions with oxo salts [1].

$$XOSO_2F + CsOClO_3 \rightarrow XOClO_3 + CsOSO_2F$$

$(X = Cl,Br)$

In related work with the very electronegative $(CF_3SO_2)_2N$ group, we found that the reaction of chlorine on $(CF_3SO_2)_2NAg$ or $[(CF_3SO_2)_2N]_2Hg$ produced the *N*-chloro derivative in very high yield. However, bromine failed to react with either the silver(I) or mercury(II) derivatives. When $(CF_3SO_2)_2NAg$ was reacted with $BrOSO_2F$, only a modest yield of $(CF_3SO_2)_2NBr$ was obtained owing to side-reactions while the reaction of $[(CF_3SO_2)_2N]_2Hg$ with $BrOSO_2F$ gave an excellent yield of $(CF_3SO_2)_2NBr$ (92%) [2]. These results prompted us to try $BrOSO_2F$ to prepare a fluoroalkyl hypobromite by reaction with the corresponding metal alkoxide. Preliminary studies by Singh and DesMarteau [3] indicated that an α-fluorine or α-hydrogen in the alkoxide prevented isolation of the corresponding hypobromite as shown below.

$$(CF_3)_2CXONa + BrOSO_2F \longrightarrow$$

$$'(CF_3)_2CXOBr' + FSO_2O^-Na^+$$

$$\hookrightarrow (CF_3)_2CO + XBr$$

$(X = H, F)$

For X = F, this result was consistent with other hypohalites where $(CF_3)_2CFOCl$ (one α-fluorine) has about the same stability as CF_3CF_2OCl (two α-fluorines), indicating that an α-fluorine in the hypochlorite is a prime source of the low thermal stability of these compounds [4]. Fluorine atoms in the α-position provide a convenient pathway for the elimination of chlorine monofluoride in hypochlorites. For X = H, the corresponding hypochlorite is quite thermally stable. To determine whether the absence of an α-fluorine or α-hydrogen would help to stabilize hypobromites, alkoxides of perfluorinated tertiary alcohols were tried. These reactions led to the isolation of the first examples of perfluoroalkyl hypobromites.

2. Experimental details

2.1. General methods

Gases and volatile materials were handled in glass vacuum systems, equipped with glass–Teflon valves. Amounts of volatile compounds were determined by PVT measurements

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using a Wallace & Tiernan series 1500 differential pressure gauge. All trap-to-trap fractionational condensations were performed under dynamic vacuum. The reaction vessel for the preparation of the perfluoroalkyl hypobromites consisted of a 50 ml Pyrex flask with a glass–Teflon valve attached through an Ace-Thred O-ring seal. The reactors contained a Teflon-coated magnetic stirring bar.

Infrared spectra were recorded in a 10 cm glass cell fitted with KCl or AgCl windows. NMR spectra were acquired at 200.13 MHz for ^{1}H, 188.31 MHz for ^{19}F and 75.47 for ^{13}C. Chemical shifts are reported relative to $Si(CH_3)_4$ or $CFCl_3$ with shifts upfield from these designated as negative. Mass spectra were recorded on a Hewlett Packard 5985B spectrometer at 70 eV for EI and CI (CH_4) with samples introduced by direct gas injection.

Most NMR samples were prepared by using about 6.0 mmol of deuterated solvent ($CDCl_3$ or acetone-d_6) and 0.10–0.20 mmol of sample. The ^{19}F NMR spectrum of $CF_3CF_2C(CF_3)_2OBr$ was run in $C_4F_9SO_2F$ as a solvent. A ^{19}F NMR spectrum was then acquired in the absence of a lock solvent. High-temperature NMR experiments of hypobromite–alkene adducts employed 1,1,2,2-tetrachloroethane-d_2 ($Cl_2CDCDCl_2$) as the lock solvent.

In preparing the perfluoroalkyl hypobromites, special care was taken to minimize their exposure to light due to their expected photosensitivity [2]. Reactors were wrapped in Al foil and room lights were turned off during vacuum line manipulations.

***Caution!* The hypohalites and their precursors are potentially hazardous. Appropriate precautions should be taken in handling these compounds.**

2.1.1. Reagents

The fluorinated alcohols $(CF_3)_3COH$ and $CF_3CF_2C(CF_3)_2OH$ were prepared as described previously [5,6]. Bromine(I) fluorosulfate [7,8] and the sodium alkoxides of $(CF_3)_3COH$ and $CF_3CF_2C(CF_3)_2OH$ were prepared by literature methods [9]. Perfluorobutanesulfonyl fluoride, $CF_2{=}CH_2$, $CF_2{=}CCl_2$ and $CF_2{=}CF_2$ were purchased from PCR, Inc. and used without further purification. Tetrafluoroethylene (PCR) was freed of its terpene inhibitor by passing it through a trap cooled to −111 °C under dynamic vacuum.

2.1.2. Preparation of $CF_3CF_2C(CF_3)_2OBr$

Sodium perfluoro-t-pentoxide (0.44 g, 1.4 mmol) was loaded into a 50 ml glass reactor in the dry box. The flask was evacuated with heating and cooled to −196 °C. Bromine(I) fluorosulfate (0.19 g, 1.1 mmol) was added by vacuum-transfer. The reactor and its contents were placed in a cold bath at −25 °C and stirred for 1 h. The volatile components were removed under dynamic vacuum for 1 h while the reaction flask warmed slowly from −25 °C to 25 °C. The resulting materials were fractionated through traps at −93 °C and −196 °C using the specially modified U-trap previously described [10]. The contents of the −93 °C trap (orange solid) were cooled to −196 °C and 6.00 mmol of $CF_3CF_2CF_2CF_2SO_2F$ as a solvent were condensed into the NMR tube. The NMR tube was flame-sealed under dynamic vacuum and placed in the NMR spectrometer at −80 °C, at which point a spectrum was acquired unlocked and referenced externally to $CFCl_3$.

The perfluoroalkyl hypobromite was characterized as follows: ^{19}F NMR $CF_3^ACF_2^BC(CF_3)_2^COBr$ δ: A −80.0 (3F, sept); B −115.9 (2F, sept); C −68.5 (6F, br mult) ppm; $J_{AC} = 5.1$, $J_{BC} = 10.7$ Hz. If a sample of $CF_3CF_2C(CF_3)_2OBr$ similarly isolated was allowed to warm to 22 °C, it decomposed quickly above ca. −20 °C to $(CF_3)_2C{=}O$ and C_2F_5Br as the only observed products.

2.2. Preparation of $(CF_3)_3COBr$

Sodium perfluoro-t-butoxide (0.50 g, 1.9 mmol) and $BrOSO_2F$ (0.29 g, 1.6 mmol) were combined as above. After 1.25 h at −25 °C, the volatile compounds were removed under dynamic vacuum over 1.25 while the flask warmed slowly from −25 °C to 24 °C and collected in traps cooled to −85 °C and −196 °C. The volatiles in the −196 °C trap (0.14 mmol) were a mixture of $CF_3C(O)CF_3$ and CF_3Br. The −85 °C trap contained $(CF_3)_3COBr$ as an orange solid. A sample collected at −85 °C and allowed to warm to 22 °C decomposed rapidly above ca. −20 °C to give CF_3Br and $(CF_3)_2C{=}O$ as the only observed products. No ^{19}F NMR spectrum was obtained for this compound.

2.3. Reactions of R_fOBr with alkenes

The reactions of $(CF_3)_3COBr$ and $C_2F_5C(CF_3)_2OBr$ were carried out by nearly identical procedures. The alkoxides (2.0 mmol) were used to prepare the hypobromites as described above. The −85 °C collection trap having a volume of 100 ml was then used as the reactor. It was cooled to −196 °C and the appropriate alkene (2–4 mmol) added by vacuum-transfer. The trap was placed in a cold bath near −85 °C and allowed to warm slowly to 22 °C over 10–12 h (see Table 1). The products were then separated by fractional condensation through a series of cold traps and the products collected were identified by IR, MS and NMR methods. The following gives the data for the respective alkenes as: trap temperature, product, followed by characterization for the addition product.

Reactions of $(CF_3)_3COBr$

$CF_2{=}CH_2$: −35 °C, $(CF_3)_3COCF_2CH_2Br$ (88)/$(CF_3)_3COCF_2CHBr_2$ (12); −89 °C, $(CF_3)_2COH$; −196 °C, $CF_2{=}CH_2$, CF_3Br, $(CF_3)_2C{=}O$. The addition products were not separated and were characterized as a mixture. IR (2 torr) (cm^{-1}): 2989 (vw); 1278 (vs); 1217 (m); 1138 (s); 1100 (m); 1062 (m); 977 (s); 849 (w); 731 (m); 675 (w); 602 (w). ^{19}F NMR of the mixture gave a series of signals ($CDCl_3$, 25 °C) at −70.3 (t, 9.3 Hz); −70.4 (br s); −70.5 (sharp s); −70.6 (br s); −70.7 (br s); −74.7 (br mult) ppm. NMR $(CF_3)_3{}^ACO{-}CF_2{}^BCH_2Br$ ^{1}H ($CDCl_3$, 25 °C) δ: 3.74

Table 1
Summary of reactions of R_fOBr with alkenes

Hypobromite	Alkene	Conditions (temp. range (°C) (time, h))	Yield of desired ether(s) (based on $BrOSO_2F$ used)	Products (relative % determined by ^{19}F NMR spectroscopy
$(CF_3)_3C{-}OBr$	$CF_2{=}CH_2$	− 88 to 24 (12)	31	$(CF_3)_3C{-}OCF_2CH_2Br$ (46) $(CF_3)_3C{-}OCF_2CHBr_2$ (6) $(CF_3)_3C{-}OH$ (47)
	$CF_2{=}CCl_2$	− 83 to 25 (12)	37	$(CF_3)_3C{-}OCF_2CCl_2Br$ (75) $(CF_3)_3C{-}OCCl_2CF_2Br$ (25)
	$CF_2{=}CF_2$	− 85 to 25 (12)	33	$(CF_3)_3C{-}OCF_2CF_2Br$ (99)
$CF_3CF_2C(CF_3)_2{-}OBr$	$CF_2{=}CH_2$	− 80 to 25 (8)	20	$CF_3CF_2C(CF_3)_2{-}OCF_2CH_2Br$ (25) $FSO_2{-}OCF_2CH_2Br$ (24) $CF_3CF_2C(CF_3)_2{-}OH$ (51)
	$CF_2{=}CCl_2$	− 80 to 25 (12)	24	$CF_3CF_2C(CF_3)_2{-}OCF_2CCl_2Br$ (90) $FSO_2{-}OCF_2CCl_2Br$ (10)
	$CF_2{=}CF_2$	− 93 to 25 (8)	23	$CF_3CF_2C(CF_3)_2{-}OCF_2CF_2Br$ (92) $FSO_2{-}OCF_2CF_2Br$ (5) $CF_3CF_2C(CF_3)_2{-}OH$ (3)

(t); $J_{HB} = 9.2$ Hz. ^{19}F ($Cl_2CDCDCl_2$, 140 °C) δ: A −69.9 (9F, t); B −69.3 (2F, mult); $J_{AB} = 9.3$ Hz. ^{13}C ($CDCl_3$, 25 °C) δ: 119.3 (CF_3, q, $J_{C-F} = 283.1$ Hz); 80.2 (C–O, ten, $J_{C-F} = 32.2$ Hz); 119.1 (CF_2, t, $J_{C-F} = 281.3$ Hz); 28.6 (CH_2Br, t, $J_{C-F} = 35.0$ Hz). NMR $(CF_3)_3{}^{A}COCF_2{}^{B}CHBr_2$ ^1H ($CDCl_3$, 25 °C) δ: 5.79 (1H, t). ^{19}F ($CCl_2CDCDCl_2$, 140 °C) δ: A −69.6 (9F, t); B −73.3 (2F, ten, d); $J_{AB} = 9.9$ Hz, $J_{HB} = 6.1$ Hz. ^{13}C ($CDCl_3$, 25 °C) δ: 119.3 (CF_3, q, $J_{C-F} = 283.1$ Hz); 79.8 (C–O, ten, $J_{C-F} = 33.5$ Hz); 119.1 (OCF_2, t, $J_{C-F} = 281.3$ Hz); 35.4 ($CHBr_2$, t, $J_{C-F} = 39.7$ Hz). MS (EI) *m/z* (^{79}Br): 378 (M^+, 5.7%); 285 [$(CF_3)_3COCF_2^+$, 15.9%]; 143 ($CF_2CH_2Br^+$, 46.3%); 69 (CF_3^+, 100.0%). MS (CI) *m/z*: 378 (M^+, 5.6%); 359 ($MH-HF^+$, 73.9%); 285 [$(CF_3)_3COCF_2^+$, 30.4%]; 143 ($CF_2CH_2Br^+$, 96.8%).

GC–MS analysis of the ether mixture indicated the presence of two compounds, i.e. 92% of $(CF_3)_3COCF_2CH_2Br$ and 8% of $(CF_3)_3COCF_2CHBr_2$.

$CF_2{=}CCl_2$: −55 °C, $(CF_3)_3COCF_2CCl_2Br$ (76)/ $(CF_3)_3COCCl_2CF_2Br$ (24); −121 °C, $CF_2{=}CCl_2$; −196 °C, CF_3Br, $(CF_3)_2C{=}O$. The two regioisomers were not separated and were characterized as a mixture. IR (2 torr) (cm^{-1}): 1282 (vs); 1224 (m); 1166 (m); 1140 (w); 1114 (w); 1029 (w); 997 (m); 980 (m); 854 (m); 815 (m); 760 (w); 732 (m); 718 (w); 537 (w). NMR $(CF_3)_3{}^{A}C{-}OCF_2{}^{B}CCl_2Br$ ^{19}F ($CDCl_3$) δ: A −70.2 (9F, t); B −79.9 (2F, 10 line mult.) ^{13}C ($CDCl_3$) δ: 119.2 (CF_3, q, $J_{C-F} = 292.4$ Hz); 80.8 (C–O, 10 line mult., $J_{C-F} = 32.7$ Hz); 118.7 (OCF_2, t, $J_{C-F} = 286.7$ Hz); 74.7 (CCl_2Br, t, $J_{C-F} = 41.3$ Hz); $J_{AB} = 9.2$ Hz. NMR $(CF_3)_3{}^{A}CO{-}CCl_2CF_2{}^{B}Br$ ^{19}F ($CDCl_3$) δ: A −67.9 (9F, s); B −61.0 (2F, s). ^{13}C ($CDCl_3$) δ: 119.2 (CF_3, q, $J_{C-F} = 292.4$ Hz); 82.0 (C–O, 10 line mult., $J_{C-F} = 32.6$ Hz); 118.7 (CF_2Br, t, $J_{C-F} = 315.6$ Hz); 107.4 ($OCCl_2$, t, $J_{C-F} = 34.0$ Hz). MS (EI) *m/z* (^{35}Cl, ^{79}Br): 411 ($M-Cl^+$, 8.9%); 367 ($M-Br^+$, 78.8%); 348 ($M-BrF^+$, 10.0%); 285 [$(CF_3)_3C-OCF_2^+$, 19.0%); 211 ($CF_2CCl_2Br^+$, 6.3%); 132 ($CCl_2CF_2^+$, 15.7%); 69 (CF_3^+, 59.5%). MS (CI) *m/z*: 427 ($MH-HF^+$, 11.3%); 411 ($MH{-}HCl^+$, 69.9%); 367 ($MH-HBr^+$, 78.8%).

$CF_2{=}CF_2$: −90 °C, $(CF_3)_3COCF_2CF_2Br$; −196 °C, trace CF_3Br, $(CF_3)_2C{=}O$, some white solid assumed to be PTFE remained in the reactor. NMR $(CF_3)_3{}^{A}CO{-}CF_2{}^{B}CF_2{}^{C}Br$ ^{19}F (acetone-d_6) δ: A −69.9 (9F, t); B −83.2 (2F, 30 line mult.); C −70.1 (2F, t); $J_{AB} = 9.1$ Hz, $J_{BC} = 3.6$ Hz. MS (EI) *m/z* (^{79}Br): 335 [$(CF_3)_3COCF_2CF_2^+$, 100.0%]; 285 [$(CF_3)_3C-OCF_2^+$, 52.2%]; 179 ($CF_2CF_2Br^+$, 6.3%); 69 (CF_3^+, 7.6%). MS (CI) *m/z*: 395 ($MH-HF^+$, 32.4%); 335 ($MH-HBr^+$, 60.1); 285 [$(CF_3)_3C-OCF_2^+$, 33.9%]; 219 [$(CF_3)_3C^+$, 15.5%)]; 179 ($CF_2CF_2Br^+$, 69.2%); 129 (CF_2Br^+, 37.7%); 100 ($CF_2CF_2^+$, 20.1%).

Reactions of $CF_3CF_2C(CF_3)_2OBr$

In contrast to the reactions of $(CF_3)_3COBr$ listed above, the preparation of $CF_3CF_2C(CF_3)_2OBr$ for reactions with alkenes always resulted in the presence of some unreacted $BrOSO_2F$. The latter also underwent additions to the alkenes, resulting in this adduct being present with the desired adduct of $CF_3CF_2C(CF_3)_2OBr$. While these resultant mixtures can probably be separated by GLC, this was not attempted and the characterization of the mixture was only by NMR which allowed unambiguous assignments for the compounds present.

$CF_2{=}CH_2$: −72 °C, $CF_3CF_2C(CF_3)_2OH$ (51), $CF_3CF_2C(CF_3)_2OCF_2CH_2Br$ (25), $FSO_2OCF_2CH_2Br$ (24); −196 °C, $CF_2{=}CH_2$, small amt. $(CF_3)_2CO$ and C_2F_5Br. NMR $CF_3{}^{A}CF_2{}^{B}C(CF_3)_2{}^{C}{-}OCF_2{}^{D}CH_2Br$ ^1H (acetone-d_6) δ: 4.18 (t). ^{19}F (acetone-d_6) δ: A −78.7 (3F, sept–t); B −115.6 (2F, sept–t); C −67.1 (6F, t–t–q); D −78.3 (2F, br s); $J_{AC} = 5.9$ Hz, $J_{AD} = 2.8$ Hz, $J_{BC} = 12.7$ Hz, $J_{BD} = 6.4$ Hz, $J_{CD} = 12.5$ Hz, $J_{HD} = 10.0$ Hz. NMR $F^{A}SO_2OCF_2{}^{B}CH_2Br$ ^1H (acetone-d_6) δ: 4.37 (t). ^{19}F (acetone-d_6) δ: A +47.6 (1F, t); B −70.6 (2F, t–d); $J_{AB} = 8.8$ Hz, $J_{HB} = 10.8$ Hz. NMR $CF_3{}^{A}CF_2{}^{B}C(CF_3)_2{}^{C}{-}OH$ ^1H (acetone-d_6) δ: 9.19 (br s); ^{19}F (acetone-d_6) δ: A -79.5 (3F, sept); B -118.5 (2F, sept); C -72.2 (6F, t–q); $J_{AC}=5.7$ Hz, $J_{BC}=11.2$ Hz.

$CF_2{=}CCl_2$: -55 °C, $CF_3CF_2C(CF_3)_2COCF_2CCl_2Br$ (90), $FSO_2OCF_2CCl_2Br$ (10); -196 °C, $CF_2{=}CCl_2$, small amt. of $(CF_3)_2CO$ and C_2F_5Br. NMR $CF_3{}^ACF_2{}^BC(CF_3)_2{}^C$–$OCF_2{}^DCCl_2Br$ 19F (acetone-d_6) δ: A -78.7 (3F, sept–t); B -115.5 (2F, sept–t); C -66.7 (6F, t–t–q); D -78.3 (2F, br s); $J_{AC}=5.9$ Hz, $J_{AD}=2.4$ Hz, $J_{BC}=12.8$ Hz, $J_{BD}=6.6$ Hz, $J_{CD}=12.3$ Hz. MS (EI) m/z (^{35}Cl, ^{79}Br): 417 ($M-Br^+$, 59.5%); 398 ($M-BrF^+$, 10.0%); 335 [$CF_3CF_2C(CF_3)_2-OCF_2{}^+$, 14.1%]; 247 [$CF_3CF_2C(CF_3)-OCF^+$, 10.5%]; 211 ($CF_2CCl_2Br^+$, 43.0%); 197 ($CF_3CF_2C-OCF_2^+$, 12.9%); 181 ($CF_3CF_2CCF_2{}^+$, 77.9%); 161 ($CCl_2Br^+$, 15.0%); 147 ($CF_3CF_2CO^+$, 12.6%); 132 ($CF_2CCl_2{}^+$, 52.8%); 119 ($CF_3CF_2{}^+$, 37.3%); 69 ($CF_3{}^+$, 87.8%). MS (CI) m/z: 477 ($MH-HF^+$, 11.3%); 461 (MH–HCl^+, 46.3%). NMR $F^ASO_2OCF_2{}^BCCl_2Br$ ^{19}F (acetone-d_6) δ: A 51.6 (1F, s), B -62.5 (2F, s).

$CF_2{=}CF_2$: -80 °C, $CF_3CF_2C(CF_3)_2OCF_2CF_2Br$ (91), $CF_3CF_2C(CF_3)_2OH$ (3), $FSO_2OCF_2CF_2Br$ (5.3); -196 °C, C_3F_4, small amount of $(CF_3)_2CO$ and C_2F_5Br. NMR $CF_3{}^ACF_2{}^BC(CF_3)_2{}^C$–$OCF_2{}^DCF_2{}^EBr$ ^{19}F (acetone-d_6) δ: A -79.0 (3F, sept–t); B -115.8 (2F, sept–t); C -67.4 (6F, 15 line mult); D -82.8 (2F, mult); E -69.9 (2F, br s); $J_{AC}=5.9$ Hz, $J_{AD}=1.8$ Hz, $J_{BC}=12.5$ Hz, $J_{BD}=6.3$ Hz. MS (EI) m/z (^{79}Br): 385 ($M-Br^+$, 100.0%); 335 ($M-CF_2Br^+$, 96.8%); 179 ($CF_2CF_2Br^+$, 34.1%); 129 (CF_2Br^+, 11.1%), 119 ($CF_3CF_2{}^+$, 15.9%), 69 (CF_3^+, 51.6%). MS (CI) m/z (^{79}Br): 445 ($MH-HF^+$, 20.6%); 385 ($MH-HBr^+$, 17.7%); 179 ($CF_2CF_2Br^+$, 77.1%); 119 ($CF_3CF_2{}^+$, 27.8%). NMR $F^ASO_2OCF_2{}^BCF_2{}^CBr$ ^{19}F (acetone-d_6) δ: A 50.2 (1F, t); B -85.7 (2F, d–t); C -70.6 (2F, t); $J_{AB}=8.4$ Hz, $J_{BC}=3.1$ Hz.

***cis*-$CFH{=}CFH$:** -80 °C, $CF_3CF_2C(CF_3)_2OCFHCFHBr$ (74), $FSO_2OCFHCHHBr$ (26); -196 °C, $CFH{=}CFH$. NMR $CF_3{}^ACF_2{}^BC(CF_3)_2{}^COCF^DH_aCF^EH_bBr$ ^{1}H (acetone-d_6) δ: H_a 6.48 (d–d–d–mult); H_b 6.98 (d–d–d). ^{19}F (acetone-d_6) δ: A -78.9 (3F, sept–t); B -116.3 (2F, sept–t); C -67.4 (6F, br mult); D -130.8 (1F, br mult); E -156.9 (1F, br s); $J_{AB}=1.2$ Hz, $J_{AC}=5.6$ Hz, $J_{BC}=12.3$ Hz, $J_{BD}=4.2$ Hz, $J_{DE}=24.2$ Hz, $J_{DH_a}=53.3$, Hz, $J_{DH_b}=4.05$ Hz, $J_{EH_b}=46.5$ Hz, $J_{EH_a}=3.42$ Hz, $J_{H_aH_b}=2.47$ Hz. MS (EI) m/z (^{79}Br): 409 ($M-F^+$, 1.3%); 317 ($M-CFHBr^+$, 100.0%); 181 [$CF_3CF_2C(CF_2)^+$, 22.4%], 143 ($CFHCFHBr^+$, 21.9%). MS (CI) m/z: 409 ($MH-HF^+$, 100%); 267 [$CF_3C(CF_3)_2OCFH^+$, 18.2%); 143 (CFHCFHBr, 32.4%). NMR $F^ASO_2OCF^BH_aCF^CH_bBr$ ^{1}H (acetone-d_6) δ: H_a 6.91 (d–d–d); H_b 7.18 (d,d,d). 19_F (acetone-d_6) δ: A $+44.5$ (1F, d); B -138.4 (1F, d,d,d,d); C -161.7 (1F, d–d–d); $J_{AB}=7.1$ Hz, $J_{BC}=19.8$ Hz, $J_{BH_a}=52.0$ Hz, $J_{BH_b}=8.9$ Hz, $J_{CH_b}=47.0$ Hz, $J_{CH_a}=7.2$ Hz, $J_{H_aH_b}=2.34$ Hz.

3. Results and discussion

Previously, Janzen and Pollitt [11] have claimed the synthesis of vicinal dihypochlorites, dihypobromites and dihypoiodites by the reaction of disodium perfluoropinacolate with Cl_2, Br_2 and ICl, respectively. This seems unlikely however based on our research in which Cl_2 or Br_2 fail to oxidize perfluorinated alkoxides.

In order to prepare an example of a perfluoroalkyl hypobromite, two possible routes were available: the use of an electropositive Br^I compound or the reaction of R_fOCl with Br_2. The latter reaction is based on the reaction of R_fSO_2OCl with Br_2 to prepare R_fSO_2OBr [12] and might be successful if the reaction were to occur at a sufficiently low temperature where the desired R_fOBr is stable, but this is not the case. The use of electropositive Br^I compounds is limited due to the low stability of many such compounds including BrF, but $BrOSO_2F$ has ideal properties. The use of $BrOSO_2F$ was successful in forming both $(CF_3)_3COBr$ and $C_2F_5C(CF_3)_2OBr$.

$$R_fONa \xrightarrow[-25\ \text{to}\ -20\ °C]{BrOSO_2F} R_fOBr$$

The yields in this reaction are only modest (20%–40%) because of several complications. The melting point of $BrOSO_2F$ is -31 °C and the reaction must be run at temperatures above this to ensure adequate contact with the alkoxide. At -25 °C, the R_fOBr is already undergoing slow decomposition and thus decreasing the isolated yield. The other main complication is the complexation of MF with $BrOSO_2F$ [13,14]. If excess $BrOSO_2F$ is added to account for this, then invariably unreacted $BrOSO_2F$ will be present in the desired R_fOBr. Using excess R_fONa minimizes the latter, but clearly this heterogeneous reaction is not stoichiometric at the required low temperature and some unreacted $BrOSO_2F$ was generally found in $C_2F_5C(CF_3)_2OBr$ preparations.

These new hypobromites readily decompose above ca. -20 °C by an assumed free radical β-elimination. As has been observed for a variety of hypochlorites and fluoroxy compounds, the rates of the decompositions are highly pressure-dependent, consistent with this proposal [15,16]. As mentioned in the Introduction, attempts to isolate $(CF_3)_2CFOBr$ and $(CF_3)_2CHOBr$ by the same route were unsuccessful. Under the same conditions the elimination of BrF and HBr occurred faster than the rate of product formation, resulting in $(CF_3)_2C{=}O$ as the only fluorocarbon product.

Due to their low thermal stability, evidence for these new hypobromites is mainly from their observed decomposition products and trapping by addition to alkenes. Pure samples of the hypobromites isolated as described under Experimental details decomposed to $(CF_3)_2CO$ and the alkyl bromide as the only observed products.

$$(CF_3)_3COBr \xrightarrow{>-20°\ C} (CF_3)_2CO + CF_3Br$$

$$C_2F_5C(CF_3)_2OBr \xrightarrow{>-20\ °C} (CF_3)_2CO + C_2F_5Br$$

While the t-pentyl derivative could conceivably form both C_2F_5Br and CF_3Br during decomposition, no evidence was found for this alternative decomposition to $C_2F_5C(O)CF_3$ and CF_3Br.

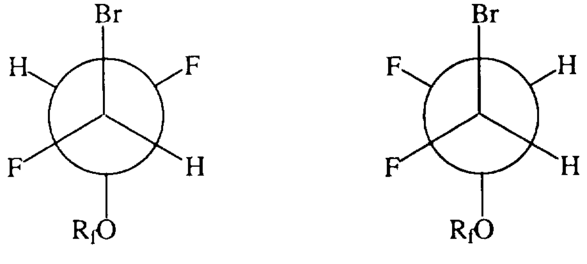
Direct spectroscopic evidence for $C_2F_5C(CF_3)_2OBr$ was obtained by ^{19}F NMR spectroscopy in n-$C_4F_9SO_2F$ as a solvent at −80 °C. The spectrum contained resonances for the three nonequivalent fluorine groups at −68.5; −80.0; −115.9 ppm in the ratio of 6:3:2 with the expected J_{FF} couplings (see Experimental details). The chemical shift values were similar to the alcohol $C_2F_5C(CF_3)OH$ (−72.2; −79.5; −118.5 ppm; acetone-d_6) with significant shifts to lower field for the CF_2 and CF_3 groups on the tertiary carbon as expected [5,6]. The δ_F value for $(CF_3)_3COBr$ would be expected to be near −70.0 ppm compared to −74.7 ppm ($CDCl_3$) for $(CF_3)_3COH$ and based on values of −69 to −70 ppm ($CFCl_3$) for a variety of $(CF_3)_3COX$ and $(CF_3)_3COO$– derivatives [17,18]. Unfortunately, long after the completion of this work, it was discovered that the ^{19}F NMR spectrum of $(CF_3)_3COBr$ had not been attempted under conditions that would have allowed it to be observed.

The reactions of the hypobromites were carried out in each case with $CF_2{=}CH_2$, $CF_2{=}CCl_2$ and $CF_2{=}CF_2$ in order to compare their reactivity and regiospecificity with related hypochlorites. The polyfluorinated ethers produced from these reactions are stable, inert, colorless liquids at room temperature. The use of ^{19}F, ^1H and ^{13}C NMR spectroscopy allowed easy identification of the products and their ratios in the case of the regio isomers. The ^{19}F NMR spectrum of the material obtained by reaction of $(CF_3)_3COBr$ and $CF_2{=}CH_2$ initially posed some problem. At 25 °C the signals due to the expected ether and another ether gave overlapping signals at −70.3; −70.4; −70.5; −70.6; −70.7 ppm. However upon heating to 140 °C in $Cl_2CD/DCCl_2$, the signals shifted so as to allow easy interpretation of the spectrum. In general, there was almost a complete lack of parent ions in the EI or CI mass spectra. This is quite general for halogenated compounds of this type where intense ion peaks are observed for the $(M-X)^+$ species where X = F, Cl [10,19]. This observation may be explained by protonation at oxygen in the ethers to form an unstable oxonium ion, which immediately undergoes loss of HX involving the adjacent α-halogen atoms.

The products of the addition reactions are summarized in Table 1. The yields of the polyfluorinated ethers are based on the amount of bromine(I) fluorosulfate ($BrOSO_2F$) used and were in general between 25%–30%. This is a result of the low stability of the hypobromites and the limitations in their synthesis as discussed above. In some cases the desired ether(s) were contaminated with small amounts of fluorosulfates formed by reaction of $BrOSO_2F$ with the olefins, due to the failure of the $BrOSO_2F$ to react completely with excess $NaOR_f$. This can be avoided by first separating the hypobromite, but the large loss of R_fOBr in a single pass through appropriate cold traps made this undesirable for the purpose of screening their reactivity with alkenes.

The regioselectivity of the reaction involving hypobromites with alkenes is such that a bond is usually formed between the halogen atom of the hypobromite and the most electron-rich carbon of the alkene. However when the difference in electron density on both carbons is small, as in the case of $CF_2{=}CCl_2$, the reaction with $(CF_3)_3COBr$ gave both regio isomers in the ratio of 75 (–CCl_2Br) to 25 (–CF_2Br). In the reactions involving 1,1-difluoroethylene, the reactions were regiospecific but the formation of some R_fOH was observed with both hypobromites. This may be due to side-reactions involving hydrogen abstraction by decomposition of the hypobromites. The formation of some $(CF_3)_3COCF_2CHBr_2$ may have arisen in the same way. No alcohol was produced in reactions involving the olefins $CF_2{=}CCl_2$ and $CF_2{=}CF_2$ with the hypobromites.

In order to examine the stereochemistry of the addition of perfluoroalkyl hypobromites to olefins and to determine whether their addition is *cis* (*syn*) or *trans* (*anti*), the reaction of $CF_3CF_2C(CF_3)_2OBr$ was carried out with *cis*-CFH=CFH. The $^3J_{HF}$, $^3J_{FF}$ and $^3J_{HH}$ couplings in the adduct can then be used to determine the stereospecificity of the reaction. The $^3J_{FF}$ coupling is the easiest value to ascertain; however, it is the least reliable as a probe for structural determination because substituent effects dominate any possible dependence on the dihedral angle [20]. While the $^3J_{HH}$ coupling is the most useful, it is often the most difficult to extract from the observed ^1H spectrum. Assuming that the most abundant rotomer in both *erythro* and *threo* stereoisomers has the R_fO group *trans* to Br, then the vicinal fluorines are *trans* for *erythro* and *gauche* for *threo*. For a series of related compounds it may be a reasonable conclusion that the larger $^3J_{FF}$ value belongs to the *threo* isomer and the smaller $^3J_{FF}$ value to the *erythro* isomer.



Erythro *Threo*

DesMarteau and coworkers have reported the $^3J_{FF}$ values for the *erythro* and *threo* isomers obtained by the reaction of CF_3SO_2OBr and CF_3CO_2Cl with *cis*- and *trans*-CFH=CFH [21–24] to be 19.5 and 25.5, and 15.4 and 20.4 Hz, respectively. Such results, in conjunction with the idea that the larger $^3J_{FF}$ value belongs to the *threo* isomer, were used to argue in favor of *cis* addition mechanism. In the case of the reaction of $CF_3CF_2C(CF_3)_2OBr$ with CFH=CFH, the value of the $^3J_{FF}$ coupling constant obtained for the *cis* adduct was 24.2 Hz, suggesting that the addition is *trans*, just the opposite of what is observed for the addition of CF_3SO_2OBr.

Fortunately the $^3J_{HH}$ coupling was easily observed in the ^1H NMR spectrum for the ether produced by the reaction of *cis*-CFH=CFH with the hypobromite and found to be 2.47 Hz. Using the Karplus equation (25) and the $^3J_{H_aH_b}$ coupling constant, the dihedral angle between the vicinal hydrogens (ϕ) was calculated to be 54.4°, implying that the vicinal hydrogens are *gauche*.

Only a few $^3J_{HH}$ values have been assigned in related compounds and in general $^3J_{HH}$(*erythro*)$^3J_{HH}$ (*threo*). Two compounds which provide an interesting comparison are $CF_3CHBrCHBrF$ and $CF_3CHICHFCF_3$ [26,27]. In these two compounds the $^3J_{HH}$ values in Hz for the *erythro* and *threo* diastereomers are as follows: $CF_3CHBrCHBrF$ (5.5, 2.8); $CF_3CHICHFCF_3$ (7.2, 1.8). Thus the available data suggest that the *threo* diastereomer is formed via an *anti* addition. Due to the unavailability of a sample of *trans*-CFH=CFH to confirm the *erythro* isomer expected for the same addition with smaller $^3J_{FF}$ and larger $^3J_{HH}$ values, this conclusion is tentative.

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