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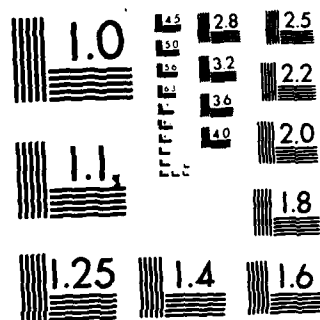
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A Simple Photochemical Conversion of Perfluoroalkyl Hydrides to
Perfluoroalkyl Bromides Using Interhalogen Compounds

by

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A Simple Photochemical Conversion of Perfluoroalkyl Hydrides to
Perfluoroalkyl Bromides Using Interhalogen Compounds

by

James L. Adcock and William D. Evans

It is an accepted principle that the inductive effects of halogen substituents reduces the reactivity of hydrogen to radical abstraction by chlorine¹⁻³ or bromine atoms.⁴ Furthermore it is accepted that resonance effects of halogen substituents have an effect on geminal hydrogen reactivity which is opposite that of their inductive effects.³ Copp and Tedder have shown that substitution of hydrogen by chlorine lowers the activation energy for radical abstraction of geminal hydrogen by bromine, while substitution of hydrogen or chlorine by fluorine raises the activation energy for radical abstraction by bromine.⁴ The increase in activation energy for hydrogen abstraction on fluorinated and chlorofluorinated methanes for bromination would seem to apply to direct fluorinations as well. For example, fluorine substitution of neopentanes tends to produce preferentially the symmetrically substituted polyfluoro neopentanes.⁵

Despite the deactivation of hydrogens toward radical abstraction in fluorocarbons, photochemical bromination and chlorination of hydryl-F-alkanes have been previously reported in early work by Haszeldine⁶ and by Benning and Park.⁷ Thermal brominations of hydryl-F-alkanes have been studied by Amphlett and Whittle at temperatures in excess of 400°C.⁸ They have also shown increases in the activation energies in hydrogen abstraction by bromine in the fluoromethane series: CFH_3 , CF_2H_2 , CF_3H , and also document the reversibility of the bromination reaction due to its inhibition by HBr .⁸

As part of a research effort directed at the construction of highly branched fluorocarbon networks, we sought convenient ways to introduce

reactive groups onto hydryl-F-neopentanes and other fluorocarbons. This led us to attempt several photochemical bromination schemes. We were able to confirm the very facile room temperature, gas phase photo-chlorination of hydryl-F-alkanes but were not able to achieve significant photo-bromination of these molecules at ambient temperatures. Thermal bromination was unsuccessful at 250°C, and, higher temperatures resulted in significant fluorocarbon skeletal fragmentation. Efforts were then directed toward interhalogen compounds as potential bromination reagents. It is the results of those investigations which are the basis of this report.

Results and Discussion

Because the reactivity of chlorine with hydryl-F-neopentane was high and that for bromine was so low, the first interhalogen which suggested itself was bromine chloride. A search of the literature produced many instances where bromine chloride was used as a reactive electrophilic brominating agent but far fewer instances where it was used as a free radical brominating agent. These examples have been reviewed in some detail by Mills and Schneider.⁹ Among the free radical reaction examples was a reference to the bromination of fluoroform by bromine chloride which reportedly produced exclusively bromotrifluoromethane.¹⁰

Bromine chloride (mp -66°C, bp 5°C) is approximately 40% dissociated at 25°C ($k_d^\circ = 0.34$) into bromine (mp -7.2°C, bp 58.8°C) and chlorine (mp -103°C, bp -34.6°C).¹¹ It is a polar, reactive electrophile and its selectivity as a brominating agent is apparently due to the attraction of the electron rich radical to the positive (bromine) end of the molecular dipole of BrCl.⁹ Given this hypothesis, the more electrophilic the radical the less selective will be the bromination.

The reaction of hydryl-F-neopentane with bromine chloride was much slower (100 hrs) than the ambient temperature chlorination of that compound (10 minutes). The reaction was followed by gas phase infrared spectroscopy. Although bromo-F-neopentane formed much faster initially than chloro-F-neopentane, the latter compound was negligible in yields only for overall conversions of less than 10%. As the reaction reached completion (304 hrs) the percentages of bromo- to chloro-F-neopentane was 48% to 43%. A slight excess of bromine to chlorine and a slightly shorter (254 hrs) reaction time slightly increases the yield of bromo-F-neopentane. The ^{19}F NMR data (Table 1) are characteristic and easily interpretable.

The reactions of 1,3-dihydryl-F-neopentane under similar conditions are summarized in Table 2. All possible products were produced. For example in Rxn. 1, 1,3-dibromo-(31.5%), 1-bromo-3-chloro-(18.6%), 1-bromo-3-hydryl-(29.2%), 1,3-dichloro-(6.5%) and 1-chloro-3-hydryl-(11.4%) were produced. The overall ratio of chlorination to bromination was 1:2.6. Increases in chlorine concentration (Rxn. 2) and increases in overall reaction time (Rxn. 3) markedly increased the yield of 1-bromo-3-chloro-F-neopentane (29.4% and 32%, respectively). Decreases in chlorine concentration (or increases in bromine concentration), Rxn. 4, significantly increased the yield of 1-bromo-3-hydryl-F-neopentane (48%) and recovered starting material (10%). The optimum reaction (Rxn. 1) for making 1,3-dibromo-F-neopentane produced 2.6 times as much bromination as chlorination products, however, optimal bromination (4.4:1) occurred for reaction 4 which produced predominately 1-bromo-3-hydryl-F-neopentane (48%).

It is apparent from these results that the proportion of chlorination to bromination increases both with the concentration of chlorine and with overall reaction time. Conversely, the proportions of brominated to chlorinated products decreased with reaction time.

In a set of control experiments F-neopentyl bromide and chlorine gas irradiated for 30 hours produced approximately 8% F-neopentyl chloride, 90% recovered F-neopentyl bromide and 2% F pivaloyl chloride. The converse reaction of F-neopentyl chloride with bromine did not occur. Furthermore F-neopentyl bromide plus hydrogen (and also deuterium) did not react. The reaction of F-neopentyl bromide with mercury, however, produced 20% F-2,2,5,5-tetramethylhexane (F-dineopentyl) after 47 hours of irradiation. The chloride produced only a trace of the coupled product under similar conditions.

These experiments suggest that although the bromides are produced faster, they are more reactive and are gradually consumed, i.e. converted to the chlorides in the interhalogen reactions.

The reaction of 2-difluoromethyl-2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane with BrCl produced much higher yields of perhalogenated products: 59.5% bromo- and 37.5% chloro-F-dioxolanes. This is likely a result of the increased reactivity of the starting compound. The reaction of BrCl and 1-hydryl-F-2,5-dioxohexane (hydryl-F glyme, $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$) however, does not go to completion but "equilibrates" at 37.1% chloro-, 34.5% bromo and 28.4% starting material.

The reactions of BrCl with 2-hydryl-F-dioxane and 4-hydryl-F-2,2-dimethyl-1,3-dioxolane result in extensive decomposition of both fluorocarbons. Neither reaction produced identifiable amounts of the chloro- or bromo- analogs, nor were significant amounts of starting material recovered in either case.

The "chlorobromination" reaction is a significant improvement over the metallation-bromination of hydryl-F-neopentane; the only previously reported route to bromo-F-neopentane.¹² The metallation route, however, remains the

preferred route to iodo-F-neopentane. Photolysis of ICl and hydryl-F-neopentane produced chloro-F-neopentane, HCl and I₂. This failure is not surprising because of the photo-lability of F-alkyl iodides and the low reactivity of iodine atoms.

Despite the improvement in convenience of the chlorobromination over the metallation route, it is still slow and produces considerable amounts of undesired chlorofluorocarbons. In search of a faster, more efficient brominating agent, we immediately began to investigate the possibility of using bromine fluoride, BrF. Bromine monofluoride (mp -33°C, bp 20°C) is not stable but disproportionates extensively (55% at 55°C; 55 torr) to bromine (mp -7.2°C, bp 58.8°C) and bromine trifluoride (mp 9°C, bp 126°C). Dissociation to the elements is not appreciable at room temperature ($K_d^\circ = 8 \times 10^{-3}$). Because of the disproportionation of BrF to BrF₃ and Br₂, special techniques were required to minimize contact between the hydryl-fluorocarbons and BrF₃ and to prevent the liquid BrF₃ from attacking the quartz reactor. The net reaction: $\text{BrF} + \text{R}_\text{F}\text{H} \rightarrow \text{R}_\text{F}\text{Br} + \text{HF}$, also requires a hydrogen fluoride scavenger to prevent HF attack on the quartz. These conditions were met relatively easily by placing a 9mm x 50mm "Teflon" FEP¹⁴ test tube vertically in the bottom of the cylindrical quartz reactor (170mL) surrounded by anhydrous sodium fluoride pellets to absorb HF and support the "Teflon" tube. A threefold stoichiometric amount of BrF₃ was syringed into the teflon test tube. The tube was cooled and evacuated. Then the stoichiometric amount of hydryl fluorocarbon and a threefold stoichiometric amount of bromine were introduced. Photolysis began as soon as frost cleared the tube and the fluorocarbon and bromine evaporated. The much lower vapor pressure of BrF₃ and the large vapor phase excess of bromine maintained the disproportionation substantially toward BrF. Some BrF and BrF₃ evidently

form adducts with the NaF because at the completion of the reaction (24 hrs) all of the volatile BrF_3 had been consumed.

"Fluorobromination" of hydryl-F-neopentane produced 78.6% bromo-F-neopentane and 6.6% F-neopentane. The remainder consisted of recovered starting material plus, occasionally, an unidentified F-acid fluoride probably formed by contaminant oxygen from attack by BrF_3 on the quartz. "Fluorobromination" of 1,3-dihydryl-F-neopentane produced 20% 1,3-dibromo-F-neopentane, 15% 1-bromo-3-hydryl-F-neopentane with 60% of the starting material recovered. No traces of bromo-F-neopentane or F-neopentane were found.

Experimental Part

Hydryl-F-neopentane, 1,3-dihydryl-F-neopentane, 4-hydryl-F-2,2-dimethyl-1,3-dioxolane, 2-difluoromethyl-2-trifluoromethyl-F-1,3-dioxolane, 2-hydryl-F-1,4-dioxane were major products isolated from nonphotochemically finished, aerosol direct fluorinations of neopentane, 2,2-dimethyl-1,3-dioxolane and 1,4-dioxane respectively.⁵ Some 2-hydryl-F-1,4-dioxane, 1-hydryl and 1,3-dihydryl-F-neopentanes and all of the 1-hydryl- and 3-hydryl-F-2,5-dioxahexanes [hydryl-F-(ethyleneglycol dimethylethers)] were produced by LTG direct fluorination techniques.^{12,15} Bromine (Fisher), chlorine (Linde) and bromine trifluoride (Matheson) were commercial products which were purified by vacuum line fractionation, using flexible "Teflon" PTFE tubing as traps in the case of BrF_3 . Photolysis reactions were conducted in a 170 mL cylindrical quartz vessel (~40mm x ~135mm) fitted with a Kontes 0-4mm "Hivac" stopcock through a graded seal. Contents were irradiated using a 125W Hanovia medium pressure mercury vapor arc lamp. Ambient temperature inside the enclosure was approximately 35°C during operation. The reaction was monitored at half day intervals by withdrawing some

of the gas phase products into a 10cm gas infrared cell (KCl windows). Following the reaction, excess halogens were absorbed by condensation of the product into a tube containing a filter paper wet with oleic acid. Nonreactive products were vacuum transferred and subjected to a work-up which consisted of vacuum line fractionation; infrared assay of fractions; gas chromatographic separation of components using either a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed, chromosorb p conditioned at 225°C (12 hrs) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb p, conditioned at 225°C (12 hrs). Following gas chromatographic separation (Bendix Model 2300, subambient multi-controller), all products of "significance" were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry, PE1330; electron impact (70eV) and chemical ionization (CH₄ plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980A MS, 5934A Computer); and ¹H and ¹⁹F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in CDCl₃ with 1% CFCl₃ internal standard. Elemental analyses, where necessary, were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Hydryl-F-Neopentane: BrCl - Hydryl-F-neopentane (0.508 mmol, 0.1371 g), chlorine (0.480 mmol, 0.340 g) and bromine (0.572 mmol, 0.0915 g) were condensed into the evacuated quartz cylindrical bulb. The contents of the bulb were warmed to ambient temperature, until all reactants were evaporated. The contents were then irradiated for a total of 254 hours. The irradiation was interrupted at half day intervals for infrared examination. Workup of the products produced 52% bromo-F-neopentane, 45% chloro-F-neopentane with 3% recovered starting material. See Table I for characterization.

1,3-Dihydril-F-neopentane: BrCl - 1,3-Dihydril-F-neopentane was reacted with bromine chloride under several sets of conditions which are outlined in Table 2. The effect on product distributions by changes in Cl_2/Br_2 ratios and reaction times are tabulated. Reactions were performed in a manner similar to the hydril-F-neopentane reactions. Characterizations of products are also given in Table 1.

F-Neopentyl Bromide: Cl_2 - Bromo-F-neopentane (0.03 mmol, 0.010 g) and chlorine (0.09 mmol, 0.0064 g) were condensed into the evacuated quartz cylindrical bulb. The contents were warmed to ambient temperature, and then irradiated with the 125 watt mercury vapor lamp for a total of 30 hours. The irradiation was interrupted three times at 2 hour intervals and at 6 hour intervals thereafter for infrared examination. The C-Cl band of F-neopentyl chloride at 860 cm^{-1} was noticeable after two hours as a shoulder on the C-Br band of F-neopentyl bromide at 840 cm^{-1} . Gas chromatographic assay of the total product indicated 90% F-neopentyl bromide, 8% F-neopentyl chloride and 2% F-pivaloyl chloride.

F-Neopentyl Bromide: Hg - Bromo-F-neopentane (0.04 mmol, 0.014 g) and mercury (0.5 mmol, 0.1 g) were combined in the evacuated quartz cylindrical bulb and irradiated for 47 hours with the 125 watt mercury lamp. Gas chromatographic assay of the total product indicated a mixture of 20% dimer, F-2,2,5,5-tetramethylhexane identified by its infrared spectra.^{12,16} The remainder consisted of unchanged starting material.

F-Neopentyl Chloride: Hg - Chloro-F-neopentane (0.20 mmol 0.062 g) and mercury (1 mmol, 0.2 g) were combined in a second quartz vessel and the

reaction carried out simultaneously with the bromo-F-neopentane reaction. Only a trace of dimer was produced in this reaction. Identification was made by g/c retention time comparison of products with the bromo-F-neopentane run.

1-Hydril-F-2,5-dioxahexane: BrCl - 1-Hydril-F-2,5-dioxahexane (0.3077 mmol, 0.075 g), chlorine (0.318 mmol, 0.0225 g) and bromine (0.3206 mmol, 0.0521 g) were condensed into the quartz bulb. On warming, the mixture was irradiated for 302 hours before coming to equilibrium. Workup produced 1-bromo-F-2,5-dioxahexane (34.5%), 1-chloro-F-2,5-dioxahexane (37.1%) and recovered starting material (28.4%). Characterizations are given in Table 3.

2-Difluoromethyl-2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane¹⁷: BrCl - The starting material (0.563 mmol, 0.150 g), chlorine (0.588 mmol, 0.0417 g) and bromine (0.588 mmol, 0.0939 g) were condensed into the quartz bulb. On warming, the mixture was irradiated for 192 hours. Workup produced 2-bromodifluoromethyl-2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane (59.5%), the analogous chloro-F-dioxolane (37.5%),¹⁷ and recovered starting material (2.3%). Characterizations are given in Table 4.

Hydril-F-neopentane: BrF - The quartz bulb used in the BrCl reactions was fitted with a 9 mm x 50 mm "Teflon" FEP test tube, supported vertically in the bottom, and charged with approximately 25 g of sodium fluoride, 1/8" pellets (Harshaw). Approximately 1.80 mmol (0.10 ml, 0.25 g) of bromine trifluoride was syringed into the test tube under a nitrogen atmosphere. The quartz bulb was cooled with liquid nitrogen, evacuated, and 0.167 g (0.620 mmol) hydril-F-neopentane and 0.290 g (1.80 mmol) bromine were condensed into the bulb. On warming, the mixture was irradiated for a total of 108 hours,

although infrared assay showed little change after 24 hours. Workup produced bromo-F-neopentane (78.6%), F-neopentane (6.6%) and recovered starting material (14%). See Table 1 for characterization.

1,3-Dihydril-F-neopentane: BrF - 1,3-Dihydril-F-neopentane (0.345 mmol, 0.0868 g) and bromine 0.313 mmol, 0.050 g) were condensed into the quartz bulb containing the bromine trifluoride (0.90 mmol, 0.05 ml, 0.12 g). On warming, the mixture was irradiated for 64 hours with most of the reaction occurring within the first 24 hours. Workup of the product produced 1,3-di-bromo-F-neopentane (20%), 1-bromo-3-hydril-F-neopentane (15%), hydril-F-neopentane (trace) and unreacted starting material (60%). See Table 1 for characterization.

TABLE I
¹⁹F NMR^a DATA AND ELEMENTAL ANALYSES OF SUBSTITUTED F-HEOPENTANES

	Chemical Structure	CF ₃	CF ₂ Br	CF ₂ Cl	Remarks	Elemental Analysis	
						Theor.	Obs.
1)	$\begin{array}{c} \text{CF}_3 \\ \\ \text{CF}_3-\text{C}-\text{CF}_2\text{Br} \\ \\ \text{CF}_3 \end{array}$	-63.84 ppm (t) J _{FF} = 10.5 Hz	-47.94 ppm (detect)	—	mp. 51.5-52.0°C		
2)	$\begin{array}{c} \text{CF}_3 \\ \\ \text{CF}_3-\text{C}-\text{CF}_2\text{Cl} \\ \\ \text{CF}_3 \end{array}$	-64.18 ppm (t) J _{FF} = 10.7 Hz	—	-52.29 ppm (detect)	mp. 77.5-78.0°C	%C 19.72% %F 68.63%	19.67% 68.60%
3)	$\begin{array}{c} \text{CF}_2\text{Br} \\ \\ \text{CF}_3-\text{C}-\text{CF}_2\text{Br} \\ \\ \text{CF}_3 \end{array}$	-62.29 ppm (p) J _{FF} = 9.77 Hz	-46.56 ppm (hept.)	—		%C 14.65% %F 46.35%	14.74% 46.56%
4)	$\begin{array}{c} \text{CF}_2\text{Cl} \\ \\ \text{CF}_3-\text{C}-\text{CF}_2\text{Br} \\ \\ \text{CF}_3 \end{array}$	-63.35 ppm (p) J _{FF} = 11.4 Hz	-47.30 ppm (mult.)	-51.35 ppm (mult.)			
5)	$\begin{array}{c} \text{CF}_2\text{Cl} \\ \\ \text{CF}_3-\text{C}-\text{CF}_2\text{Cl} \\ \\ \text{CF}_3 \end{array}$	-62.95 ppm (p) J _{FF} = 10.5 Hz	—	-51.05 ppm (hept.)		%C 18.71% %F 59.20%	18.85% 58.91%
6)	$\begin{array}{c} \text{CF}_2\text{Br} \\ \\ \text{CF}_3-\text{C}-\text{CF}_2\text{H} \\ \\ \text{CF}_3 \end{array}$	-63.45 ppm (p) J _{FF} = 9.77 Hz	-47.95 ppm (m)	—	$\delta_{\text{CF}_2\text{H}} = -125.36 \text{ ppm (d.mult.)}$ $\delta_{\text{CF}_2\text{H}} = 6.29 \text{ ppm (t)}$ $J_{\text{CF}_2\text{H}} = 51.0 \text{ Hz (}^1\text{H)}, 53.7 \text{ Hz (}^1\text{F)}$		
7)	$\begin{array}{c} \text{CF}_2\text{Cl} \\ \\ \text{CF}_3-\text{C}-\text{CF}_2\text{H} \\ \\ \text{CF}_3 \end{array}$	-63.85 ppm (p) J _{FF} = 9.77 Hz	—	-52.44 ppm	$\delta_{\text{CF}_2\text{H}} = -125.51 \text{ ppm (d.mult.)}$ $\delta_{\text{CF}_2\text{H}} = 6.28 \text{ ppm (t)}$ $J_{\text{CF}_2\text{H}} = 50.9 \text{ Hz (}^1\text{H)}, 48.8 \text{ Hz (}^1\text{F)}$		

(a) Relative to CFCl₃ (10% internal) = 0.0 ppm, CCl₄.
 (b) See Reference 12.

TABLE 2

Reaction of 1,3-Dihydril-F-neopentane with BrCl
Product Distributions Versus Reaction Conditions

Rxn No.	1,3-DiH g	Mole Ratios ^a of		Reaction Time (Hr)	H, H ^b	1,3-Product Distribution (mole %)				Br, Br	Bromination to Chlorination Ratio ^c
		Cl ₂	Br ₂			H, Cl	Cl, Cl	H, Br	Br, Cl		
1.	0.663	1.113	1.165	186	2.7	11.4	6.5	29.2	18.6	31.5	2.6
2.	0.302	1.311	1.315	180	2.0	9.8	9.8	24.6	29.4	24.5	1.75
3.	0.608	0.975	0.980	302	1	7	9	35	32	16	1.74
4.	0.354	0.93	1.75	173	10	8	3	48	9	22	4.4

(a) Relative to 1,3-dihydril-F-neopentane.

(b) Recovered 1,3-dihydril-F-neopentane.

(c) Calculated as mmoles C-Br bonds to mmoles C-Cl bonds in 1,3- Product Distribution.

TABLE 3

¹⁹F NMR Data¹ on 1-Substituted-F-2,5-dioxahexanes

Derivative	CF ₃ -O-CF ₂ -CF ₂ -O-CF ₂ -X				
	a	b	c	d	e
	CF ₃ (a)	CF ₂ (b)	CF ₂ (c)	CF ₂ (d)	X(e)
1-Hydryl	-59.23 ppm (t) J _{ab} = 9.4 hz	-93.63 ppm (q) J _{bc} ≈ 0 hz	-92.47 ppm (t) J _{cd} = 4.5 hz	-88.36 ppm (d·t) J _{de} = 68.9 hz	δ = 3.74 ppm (t)
1-Bromo	-55.75 ppm (t) J _{ab} = 8.79 hz	-91.06 ppm (q) J _{bc} ≈ 0 hz	-90.13 ppm (t) J _{cd} = 10.74 hz	-19.19 ppm (t)	
1-Chloro	-55.74 ppm (t) J _{ab} = 8.79 h	-91.06 ppm (q) J _{bc} ≈ 0 hz	-90.52 ppm (t) J _{cd} = 10.74 hz	-27.46 ppm (t)	

(1) Relative to CFCl₃ (10% internal) = 0.0 ppm, CDCl₃.

(2) See reference 14.

(3) Elemental Analysis: Calculated for C₄F₉O₂Br: %C 14.52%, %F 51.67%; Found %C 14.38%, %F 51.31%.

TABLE 4

 ^{19}F NMR¹ Data of Some F-1,3-Dioxolane Derivatives

F-1,3-Dioxolane	CF ₂	CF ₃	CF ₂ (X)	X
$ \begin{array}{c} \text{CF}_2\text{-O} \quad \text{CF}_3 \\ \quad \diagdown \\ \text{C} \\ \quad \diagup \\ \text{CF}_2\text{-O} \quad \text{CF}_2\text{H} \end{array} $	-83.35 ppm (hexet) [4] 3	-82.35 ppm (t·p·d) [3]	-138.01 ppm (d·q·p) [2] $J_{\text{HF}} = 53.1 \text{ hz } (^{19}\text{F})$	$\delta_{\text{CF}_2\text{H}} = 5.996 \text{ ppm } (t)^2$ $J_{\text{HF}} = 52.2 \text{ hz } (^1\text{H})$
	$J_{\text{CF}_2\text{X}-\text{CF}_2} = J_{\text{CF}_3-\text{CF}_2} = 2.0 \text{ hz}$			
$ \begin{array}{c} \text{CF}_2\text{-O} \quad \text{CF}_3 \\ \quad \diagdown \\ \text{C} \\ \quad \diagup \\ \text{CF}_2\text{-O} \quad \text{CF}_2\text{Br} \end{array} $	-81.40 ppm (s) ⁴ [4]	-78.76 ppm (t) [3]	-63.71 ppm (q) [2]	
$ \begin{array}{c} \text{CF}_2\text{-O} \quad \text{CF}_3 \\ \quad \diagdown \\ \text{C} \\ \quad \diagup \\ \text{CF}_2\text{-O} \quad \text{CF}_2\text{Cl} \end{array} $	-81.78 ppm (s) ⁴ [4]	-79.43 ppm (t) [3]	-68.54 ppm (q) [2]	

(1) Relative to CFCl_3 (10% internal) $\equiv 0.0 \text{ ppm}$, CDCl_3 .

(2) See ref. 15.

(3) [integral].

(4) $J_{\text{CF}_2\text{CF}_2}$ and $J_{\text{CF}_3-\text{CF}_2} < 2 \text{ hz}$.(5) Elemental Analysis: Calculated for $\text{C}_5\text{F}_9\text{O}_2\text{Br}$: %C = 17.51%, %F = 49.86%; Found %C 17.52%, %F 49.35%.

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