Journal of Fluorine Chemistry, 21 (1982) 287–293

Received: March 22, 1982

THE PREPARATION AND PROPERTIES OF PERFLUORO-n-HEPTYLBROMINE(V) TETRAFLUORIDE

M. H. HABIBI and L.C. SAMS

Department of Chemistry, The Texas Woman's University,
Denton, Texas 76204 (U.S.A.)

SUMMARY

Reactions of n-$C_7F_{15}Br$ with elemental fluorine at 0°C have produced perfluoro-n-heptylbromine(V) tetrafluoride (n-$C_7F_{15}BrF_4$). This derivative of BrF_5 was characterized by IR, ^{19}F-NMR, mass spectroscopy and elemental analysis. The reactions of n-$C_7F_{15}BrF_4$ with 1,2-dichlorohexafluorocyclopentene-1 ($C_5F_6Cl_2$) and 1,2-dichlorooctafluorocyclohexene-1 ($C_6F_8Cl_2$) were used to demonstrate in the fluorinating ability of n-$C_7F_{15}BrF_4$.

INTRODUCTION

The syntheses of several perfluoroalkyliodine(V) tetrafluorides have been reported. These compounds were prepared by fluorination of perfluoroalkyl iodides with elemental fluorine [1,3], ClF_3[2,3] and BrF_3[3]. The preparation of pentafluorophenylbromine(V) tetrafluoride has been reported [4].

RESULTS AND DISCUSSION

Preparation

Perfluoro-n-heptylbromine(V) tetrafluoride was synthesized by allowing n-$C_7F_{15}Br$ and elemental fluorine to react in a Monel cylinder at 0°C for eighteen hours. The reaction

0022-1139/82/0000-0000/$02.75

products were dissolved in n-C_6F_{14} and a colorless liquid was isolated from the reddish-brown solution by gas chromatography. It oxidized four equivalents of KI per mole.

$$n\text{-}C_7F_{15}BrF_4 + 4KI \longrightarrow n\text{-}C_7F_{15}Br + 2I_2 + 4\ KF$$

Mass Spectrum

The mass spectrum, detailed in Table 1, consists of molecular ions at m/e 524 and 526 and expected fragment ions. The expected isotope pattern (1:1) for ^{79}Br and ^{81}Br was observed for fragments containing Br, and the peak at m/e 69 was assigned to CF_3^+ as the base peak.

TABLE 1

Mass Spectrum

m/e	Relative Abundance	Ion
526	3	$[C_7BrF_{19}]^+$
524	3	$[C_7BrF_{19}]^+$
469	12	$[C_7BrF_{16}]^+$
467	12	$[C_7BrF_{16}]^+$
369	75	$[C_7F_{15}]^+$
281	45	$[C_4BrF_8]^+$
279	43	$[C_4BrF_8]^+$
169	80	$[C_3F_7]^+$
157	40	$[BrF_4]^+$
155	38	$[BrF_4]^+$
69	100	$[CF_3]^+$

NMR spectra

A comparison of the NMR spectra of n-$C_7F_{15}Br$ and n-$C_7F_{15}BrF_4$ is given in Table 2. The integration of the +140.2 ppm signal is consistent with four fluorines (relative to fluorines of the α-CF_2 group) in the same magnetic environment, similar to the equatorial fluorines of BrF_5. The R_F chemical shifts are as expected by comparison with perfluoro-n-heptyl bromide.

TABLE 2

The ^{19}F-NMR spectra of n-$C_7F_{15}Br$ and n-$C_7F_{15}BrF_4$

$$CF_3-\underset{\xi}{CF_2}-\underset{\varepsilon}{CF_2}-\underset{\delta}{CF_2}-\underset{\gamma}{CF_2}-\underset{\beta}{CF_2}-\underset{\alpha}{CF_2}-Br$$

$$CF_3-\underset{\xi}{CF_2}-\underset{\varepsilon}{CF_2}-\underset{\delta}{CF_2}-\underset{\gamma}{CF_2}-\underset{\beta}{CF_2}-\underset{\alpha}{CF_2}-BrF_4$$

Compound	Chemical Shifts (ppm)[a]			Coupling Constant (Hz)		
	$\delta(CF_3)$	$\delta(CF_2)$	$\delta(BrF_4)$	J(FBrCF)	J(FBrCCF)	Others
n-$C_7F_{15}Br$	-81.3	-63.1(F_α)[b]	-	-	-	-
		-126.7 F_β				
		-123.0 F_γ				
		-122.2 F_δ				
		-121.3 F_ε				
		-117.7 F_ξ				
n-$C_7F_{15}BrF_4$	-82.8	-65.3(F_α)[b]	+ 140.2	28	28	J(CF_α-CF_3) 28
		-127.5 F_β				
		-123.8 F_γ				
		-122.9 F_δ				
		-122.0 F_ε				
		-118.4 F_ξ				

[a] From CCl_3F as internal reference, upfield is negative.

[b] First order spectra.

IR spectra

The liquid phase infrared spectrum consists of absorption bands at 1230(s), 1200(vs), 1147(s), 1115(m), 978(m), 820(w), 720(w), 700(m), 680(s), 648(m), 570(vs), and 530(m) cm^{-1}. This spectrum is comparable with that of other n-C_7F_{15} groups [5] and the strong bands at 680 and 570 cm^{-1}comparable to the 683 and 587 cm^{-1} bands of bromine pentafluoride [6]. This spectrum is also comparable with the IR of $C_6F_5BrF_4$[4].

Stability and hydrolysis

Perfluoro-*n*-heptylbromine(V) tetrafluoride decomposes slowly at room temperature, giving a mixture of *n*-C_7F_{16}, Br_2, and n-$C_7F_{15}Br$. It hydrolyzes and ^{19}F-NMR analysis of the hydrolysis products showed the presence of *n*-$C_7F_{15}Br$ and HF.

Reaction with $C_5F_6Cl_2$

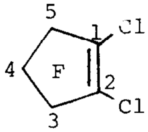
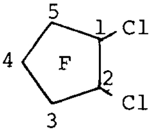
When excess of 1,2-dichlorohexafluorocyclopentene-1 [7] ($C_5F_6Cl_2$) was allowed to react with *n*-$C_7F_{15}BrF_4$ in a Monel reactor at 120°C for 8 hours, NMR and mass spectra showed that 1,2-dichlorooactafluorocyclopentane ($C_5F_8Cl_2$) and *n*-$C_7F_{15}Br$ has been formed according to the equation:

$$2\ C_5F_6Cl_2 + \underline{n}\text{-}C_7F_{15}BrF_4 \longrightarrow 2C_5F_8Cl_2 + \underline{n}\text{-}C_7F_{15}Br$$

The NMR data for $C_5F_6Cl_2$ and $C_5F_8Cl_2$ are given in Table 3.

TABLE 3

The Chemical Shifts of $C_5F_6Cl_2$ and $C_5F_8Cl_2$

Compound	Structure	^{19}F nucleus	Chemical Shifts*
$C_5F_6Cl_2$		3,5	-115.0
		4	-131.0
$C_5F_8Cl_2$		3,5-eq	-117.1
		3,5-ax	-124.0
		4-eq	-125.4
		4-ax	-126.7
		1,2-ax	-139.0

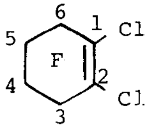
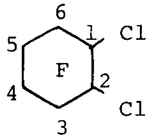
*In ppm from $CFCl_3$ as internal references, upfield is negative.

Reaction with $C_6F_8Cl_2$

Excess of 1,2-dichlorooctafluorocyclohexene-1 ($C_6F_8Cl_2$) was allowed to react with *n*-$C_7F_{15}BrF_4$ in a Monel reactor at 140°C for eight hours. The product was isolated by GC. The NMR and mass spectra showed that 1,2-dichlorodecafluorocyclohexane ($C_6F_{10}Cl_2$) and *n*-$C_7F_{15}Br$ had been formed. The NMR data for $C_6F_8Cl_2$ [8,9] and $C_6F_{10}Cl_2$ [10] are given in Table 4.

TABLE 4

The Chemical Shifts of ^{19}F nuclei in $C_6F_8Cl_2$ and $C_6F_{10}Cl_2$

Compound	Structure	^{19}F nucleus	Chemical Shifts*
$C_6F_8Cl_2$		3,3′,6,6′	-110.0
		4,4′,5,5′	-133.5
$C_6F_{10}Cl_2$		3,6-eq	-116.8
		3,6-ax	-120.5
		4,5-eq	-124.6
		4,5-ax	-128.2
		1,2-ax	-132.0

*In ppm from $CFCl_3$ as internal references, upfield is negative.

EXPERIMENTAL

Perfluoro-n-heptyl bromide was purchased from Columbia Organic Chemical Co., Inc., and the ^{19}F-NMR was observed and the product was used without further purification. Elemental fluorine was purchased from Air Products, Incorporated, and passed through a NaF trap before use.

The ^{19}F-NMR spectra were obtained on a Varian Model EM-390 spectrometer operating at 84.67 MHz using $CFCl_3$ as an internal reference. The mass spectra were determined with a Consolidated Electrodynamics Corporation Model 21-104 mass spectrometer IR spectra were recorded with a Perkin-Elmer Model 225 infrared spectrophotometer using a 0.1 mm liquid cell fitted with polyethylene windows.

Preparation of n-$C_7F_{15}BrF_4$

A vacuum manifold was used to condense 10 mmoles of perfluoro-n-heptyl bromide and 20 mmoles of elemental fluorine into a previously evacuated Monel reactor. The 0.304 liter Monel reactor was equipped with a Monel valve with "Teflon" packing.

At the completion of the reaction period, perfluoro-n-hexane was vacuum distilled into the reactor to dissolve the products. Dry helium gas was allowed to flow into the reactor and the products were transferred into a helium flushed sample holder through a septum. Moisture was rigorously excluded in all handling of the sample. The product, $C_7F_{15}BrF_4$ was isolated by trapping the appropriate peak from a Varian 90-P3 gas chromatograph equipped with a 3/8 inch x 20 foot column packed with 30% SE-30 on Chromosorb P. The column temperature was 100°C and the rate of helium flow was 65 ml/min. Analysis showed the product to be 38% $C_7F_{15}BrF_4$, 30% $C_7F_{15}Br$ and 32% unidentified. Anal. Calcd. for $C_7F_{15}BrF_4$: C, 16.0; F, 68.8; Br, 15.2. Found: C, 16.2; F, 68.6; Br, 14.8.

Reaction of n-$C_7F_{15}BrF_4$ with $C_5F_6Cl_2$

Excess $C_5F_6Cl_2$ (22 mmole) and n-$C_7F_{15}BrF_4$ (10 mmole) were allowed to react in a previously evacuated cylinder at 120°C for eight hours. The NMR spectrum of the products showed the presence of 1,2-dichlorooctafluorocyclopentane ($C_5F_8Cl_2$), n-$C_7F_{15}Br$ and unreacted $C_5F_6Cl_2$. The ^{19}F-NMR of the GC separated products were consistent with the above results.

Reaction of n-$C_7F_{15}BrF_4$ with $C_6F_8Cl_2$

The reaction of n-$C_7F_{15}BrF_4$ (0.4 mmole) with excess of $C_6F_8Cl_2$ (10 mmole) were carried out in Monel reactor, at 140°C for eight hours. ^{19}F-NMR spectra of products showed that 1,2-dichlorodecafluorocyclohexane ($C_6F_{10}Cl_2$), n-$C_7F_{15}Br$ and unreacted $C_6F_8Cl_2$ were present.

REFERENCES

1 D. Naumann, M. Schmeisser and L.J. Deneken, J. Inorg. Nucl. Chem., (1976) Supplement, 13.

2 G. Oates and J.M. Winfield, J. Chem. Soc., Dalton (1974) 119.

3 C.S. Rondestvedt, Jr., J. Am. Chem. Soc., 91 (1969) 3054.

4 J.A. Obaleye and L.C. Sams, Inorg. Nucl. Chem. Letters, 16 (1980) 343.

5 J.K. Brown and K.J. Morgan, Adv. Fluorine Chem., 4 (1965) 253

6 G.M. Begun and W.M. Fletcher, J. Chem. Phys., 42 (1965) 2236.

7 M.I. Bruce and P.W. Jolly, J. Chem. Soc. (a), (1966) 1602.

8 S.F. Campbell and A.C. Hudson, Spec. Acta, 23A (1967) 2119.

9 G.M. Birch and J.R. Van Wazer, J. Chem. Soc. (A), (1966) 586.

10 J.W. Emsley, Mol. Phys., 9 (1965) 381.