Journal of Fluorine Chemistry, 18 (1981) 277–280
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
Received: March 5, 1981

PERFLUORO-n-PROPYLBROMINE(V) TETRAFLUORIDE

MOHAMMAD H. HABIBI and LEWIS C. SAMS

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

SUMMARY

Perfluoro-n-propylbromine(V) tetrafluoride has been prepared by fluorination of perfluoro-n-propyl bromide at 0°C with elemental fluorine. It has been characterized by ^{19}F-NMR, mass spectroscopy and elemental analysis.

INTRODUCTION

The synthesis of several perfluoroalkyliodine(V) tetrafluorides have been reported. These compounds were prepared by fluorination of perfluoroalkyl iodide with elemental fluorine [1,3], ClF_3 [2,3] and BrF_3 [3]. The preparation of pentafluorophenylbromine(V) tetrafluoride has been reported [4], but no report of perfluoroalkylbromine(V) tetrafluorides has been found.

This paper reports the preparation and characterization of perfluoro-n-propylbromine(V) tetrafluoride.

RESULTS AND DISCUSSION

Perfluoro-n-propylbromine(V) tetrafluoride was synthesized by allowing perfluoro-n-propyl bromide and elemental fluorine to react in a Monel cylinder at 0°C for 15 hours. The reaction products were dissolved in perfluoro-n-hexane and a colorless liquid was isolated from the reddish-brown solution by G.C. This colorless product was identified as perfluoro-n-propylbromine(V) tetrafluoride on the basis of elemental analysis, mass spectra, ^{19}F-NMR and its ability to oxidize four equivalents of KI per mole.

A comparison of the NMR spectra of n-C_3F_7Br and n-$C_3F_7BrF_4$ is given in Table I. The integration of the +141.8 ppm signal is consistent with four fluorines in the same magnetic environment, similar to the equatorial fluorines of BrF_5. The R_F chemical shifts are as expected in comparison with perfluoro-n-propyl bromide

The mass spectrum,detailed in Table II ,consists of molecular ions at m/e 324 and 326 and expected fragment ions. The expected isotope patterns (1:1) for ^{79}Br and ^{81}Br were observed and the peak at m/e 169 was assigned to $C_3F_7^+$ as the base peak.

The liquid phase infrared spectrum consists of absorption band at 1340(s), 1250(vs), 1145(s), 1080(s), 910(w), 710(m), 685(vs), 665(s), 640(m), 620(m), 550(m) and 475(s) cm^{-1}. IR spectra of $C_3F_7BrF_4$ contained bands comparable to those of the C_3F_7 group [5] and a strong band at 685 cm^{-1} which is comparable to the 683 cm^{-1} band of BrF_5 [6].

Perfluoro-n-propylbromine(V) tetrafluoride decomposes slowly at room temperature in contact with air (decomposition was detectable after 30 minutes). Under dry helium at -30°C the compound was stable for a month.

Perfluoro-n-propylbromine(V) tetrafluoride hydrolyzes and NMR analysis of the hydrolysis products showed that fluorines attached to bromine in $C_3F_7BrF_4$ were liberated.

EXPERIMENTAL

Perfluoro-n-propyl bromide was purchased from PCR, Incorporated, and used without further purification. Elemental fluorine was purchased from Air Products, Incorporated, and passed through a NaF trap before use.

A vacuum manifold was used to condense 10 mmoles of perfluoro-n-propyl 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, $C_3F_7BrF_4$ was isolated by

TABLE I

The ^{19}F-NMR spectra of perfluoro-n-propylbromine(V) tetrafluoride

	Chemical Shifts (ppm)*				Coupling Constants (Hz)		
Compound	CF_3	CF_2	CF_2	BrF_4	J(FBrCF)	J(FBrCCF)	Others**
n-C_3F_7Br	-80.0	-121.8	-58.6	-	-	-	
n-$C_3F_7BrF_4$	-80.1	-123.1	-63.2	+141.8	32.0	32.0	$J(F_1F_2)$ 32.0 $J(F_1F_3)$ 11.8 $J(F_2F_3)$ 1.2

* From CCl_3F as internal references, upfield is negative to CCl_3F.

** ^{19}F nuclei in C_3F_7 numbered from the alpha-position.

TABLE II

Mass Spectrum of $C_3F_7BrF_4$

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
326	30	$C_3BrF_{11}^+$	286	6	$C_3BrF_9^+$
324	30	$C_3BrF_{11}^+$	257	19	$C_2BrF_8^+$
307	23	$C_3BrF_{10}^+$	255	19	$C_2BrF_8^+$
305	23	$C_3BrF_{10}^+$	169	100	$C_3F_7^+$
288	6	$C_3BrF_9^+$	69	70	CF_3^+

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 Chromsorb P. The column temperature was 80°C and the rate of helium flow was 80 ml/min.

Analysis: Found: C, 10.58; F, 64.14; Br, 24.05; $C_3F_7BrF_4$ requires C, 11.07; F, 64.30; Br, 24.61.

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 spectrum was 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.

REFERENCES

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