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New pentafluorothio (SF_5)-containing alkyl dibromides

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Abstract

Preparation of two new SF_5-containing compounds and one telomer was achieved by reaction of the olefins $CH_2{=}CHBr$ and $CF_2{=}CFBr$ with SF_5Br to form $SF_5CH_2CHBr_2$ and $SF_5CF_2CFBr_2$. In the reaction of SF_5Br with $CF_2{=}CFBr$, a waxy solid formed with an average formula of $SF_5(CF_2CFBr)_{10}Br$.

Keywords: Pentafluorothio group; Alkyl dibromides; Preparation; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

Fluorinated alkyl bromides and dibromides with end groups such as $-CFBr_2$, $-CFClBr$ and $-CF_2Br$ have been studied as telogens in reactions with fluoroolefins [1–4]. Pentafluorosulfur bromide, SF_5Br, has been shown to be a useful reagent for incorporating SF_5- groups into carbon compounds by reaction with olefins [5–8] and should be effective in forming the corresponding dibromides by reaction with bromides. SF_5 polymers/telomers have been prepared by reactions of SF_5Cl with $CF_2{=}CF_2$ [9–11], $CF_3CF{=}CF_2$ with S_2F_{10} [12], $SF_5CF{=}CF_2$ with $CF_2{=}CF_2$ [13] and $CF_2{=}CH_2$ [14], and SF_5Br with $CF_2{=}CH_2$, $CF_2{=}CFH$, $CF_2{=}CF_2$ and $CFH{=}CH_2$ [15].

2. Results and discussion

We have found that SF_5Br reacts readily with bromoethene ($CH_2{=}CHBr$) at room temperature in a Pyrex glass vessel for 18 h, while more stringent conditions were needed to form the polymer/telomer with perfluorobromoethene ($CF_2{=}CFBr$); in this case, a metal vessel containing the reactants under autogenous pressure was heated for 51 h at 76 °C. Under these conditions a waxy solid material formed in addition to the adduct $SF_5CF_2CFBr_2$. Dehydrobromination of $SF_5CH_2CHBr_2$ with KOH indicated the formation of $SF_5CH{=}CHBr$ and $SF_5C{\equiv}CH$.

The infrared spectra of $SF_5CF_2CFBr_2$, $SF_5(CF_2CFBr)_{10}Br$ and $SF_5CH_2CHBr_2$ have been measured. All spectra exhibit strong SF_5- stretching modes in the region 878–903 cm^{-1}. The CF stretching frequencies between 1100 and 1208 cm^{-1} are present in $SF_5CF_2CFBr_2$ and $SF_5(CF_2CFBr)_{10}Br$. The deformation modes for SF_5- appear at 603, 599 and 581 cm^{-1} in $SF_5CF_2CFBr_2$, $SF_5(CF_2CFBr)_{10}Br$ and $SF_5CH_2CHBr_2$, respectively. Cross and coworkers have reported the SF_5- stretching frequency as a strong band in the 850–920 cm^{-1} region with a deformation mode near 600 cm^{-1} [16]. The CH and CH_2 vibrations in $SF_5CH_2CHBr_2$ occur at 3034 and 2978 cm^{-1}.

The major mass spectral peaks for each compound are listed under Experimental details. For the adducts $SF_5CF_2CFBr_2$ and $SF_5CH_2CHBr_2$, the peaks are representative of the isotopic ratios of bromine. With both adducts, molecular ion peaks were observed. For the compound $SF_5CH_2CHBr_2$, the base peak was (127) FCH_2CHBr^+, SF_5^+, and for $SF_5CF_2CFBr_2$ it was (179) $C_2F_4Br^+$.

The ^1H and ^{19}F NMR spectral data for the compounds are listed in Table 1. The ^{19}F NMR spectra for the adduct $SF_5CF_2CFBr_2$ showed an AB_4 pattern for the SF_5 grouping at δ 64.8 ppm (9-line) and 48.4 ppm (doublet). Interestingly, with $SF_5CH_2CHBr_2$, the axial fluorine splitting pattern reduced to a distorted pentet at δ 79.9 ppm with the doublet at δ 64.9 ppm. By comparison, $SF_5CF_2CF_2Br$ and $SF_5CH_2CH_2Br$ exhibited the AB_4 splitting pattern at δ 61.5 (9-line) and 44.3 ppm (doublet) [15], and at δ 80.8 ppm and 63.1 ppm [17], respectively. In $SF_5CF_2CFBr_2$, the CF_2 chemical shift occurred at δ −86.1 ppm with the CF resonance occurred at δ −78.5 ppm; for the polymer, these peaks consisted of broad multiplets over a range of chemical shifts.

The ^1H NMR assignments for $SF_5CH_2CHBr_2$ are δ 4.60 ppm for the CH_2 group and δ 5.95 ppm for the CH group. This is somewhat different from the compound SF_5CH_2-

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Table 1
Proton and fluorine-19 NMR data for new compounds

Compound	Chemical shifts (δ, in ppm from $CFCl_3$ or TMS) *			
	a	b	c	d
$F^{a}-SF_4^{b}-CF_2^{c}-CF^{d}Br_2$	64.8 (9-line)	48.4 (d)	−86.1 (s)	−78.5 (m)
ratio	1.0	4.1	1.0	2.0
	$J_{a,b} = 152$ Hz, $J_{a,c} = 5.4$ Hz			
$F^{a}-SF_4^{b}-(CF_2^{c}-CF^{d}Br)_{10}Br$	65.1	46.0	*	*
	$J_{a,b} = 148$ Hz			
$F^{a}-SF_4^{b}-C^{\alpha}H_2^{c}-C^{\beta}H^{d}Br_2$	79.9 (p,m)	64.9 (d,m)	4.60 (d,p)	5.95 (t)
ratio	1.0	4.3	2.1	1.0
	$J_{a,b} = 147.3$ Hz, $J_{b,c} = 6.7$ Hz, $J_{c,d} = 6.0$ Hz			

* Broad peaks (integration ratio) occur at 58.2 (14); 71.0 (11); 82.5 (9); 86.2 (5); 93.0 (17); 100.9 (70); 106.2 (53); 129.5 (52); 137.5 (7) ppm.

Table 2
^{13}C NMR spectral data (proton-decoupled) *

Compound	C_α	C_β	$J_{\alpha,b}$	$J_{\beta,b}$	$J_{\beta,c}$	$J_{\beta,d}$
$F^{a}-SF_4^{b}-C^{\alpha}H_2^{c}-C^{\beta}H_2^{d}Br$ **	71.3 (p)	23.15 (p)	13.90	6.36	–	–
$F^{a}-SF_4^{b}-C^{\alpha}H_2^{c}-C^{\beta}H^{d}Br_2$	79.76 (d,p)	30.7 (br,p)	14.75	4.77	–	–
$F^{a}-SF_4^{b}-C^{\alpha}F_2^{c}-C^{\beta}F^{d}Br_2$	121.8 (t,m)	85.7 (d,t)	–	–	34.5	327.6
$F^{a}-SF_4^{b}-C^{\alpha}HF^{c}-C^{\beta}F_2^{d}Br$ ***	108.15 (d,d,d,p)	114.87 (d,d,d)	23.3	–	30.2	315.4 (F_d) 307.8 (F_d)
			$J_{\alpha,c} = 249.0$, $J_{\alpha,d} = 36.0$			

* Chemical shifts in ppm from TMS and coupling constants in Hz.
** Ref. [13].
*** Ref. [14].

CH_2Br where the values are δ 3.93 and 3.60 ppm [17], with the δ 3.93 ppm resonance assigned to the protons closest to the SF_5 group. In SF_5CH_2CHFBr, the chemical shift of the protons in the CH_2 group was δ 4.27 ppm and in $SF_5CH_2CF_2Br$ it was at δ 4.46 ppm; the CH hydrogen in the former compound had a chemical shift of δ 6.95 ppm [1]. With $SF_5CHBrCHBr_2$, the protons were at δ 6.29 and 5.86 ppm for CHBr and $CHBr_2$, respectively [18].

Table 2 lists the ^{13}C NMR data for $SF_5CH_2CHBr_2$ and $SF_5CF_2CFBr_2$, as well as data for $SF_5CH_2CH_2Br$ [17] and SF_5CFHCF_2Br [19] for comparison. Chemical shifts for the α carbon range from δ 71.3 ppm to δ 121.8 ppm, and for the β carbon from δ 23.15 to 114.87 ppm. These ranges are consistent with literature values reported for the sulfonic acids $SF_5CH_2CH_2SO_3H$, $SF_5CH_2CF_2SO_3H$, and $SF_5CHFCF_2SO_3H$ [20]. In both groups of compounds there is a reversal of the α- and β-carbon pattern when the SF_5CHFCF_2 grouping appears; the chemical shifts differ by less than 10 ppm. Assignment of peaks was made by comparing the magnitude of the B_4 fluorine to carbon coupling constants with $J_{\alpha,b}$ ranging from 13.9 to 23.3 Hz and $J_{\beta,b}$ ranging from 4.77 to 6.36 Hz. Coupling of the axial fluorine to the carbons was not observed.

3. Experimental details

SF_5Br was prepared and handled as previously reported [1] or as modified in our laboratory. The reactants $CF_2{=}CFBr$ and $CH_2{=}CHBr$ were purchased from Peninsular Chem. Research and used as received. Infrared spectra were obtained using a Nicolet 20 DX FT-IR spectrometer operating at 2.0 cm^{-1} resolution or a Perkin-Elmer System 2000 FT-IR spectrometer operating at 1.0 cm^{-1} resolution using KBr cells for liquids and solids. Mass spectra were measured on a VG 7070 HS mass spectrometer operated at 70 keV. NMR spectra were obtained on a Varian EM-390 spectrometer operating at 90.00 MHz for ^1H and 84.67 MHz for ^{19}F or on a Bruker AMX-400 instrument operating at 100.6 MHz for ^{13}C and 400.1 MHz for ^1H. Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Germany.

3.1. Preparation of $SF_5CF_2CFBr_2$ and the telomer $SF_5(CF_2CFBr)_{10}Br$

Into a 150 ml Hoke stainless-steel metal vessel equipped with a Whitey stainless-steel valve, 29.86 g (144.0 mmol) of SF_5Br and 20.46 g (127.0 mmol) $CF_2{=}CFBr$ were condensed at − 196 °C. The mixture was warmed to room temperature. The reaction vessel was placed in an oven at 76 °C for 51 h. The contents of the vessel were transferred to a 50 ml round-bottom flask and allowed to warm to room temperature. Distillation of the mixture gave $SF_5CF_2CFBr_2$ mixed with other minor components; 22.94 g and 48.8% yield based upon SF_5Br. The reaction vessel was rinsed with acetone and the rinsing set aside to dry. The solid material (3.82 g) collected from these rinsings was the telomer with the average formula $SF_5(CF_2CFBr)_{10}Br$ calculated from the elemental analysis data. In a subsequent preparative run in a 2 l Pyrex glass vessel equipped with a Kontes Teflon valve, 5.80 g (28.0 mmol) SF_5Br and 4.93 g (30.6 mmol) of $CF_2{=}CFBr$ were condensed at −196 °C. The mixture was allowed to warm to room temperature and placed under a Sylvania 90-W Halogen Par 38 lamp for 19 h. Distillation of the mixture gave 6.63 g of $SF_5CF_2CFBr_2$ with a boiling point of 115–116 °C in 64.3% yield.

The infrared spectrum for $SF_5CF_2CFBr_2$ shows the following peaks (cm^{-1}): 1208 (s); 1118 (s); 1031 (w); 903 (vs); 886 (vs); 828 (m); 811 (w); 717 (s); 686 (m); 643 (w); 602 (s); 575 (w). The infrared spectrum for $SF_5(CF_2CFBr)_{10}Br$ shows (cm^{-1}): 1411 (m); 1384 (m); 1249 (s); 1208 (vs); 1183 (vs); 1122 (vs); 1115 (m); 927 (s); 884 (vs); 841 (s); 796 (w); 763 (m); 712 (m); 683 (m); 653 (m); 636 (w); 599 (s); 573 (m); 532 (w); 495 (w).

A molecular ion peak and appropriate fragments were observed in the mass spectrum of $SF_5CF_2CFBr_2$. Major peaks include (*m/z*, mol, ion): 368 ($SF_5CF_2CFBr_2^+$); 239, 241, 243 ($CF_2CFBr_2^+$); 189, 191, 193 ($CFBr_2^+$); 179, 181 ($C_2F_4Br^+$); 160, 162 ($C_2F_3Br^+$); 129, 131 (CF_2Br^+); 127 (SF_5^+); 110, 112 ($CFBr^+$); 91, 93 (CBr^+); 89 (SF_3^+); 70 (SF_2^+); 50 (CF_2^+).

Analysis: Calc. for $SF_5CF_2CFBr_2$: C, 6.52; S, 8.7; F, 41.3; Br, 43.37%. Found: C, 6.48; S, 8.59; F, 41.5; Br, 43.33%. Calc. for $SF_5(CF_2CFBr)_{10}Br$: C, 13.22; S, 1.77; F, 36.6; Br, 48.39%. Found: C, 13.56; S, 1.85; F, 37.1; Br, 47.53%.

3.2. Preparation of $SF_5CH_2CHBr_2$

Into a 3 l Pyrex glass vessel equipped with a Kontes Teflon valve, 11.70 g (56.5 mmol) of SF_5Br and 6.55 g (61.2 mmol) of $CH_2{=}CHBr$ were condensed at −196 °C. The mixture was allowed to warm to room temperature overnight and the products transferred to a 25 ml distillation flask. Vacuum distillation gave 16.4 g for $SF_5CH_2CHBr_2$; b.p. 46 ± 2 °C/16 mmHg with a 92.4% yield based upon SF_5Br.

The infrared spectrum for $SF_5CH_2CHBr_2$ shows the following peaks (cm^{-1}): 2978 (w); 3034 (w); 1218 (m); 1177 (w); 1150 (m); 929 (s); 878–829 (vs); 720 (w); 595 (m); 581 (s); 565 (m).

A molecular ion peak and appropriate fragments were observed in the mass spectrum of $SF_5CH_2CHBr_2$. Major peaks include (*m/z*, mol, ion): 312, 314, 316 ($SF_5CH_2CHBr_2^+$, ratio 1:2:1); 233, 235 ($SF_5CH_2CHBr^+$); 185, 187, 189 ($CH_2CHBr_2^+$); 127 (SF_5^+, FCH_2CHBr^+); 125 (FCH_2CHBr^+); 105, 107 ($C_2H_2Br^+$); 106, 108 (CH_2CHBr^+); 89 (SF_3^+); 79, 81 (Br^+); 45 (SCH_2^+); 27 ($CHCH_2^+$); 26 ($C_2H_2^+$).

Analysis: Calc. for $SF_5CH_2CHBr_2$: C, 7.6; H, 0.96; Br, 50.90%. Found: C, 7.74; H, 0.97; Br, 50.97%.

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