

## Pentafluoro- $\lambda^6$ -sulfanyl ( $\text{SF}_5$ ) fluoroalkyl iodides

Robin J. Terjeson, Julia Renn, Rolf Winter, Gary L. Gard \*

*Department of Chemistry, Portland State University, Portland, OR 97207, USA*

Received 17 May 1996; accepted 9 September 1996

### Abstract

Fluoroalkyl iodides are an important class of compounds used in the preparation of large numbers of fluoro-organo and fluoro-organometallic derivatives. We report the synthesis of several  $\text{SF}_5$ -containing fluoroalkyl iodides derived from an improved synthesis of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ . They are:  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$ /isomer and  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CHF}\text{CF}_2\text{I}$ /isomer. In addition, the higher homologs  $\text{SF}_5(\text{CF}_2)_6\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CHF}\text{CF}_2)_2\text{I}$ /isomer and  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_3\text{I}$  have been identified. © 1997 Elsevier Science S.A. All rights reserved.

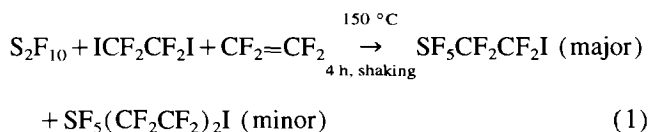
**Keywords:** Fluoroalkyl iodides; Mass spectroscopy; NMR spectroscopy; Pentafluorothio; Preparation

### 1. Introduction

Fluoroalkyl iodides are an important class of compounds used in the preparation of many useful fluoro-organo and fluoro-organometallic derivatives [1]. The  $\text{SF}_5$ -containing fluoroalkyl iodides  $\text{SF}_5\text{CF}_2\text{I}$  [2],  $\text{SF}_5(\text{C}_2\text{F}_4)_n\text{I}$  ( $n = 1, 2, 3$ ) [3],  $\text{SF}_5\text{CF}(\text{I})\text{CF}_3$  [4],  $\text{SF}_5\text{CF}=\text{CFI}$  [5,6],  $\text{SF}_5\text{C}\equiv\text{CI}$  [7] and  $\text{SF}_5\text{CF}(\text{I})\text{CF}_2\text{CF}_3$  [8] have been reported. The iodides  $\text{SF}_5\text{R}_f\text{I}$  and their ethylene adducts,  $\text{SF}_5\text{R}_f\text{CH}_2\text{CH}_2\text{I}$ , where  $\text{R}_f$  represents at least three fully fluorinated carbon atoms, have also been reported [9–11]; very little information has been given regarding the preparation, identification and properties of these compounds. The characterization and isolation of the known  $\text{SF}_5$  fluoroalkyl iodides listed above have, in many cases, proved difficult. The incorporation of the  $\text{SF}_5$  group into a carbon-containing system is well known using  $\text{SF}_5\text{X}$  ( $\text{X} = \text{Br}, \text{Cl}$ ). Since  $\text{SF}_5\text{I}$  is unknown, the chemistry of the readily accessible  $\text{SF}_5\text{C}_2\text{F}_4\text{I}$  was studied. We report the preparation and properties of a number of  $\text{SF}_5$ -containing fluoroalkyl iodides derived from an improved synthesis of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  [3]:  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$ /isomer and  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CHF}\text{CF}_2\text{I}$ /isomer. In addition, higher molecular weight  $\text{SF}_5$  fluoroalkyl iodides,  $\text{SF}_5(\text{CF}_2)_6\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CHF}\text{CF}_2)_2\text{I}$ /isomer and  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_3\text{I}$ , have been identified via gas chromatography–mass spectroscopy (GC–MS).

### 2. Results and discussion

In order to prepare  $\text{SF}_5$ -containing iodides, it was necessary to modify the method reported by Hutchinson [3]. Hutchinson's method employs tetrafluoroethylene at high pressure (150 psi) [3]. However, since it is known that  $\text{C}_2\text{F}_4$  may explosively polymerize at this pressure, it was critical to study alternative preparative conditions. We have modified this reaction to produce safely, at lower pressure (88–103 psi),  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  in yields of about 50% with re-use of the unreacted starting material. The reactants were condensed into a metal pressure vessel, heated to 150 °C, and allowed to react with periodic shaking for 4–5 h. The reaction was quenched in cold water and stored at 0 °C until distillation. To improve and maximize the separation during distillation, a 100 mm column filled with Monel helices was used. In order to remove any iodine, the product was shaken with mercury.



The pot contained small amounts of  $\text{SF}_5(\text{CF}_2\text{CF}_2)_2\text{I}$  as identified by its characteristic  $^{19}\text{F}$  nuclear magnetic resonance (NMR) spectrum.

The reactions of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  were carried out in a Carius tube containing mercury; irradiation was performed with a halogen lamp for 3–6 weeks. In some cases, the olefin or acetylene was added in aliquots during the course of the

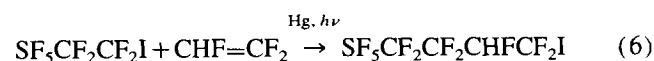
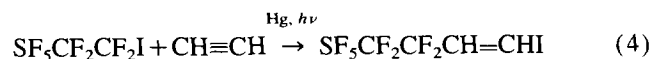
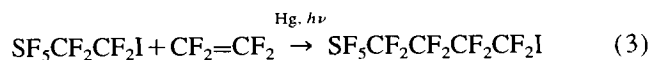
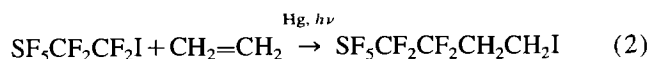
\* Corresponding author.

Table 1  
GC–MS data<sup>a</sup>

Compound	Retention time (min)	Major peaks
SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> I	7.10	316 M–F <sub>2</sub> <sup>+</sup> ; 240 M–F <sub>6</sub> <sup>+</sup> , SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> ; 189 C <sub>2</sub> F <sub>2</sub> I <sup>+</sup> , C <sub>2</sub> F <sub>7</sub> S <sup>+</sup> ; 158 SF <sub>5</sub> CF <sup>+</sup> , CFI <sup>+</sup> ; 127 SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup> ; 89 SF <sub>3</sub> <sup>+</sup> ; 31 CF <sup>+</sup>
SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> I	10.75	410 M <sup>+</sup> ; 283 M–I <sup>+</sup> , M–SF <sub>5</sub> <sup>+</sup> ; 175 F(CF <sub>2</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> <sup>+</sup> ; 156 M–I–SF <sub>5</sub> <sup>+</sup> ; 127 SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup> ; 81 CF <sub>2</sub> CF <sup>+</sup>
SF <sub>5</sub> (CF <sub>2</sub> ) <sub>4</sub> I	4.20	454 M <sup>+</sup> ; 327 M–I <sup>+</sup> , M–SF <sub>5</sub> <sup>+</sup> ; 219 F(CF <sub>2</sub> ) <sub>4</sub> <sup>+</sup> ; 181 CF(CF <sub>2</sub> ) <sub>3</sub> <sup>+</sup> ; 127 SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup> ; 69 CF <sub>3</sub> <sup>+</sup>
SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> CH=CHI	5.85 trans, 7.12 cis	380 M <sup>+</sup> ; 127 SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup>
SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub> I, SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub> I	5.45 and 4.95	436 M <sup>+</sup> ; 201 M–I–SF <sub>4</sub> <sup>+</sup> ; 127 SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup> ; 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> ; 89 SF <sub>3</sub> <sup>+</sup> ; 82 C <sub>2</sub> F <sub>3</sub> H <sup>+</sup>
SF <sub>5</sub> (CF <sub>2</sub> ) <sub>6</sub> I	6.16	554 M <sup>+</sup> ; 319 M–I–SF <sub>4</sub> <sup>+</sup> ; 127 SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup> ; 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup>
SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> (CHF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> I, SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> (CF <sub>2</sub> CHF) <sub>2</sub> I	8.31 and 8.25	518 M <sup>+</sup>
SF <sub>5</sub> CF <sub>2</sub> CF <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> I	12.6	438 M <sup>+</sup> ; 311 M–I <sup>+</sup> , M–SF <sub>5</sub> <sup>+</sup> ; 127 SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup>

<sup>a</sup>Data taken on a VG 7070 HS mass spectrometer operated at 70 eV with a 25 m DB5 column. Temperature range 50–280 °C at 18 °C min<sup>-1</sup>. Hutchinson [3] reported higher homologs identified from a mixture by gas–liquid chromatography (GLC): SF<sub>5</sub>(CF<sub>2</sub>)<sub>2</sub>I, SF<sub>5</sub>(CF<sub>2</sub>)<sub>4</sub>I, SF<sub>5</sub>(CF<sub>2</sub>)<sub>6</sub>I, SF<sub>5</sub>(CF<sub>2</sub>)<sub>8</sub>I, SF<sub>5</sub>(CF<sub>2</sub>)<sub>10</sub>I.

reaction in an attempt to keep the initial pressure below 2 atm.



In reactions (3), (5) and (6), a GC–MS study showed the presence of higher homologs (see Table 1). Reactions (4) and (6) gave isomeric products.

The infrared (IR) spectral data for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I, SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>I, SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>I, SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CHF<sub>2</sub>I (and isomer) and SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH=CHI (cis and trans isomers) are listed in Section 3. All spectra exhibit strong SF<sub>5</sub> stretching modes in the region 876–884 cm<sup>-1</sup>. The CF stretching frequencies between 1100 and 1227 cm<sup>-1</sup> are present in all compounds. One of the SF<sub>5</sub> deformation modes for the above compounds appears in the 604–610 cm<sup>-1</sup> range. Cross et al. [12] have reported the SF<sub>5</sub> stretching frequency as a strong band in the 850–920 cm<sup>-1</sup> region with a deformation mode near 600 cm<sup>-1</sup>. The CH vibrations in SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CHF<sub>2</sub>I and SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH=CHI/isomer occur at 2996 cm<sup>-1</sup> and 3083 cm<sup>-1</sup> respectively. The CH<sub>2</sub> vibrations in SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I appear at 2984 and 2967 cm<sup>-1</sup>, with absorption peaks for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>I occurring at 2958 and 2879 cm<sup>-1</sup>. The C=C vibration is found at 1618 cm<sup>-1</sup>.

The major mass spectral peaks for each compound are listed in Section 3. Molecular ion peaks are observed for all compounds, except SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I, where the highest

peak corresponds to M–2F<sup>+</sup>. A GC–MS study found that higher homologs were present in the addition reactions for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I with CF<sub>2</sub>=CF<sub>2</sub> and CHF=CF<sub>2</sub> and in the reaction of SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I with CH<sub>2</sub>=CH<sub>2</sub>. Retention times are given in Table 1 for derivatives of SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I and their higher homologs. It should be noted that Hutchinson [3] found higher homologs of SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I when reacting CF<sub>2</sub>=CF<sub>2</sub> with S<sub>2</sub>F<sub>10</sub> and I<sub>2</sub>.

The <sup>1</sup>H and <sup>19</sup>F NMR spectral data for the compounds are given in Table 2. The <sup>19</sup>F spectra for the compounds show an AB<sub>4</sub> pattern for the SF<sub>5</sub> group: A (distorted pentet or nine-line pattern) at δ=63.5–67.2 ppm; B (doublet) at δ=44.2–45.5 ppm; these chemical shifts for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I are found at δ=65.4 and 47.3 ppm. Hutchinson [3] reports finding these resonances at δ=64 and 46 ppm. For comparison, SF<sub>5</sub>CF<sub>2</sub>I and SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>Br exhibit the AB<sub>4</sub> splitting pattern at δ=66.5 and 61.5 ppm (nine-line pattern) and 36.5 and 44.3 ppm (doublet) [2,13]. The chemical shifts of the CF<sub>2</sub> fluorines adjacent to the SF<sub>5</sub> group in the above compounds are located in the range δ=–89.0 to –97.5 ppm; this shift is δ=–89 ppm for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I [3]. In SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I and SF<sub>5</sub>(CF<sub>2</sub>)<sub>4</sub>I, the CF<sub>2</sub>I fluorines have chemical shifts of δ=–61.7 and –59.5 ppm respectively; in SF<sub>5</sub>CF<sub>2</sub>I and SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I, this resonance is found at δ=–88.8 and –60 ppm respectively [2,3]. Internal CF<sub>2</sub> groups contain multiplets ranging from δ=–115.9 to –138.0 ppm. The CF<sub>2</sub> fluorines adjacent to CH or CH<sub>2</sub> groups in other iodides are in the range δ=–117.2 to –120.7 ppm [14]. The coupling constants for the AB<sub>4</sub> fluorines were consistent in all the compounds with J<sub>a,b</sub> values ranging from 146.5 to 146.7 Hz; for SF<sub>5</sub>C≡CI and SF<sub>5</sub>CF=CFI, the AB<sub>4</sub> coupling constant was found to be 147.3 Hz [5,7].

<sup>1</sup>H NMR assignments for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I and SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>I are in the range δ=1.52–3.18 ppm; in SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH=CHI, the <sup>1</sup>H chemical shifts adjacent to CF<sub>2</sub> are found at δ=6.75 ppm (trans) and δ=6.81 ppm (cis), and for the CHI proton they are at δ=7.46 ppm (trans) and 7.39 ppm (cis). Coupling constants for the hydrogens in

Table 2  
Proton and <sup>19</sup>F NMR data for new compounds

Compound	Chemical shift (in ppm from CFCl <sub>3</sub> or TMS, coupling constants in hertz)							
	a	b	c	d	e	f	g	h
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> -I	65.4(p) J <sub>ab</sub> =146.6	47.25(d) J <sub>ac</sub> =4.93	-89.0(p,t,d) J <sub>bc</sub> =10.86	-61.7(p,t) J <sub>bd</sub> =11.28	J <sub>cd</sub> =5.64 1.52			
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> -CH <sub>2</sub> <sup>e</sup> CH <sub>2</sub> <sup>f</sup> I	65.3(p) J <sub>ab</sub> =146.6	45.5(d,m) J <sub>bc</sub> =15.0	-95.89(m) J <sub>dc</sub> =21.55	-115.9(m) J <sub>ef</sub> =5.64		2.03		
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> -CF <sub>2</sub> <sup>e</sup> CF <sub>2</sub> <sup>f</sup> I	63.5(p,m) J <sub>ab</sub> =146.6	44.64(d,p) J <sub>bc</sub> =14.5	-94.6(p,m) J <sub>cd</sub> =16	-122.1(m) J <sub>de</sub> =16.9	-112.8(t,t) J <sub>ef</sub> ~3	-59.5(t,t)	J <sub>ef</sub> =15.5	
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> CH=CH <sup>e</sup> I (trans)	65.10(p,m) J <sub>ab</sub> =146.5	44.2(d,m) J <sub>ac</sub> =4.8	-96.02(p) J <sub>bc</sub> =13	-112.19(d,t) J <sub>cd</sub> =11.0	J <sub>de</sub> =2.16 6.75(d,t)	7.46(d,t)	J <sub>ef</sub> =14.9	J <sub>ed</sub> =11.16
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> CH=CH <sup>e</sup> I (cis)	65.15(p,m) J <sub>ab</sub> =146.5	44.2(p) J <sub>ac</sub> =4.8	-96.65(p) J <sub>bc</sub> =13	-110.90(d,t) J <sub>cd</sub> =11.0	6.81(d,t) J <sub>de</sub> =3.36	7.39(d,t)	J <sub>ef</sub> =9.62	J <sub>ed</sub> =13.1
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> CH <sub>2</sub> <sup>e</sup> CH <sub>2</sub> <sup>f</sup> CH <sub>2</sub> <sup>g</sup> CH <sub>2</sub> <sup>h</sup> I	67.2(m) J <sub>ab</sub> =146.7	45.0(d,m) J <sub>bc</sub> ~13	-97.7(line) J <sub>bd</sub> ~13	-117.2(m)	3.18, 2.28, 2.07, 1.82 multiplets in H			
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> CH <sup>e</sup> CF <sub>2</sub> <sup>f</sup> CF <sub>2</sub> <sup>g</sup> I	64(m)	44.7(d,m) J <sub>bc</sub> ~13	-95.7 to -97.5(m)	Fluorines next to iodine	-52 to -61.3			
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -CF <sub>2</sub> <sup>c</sup> -CF <sub>2</sub> <sup>d</sup> CF <sub>2</sub> <sup>e</sup> CF <sub>2</sub> <sup>f</sup> CF <sub>2</sub> <sup>g</sup> CF <sub>2</sub> <sup>h</sup> I	64.0(m)	44.7(d,m)	-95.7 to -97.5(m)	Fluorines next to iodine	-52 to -61.3			

Table 3  
<sup>13</sup>C NMR spectral data (proton decoupled)<sup>a</sup>

Compound	C <sub>α</sub>	C <sub>β</sub>	C <sub>γ</sub>	C <sub>δ</sub>	J <sub>αβ</sub>	J <sub>αγ</sub>	J <sub>αδ</sub>	J <sub>βγ</sub>	J <sub>βδ</sub>	J <sub>γδ</sub>
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -C <sup>c</sup> CF <sub>2</sub> <sup>d</sup> -C <sup>e</sup> CF <sub>2</sub> <sup>f</sup> I	119.0(t,p,t)	91.1(t,t)	-	-	25.9	305.5	34.5	42.06	323.0	-
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -C <sup>c</sup> CF <sub>2</sub> <sup>d</sup> -C <sup>e</sup> CF <sub>2</sub> <sup>f</sup> -C <sup>g</sup> H <sub>2</sub> <sup>h</sup> C <sup>i</sup> H <sub>2</sub> <sup>j</sup> I	121.6S(t,m)	117.4(t,t)	37.50(t)	-11.61(t)	37.4	305.9	25.5	32.7	266.6	-
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -C <sup>c</sup> CF <sub>2</sub> <sup>d</sup> -C <sup>e</sup> CF <sub>2</sub> <sup>f</sup> -C <sup>g</sup> CF <sub>2</sub> <sup>h</sup> -C <sup>i</sup> CF <sub>2</sub> <sup>j</sup> I	121.2(t,p,t)	109.4(t,t)	108.8(t,t)	93.4(t,t)	J <sub>δd</sub> =5.05 36.8	311.8	27	32.6	275.1	321.4
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -C <sup>c</sup> CF <sub>2</sub> <sup>d</sup> -C <sup>e</sup> CF <sub>2</sub> <sup>f</sup> -C <sup>g</sup> CF <sub>2</sub> <sup>h</sup> -C <sup>i</sup> CF <sub>2</sub> <sup>j</sup> -C <sup>k</sup> CF <sub>2</sub> <sup>l</sup> I	121.6(t,p,t)	114.0(t,p,t)	132.3(t)	91.72	J <sub>δe</sub> =42 37.9	306	J <sub>αβ</sub> =36.8 25.2	J <sub>γδ</sub> =31.8 31	258.0	269.7
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -C <sup>c</sup> CF <sub>2</sub> <sup>d</sup> -C <sup>e</sup> CF <sub>2</sub> <sup>f</sup> -C <sup>g</sup> CF <sub>2</sub> <sup>h</sup> -C <sup>i</sup> CF <sub>2</sub> <sup>j</sup> -C <sup>k</sup> CF <sub>2</sub> <sup>l</sup> -C <sup>m</sup> CF <sub>2</sub> <sup>n</sup> I (trans)	121.6(t,p,t)	113.9(t,p,t)	128.0(t)	89.7(t)						
F <sup>a</sup> -SF <sub>4</sub> <sup>b</sup> -C <sup>c</sup> CF <sub>2</sub> <sup>d</sup> -C <sup>e</sup> CF <sub>2</sub> <sup>f</sup> -C <sup>g</sup> CF <sub>2</sub> <sup>h</sup> -C <sup>i</sup> CF <sub>2</sub> <sup>j</sup> -C <sup>k</sup> CF <sub>2</sub> <sup>l</sup> -C <sup>m</sup> CF <sub>2</sub> <sup>n</sup> I (cis)				J <sub>δd</sub> =11.06(cis, 7.06)			J <sub>γd</sub> =24.2(cis, 23.8)			

<sup>a</sup>Chemical shifts in parts per million from TMS and coupling constants in hertz.

the isomer were assigned with the larger value corresponding to the trans isomer:  $J = 14.9$  and  $9.62$  Hz. This assignment agrees with previous results found for other cis and trans isomers [15].

Table 3 contains  $^{13}\text{C}$  NMR data for  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ ,  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$  and  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$ . The chemical shifts for the  $\alpha$  carbon adjacent to the  $\text{SF}_5$  group range from  $\delta = 119.0$  ppm to  $\delta = 121.6$  ppm and for the  $\beta$  carbon from  $\delta = 117.4$  ppm to  $\delta = 91.1$  ppm. This range is consistent with the literature values reported for  $\text{SF}_5$ -containing sulfonic acids, bromides and dibromides [14,16]. The coupling constants for the  $\alpha$  carbon to the  $\text{SF}_4$  fluorines are in the range  $J_{\alpha,b} = 37.9$ – $25.9$  Hz.

### 3. Experimental details

The reactants  $\text{CF}_2=\text{CF}_2$ ,  $\text{S}_2\text{F}_{10}$  and  $\text{CHF}=\text{CF}_2$  were obtained from PCR;  $\text{CH}\equiv\text{CH}$  and  $\text{CH}_2=\text{CH}_2$  were purchased from Air Products and Airco, respectively, and were used as received.  $\text{ICF}_2\text{CF}_2\text{I}$  was prepared in our laboratory using a modified literature method [17,18]. IR spectra were obtained using a Nicolet 20 DX FTIR spectrometer operating at  $2.0\text{ cm}^{-1}$  resolution or a Perkin Elmer System 2000 FTIR spectrometer operating at  $1.0\text{ cm}^{-1}$  resolution, using KBr cells for liquids and solids. Mass spectra were measured on a VG 7070 HS mass spectrometer operated at  $70\text{ eV}$ . NMR spectra were obtained on a Varian EM-390 spectrometer operating at  $90.00\text{ MHz}$  for  $^1\text{H}$  and  $84.67\text{ MHz}$  for  $^{19}\text{F}$  with F-11 as internal standard, or a Bruker AMX-400 operating at  $100.6\text{ MHz}$  for  $^{13}\text{C}$  and  $400.1\text{ MHz}$  for  $^1\text{H}$ , both using tetramethylsilane (TMS) as internal standard. Elemental analyses were determined by Beller Microanalytical Laboratory, Gottingen, Germany.

#### 3.1. Preparation of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$

Into a 150 ml Hoke stainless steel vessel, equipped with a Whitey stainless steel valve,  $11.68\text{ g}$  ( $32.99\text{ mmol}$ ) of  $\text{ICF}_2\text{CF}_2\text{I}$  was pipetted. The reaction vessel containing  $\text{ICF}_2\text{CF}_2\text{I}$  was cooled to  $-196^\circ\text{C}$  and evacuated, and  $10.28\text{ g}$  ( $32.09\text{ mmol}$ ) of  $\text{S}_2\text{F}_{10}$  and  $2.98\text{ g}$  ( $29.80\text{ mmol}$ ) of  $\text{CF}_2=\text{CF}_2$  were added. The mixture was heated with the lower half of the reaction vessel in an oil bath (or heating tube) at  $155 \pm 5^\circ\text{C}$  for  $4.0\text{ h}$  with shaking every  $20$ – $30\text{ min}$ . The reaction was quenched with cold water and stored at  $0^\circ\text{C}$  overnight. Distillation with a  $2.5\text{ mm} \times 100\text{ mm}$  column packed with  $0.05\text{ in} \times 0.05\text{ in} \times 0.1$  in Monel helices gave  $10.26\text{ g}$  ( $28.98\text{ mmol}$ ) of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  collected at  $82$ – $86^\circ\text{C}$  ( $48.6\%$  yield based on  $\text{CF}_2=\text{CF}_2$  used) ( $96\%$  pure by NMR). The violet liquid was treated with Hg to remove  $\text{I}_2$ .

The IR spectrum for  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  shows the following peaks:  $1217$  (ms),  $1204$  (ms),  $1163$  (s),  $1133$  (s),  $1109$  (s),  $1044$  (m),  $977$  (w),  $884$  (vs),  $835$  (w),  $814$  (w),  $764$  (vw),  $732$  (s),  $702$  (s),  $675$  (mw),  $653$  (vw),  $602$  (s),  $582$  (m),  $574$  (m),  $537$  (vw),  $417$  (w).

#### 3.2. General procedure for derivatives of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$

The reactants were pipetted or condensed at  $-196^\circ\text{C}$  into Pyrex glass Carius tubes (volume:  $50$ ,  $100$ ,  $200$  and  $300\text{ ml}$ ) equipped with Kontes Teflon stopcocks and containing a small amount of mercury. Gases were condensed into the reaction vessel at  $-196^\circ\text{C}$ . The vessel was irradiated with a Sylvania Capsylite Halogen Par 38 lamp at a distance of  $12$ – $18\text{ in}$  for several days to weeks (wavelengths of the halogen lamps were in the range of approximately  $250$ – $800\text{ nm}$ ). During this time, the reaction mixture was shaken (five times in  $24\text{ h}$ ). The temperature in the warmest portion of the irradiation zone was approximately  $54^\circ\text{C}$ . The pressure of the volatile components decreased as the reaction proceeded; a red solid,  $\text{HgI}_2$ , was also formed. The pressure of the reaction mixture was determined via the use of a vacuum line; a Heise Bourdon ( $0$ – $1000\text{ mmHg}$ ) gauge attached to the vacuum line was used to measure the pressure. When the reaction was found to be complete (no further pressure change observed), the volatile materials were transferred from the reaction vessel which had been cooled to  $-24^\circ\text{C}$ .

#### 3.3. Reaction of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ with $\text{CH}_2=\text{CH}_2$

Into a  $300\text{ ml}$  Carius tube containing  $0.48\text{ g}$  Hg was pipetted  $5.29\text{ g}$  ( $14.9\text{ mmol}$ ) of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ ;  $0.48\text{ g}$  ( $17.4\text{ mmol}$ ) of  $\text{CH}_2=\text{CH}_2$  was condensed under vacuum into the reactor cooled to  $-196^\circ\text{C}$ . The reaction mixture was irradiated for  $7\text{ days}$  with shaking (five times in  $24\text{ h}$ ). The volatile materials were removed at  $-24^\circ\text{C}$  and distillation of the non-volatile material at reduced pressure gave  $5.08\text{ g}$  ( $13.3\text{ mmol}$ ) of colorless liquid  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$  (boiling point (b.p.),  $53.5^\circ\text{C}$  at  $16\text{ mmHg}$ ) in  $89.0\%$  yield.

The IR spectrum for  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$  shows the following peaks:  $2984$  (w),  $2967$  (w),  $1496$  (vw),  $1444$  (m),  $1356$  (m),  $1310$  (m),  $1262$  (m),  $1187$  (vs),  $1165$  (w),  $1118$  (s),  $1076$  (s),  $955$  (w),  $916$ ,  $877$ ,  $825$  (vs),  $802$  (s),  $761$  (s),  $761$  (s),  $683$  (m),  $647$  (vw),  $606$  (s),  $580$  (ms),  $527$  (s),  $416$  (w).

A molecular ion peak and appropriate fragments were observed in the mass spectrum for  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ . Major peaks include:  $382$  ( $\text{M}^+$ );  $155$  ( $(\text{CF}_2)_2$ - $(\text{CH}_2)_3\text{CH}^+$ );  $141$  ( $(\text{CF}_2)_2(\text{CH}_2)_2\text{CH}^+$  or  $\text{CH}_2\text{I}^+$ );  $128$  ( $\text{HI}^+$ ,  $(\text{CF}_2)_2(\text{CH}_2)_2^+$ );  $127$  ( $\text{SF}_5^+$ ,  $\text{I}^+$ );  $100$  ( $\text{CF}_2\text{CF}_2^+$ );  $89$  ( $\text{SF}_3^+$ );  $77$  ( $\text{CF}_2\text{C}_2\text{H}_3^+$ );  $69$  ( $\text{CF}_3^+$ );  $65$  ( $\text{CF}_2\text{CH}_3^+$ );  $51$  ( $\text{SF}^+$ )  $47$  ( $\text{C}_2\text{H}_4\text{F}^+$ );  $28$  ( $\text{C}_2\text{H}_4^+$ );  $27$  ( $\text{C}_2\text{H}_3^+$ ).

Analysis: calculated for  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ : C,  $12.6\%$ ; H,  $1.05\%$ ; F,  $44.8\%$ ; found: C,  $13.3\%$ ; H,  $0.96\%$ ; F,  $44.2\%$ .

#### 3.4. Reaction of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ with $\text{CH}_2=\text{CH}_2$

Into a  $200\text{ ml}$  quartz vessel cooled to  $-196^\circ\text{C}$ ,  $1.62\text{ g}$  ( $4.24\text{ mmol}$ ) of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  and  $4.78\text{ mmol}$  of  $\text{CH}_2=\text{CH}_2$  were condensed. The reaction mixture was irradiated for  $7\text{ days}$  with shaking (five times in  $24\text{ h}$ ). The mixture was then transferred to a  $100\text{ ml}$  Carius tube containing a few drops of

tert-butylperoxide. An additional 4.52 mmol of  $\text{CH}_2=\text{CH}_2$  was added and the mixture was heated at 100 °C for 21 h and at 132 °C for 64 h. Distillation under reduced pressure gave 0.82 g (2.0 mmol) of colorless liquid (b.p., 99–103 °C at 198 mmHg) in 42.7% yield.

The IR spectrum of  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_2\text{I}$  shows the following peaks: 2958 (wm), 2879 (w), 1463 (vw), 1437 (vw), 1384 (vw), 1362 (vw), 1322 (vw), 1293 (vw), 1257 (w), 1187 (s), 1115 (m), 1000 (w), 877 (vs), 825 (vs), 738 (m), 729 (m), 681 (m), 604 (s), 574 (wm), 544 (w), 527 (w).

A molecular ion peak and appropriate fragments were observed in the mass spectrum for  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_2\text{I}$  and  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_3\text{I}$ . Major peaks for  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_2\text{I}$  include: 410 ( $\text{M}^+$ ); 175 ( $\text{C}_2\text{F}_5\text{C}_4\text{H}_8^+$ ); 155 ( $(\text{CF}_2)_2(\text{CH}_2)_3\text{CH}^+$ ); 141 ( $(\text{CF}_2)_2(\text{CH}_2)_2\text{CH}^+$  or  $\text{CH}_2\text{I}^+$ ); 135 ( $\text{C}_6\text{F}_3\text{H}_6^+$ ); 128 ( $\text{HI}^+$ ,  $(\text{CF}_2)_2(\text{CH}_2)_2^+$ ); 127 ( $\text{SF}_5^+$ ,  $\text{I}^+$ ,  $\text{C}_2\text{F}_4\text{C}_2\text{H}_3^+$ ); 115 ( $\text{CF}_2\text{CF}_2\text{CH}_3^+$ ); 95 ( $\text{C}_3\text{F}_3\text{H}_2^+$ ); 91 ( $\text{C}_4\text{F}_2\text{H}_5^+$ ); 89 ( $\text{SF}_3^+$ ); 85 ( $\text{C}_5\text{H}_6\text{F}^+$ ); 77 ( $\text{CF}_2\text{C}_2\text{H}_3^+$ ); 73 ( $\text{C}_4\text{H}_6\text{F}^+$ ); 69 ( $\text{CF}_3^+$ ); 65 ( $\text{CF}_2\text{CH}_3^+$ ); 64 ( $\text{CF}_2\text{CH}_2^+$ ); 61 ( $\text{C}_3\text{H}_6\text{F}^+$ ); 59 ( $\text{C}_3\text{H}_4\text{F}^+$ ); 55 ( $\text{C}_4\text{H}_7^+$ ); 53 ( $\text{C}_4\text{H}_5^+$ ); 51 ( $\text{SF}^+$ ,  $\text{CF}_2\text{H}^+$ ); 47 ( $\text{C}_2\text{H}_4\text{F}^+$ ); 42 ( $\text{C}_3\text{H}_6^+$ ); 41 ( $\text{C}_3\text{H}_5^+$ ); 39 ( $\text{C}_3\text{H}_3^+$ ); 29 ( $\text{C}_2\text{H}_3^+$ ); 28 ( $\text{C}_2\text{H}_4^+$ ); 27 ( $\text{C}_2\text{H}_3^+$ ). Major peaks for  $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_3\text{I}$  include: 439 ( $\text{M}+\text{H}^+$ ); 438 ( $\text{M}^+$ ); 313 ( $\text{M}-\text{I}$  or  $\text{SF}_5+2\text{H}^+$ ); 312 ( $\text{M}-\text{I}$  or  $\text{SF}_5+\text{IH}^+$ ); 311 ( $\text{M}-\text{I}$  or  $\text{SF}_5^+$ ); 155 ( $(\text{CF}_2)_2(\text{CH}_2)_3\text{H}^+$ ); 127 ( $\text{SF}_5^+$ ,  $\text{I}^+$ ); 89 ( $\text{SF}_3^+$ ); 77 ( $\text{CF}_2\text{C}_2\text{H}_3^+$ ); 69 ( $\text{CF}_3^+$ ); 55 ( $(\text{CH}_2)_3\text{CH}^+$ ); 47 ( $\text{FCH}_2\text{CH}_2^+$ ); 43 ( $(\text{CH}_2)_3\text{H}^+$ ); 42 ( $(\text{CH}_2)_3^+$ ); 41 ( $\text{C}_3\text{H}_5^+$ ); 39 ( $\text{C}_3\text{H}_3^+$ ).

### 3.5. Reaction of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ with $\text{CH}\equiv\text{CH}$

To a 50 ml Pyrex glass Carius tube containing 0.20 g of Hg, 1.49 g (4.21 mmol) of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  was added; 3.00 mmol of  $\text{CH}\equiv\text{CH}$  was then added at  $-196$  °C and the reaction mixture was warmed to room temperature and irradiated for 6 days with shaking (six times in 24 h). An additional 2.08 mmol of  $\text{CH}\equiv\text{CH}$  was added and the reaction mixture was irradiated for another 15 days. The volatile materials were removed at  $-25$  °C and the product was stored at 0 °C. A second run using 1.71 g (4.83 mmol) of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$  and 2.87 mmol of  $\text{CH}\equiv\text{CH}$  was irradiated for 8 days, after which 3.30 mmol of  $\text{CH}\equiv\text{CH}$  was added and irradiated for an additional 11 days. The volatile materials were removed, and distillation of combined runs 1 and 2, at reduced pressure, gave 2.42 g (6.38 mmol) of a colorless liquid (b.p., 99–103 °C at 198 mmHg) in 74% yield. The  $^{19}\text{F}$  NMR data showed a mixture of approximately 14% *cis*- and 86% *trans*- $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$ .

Analysis: calculated for  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$ : C, 12.6%; H, 0.53%; F, 45.0%; found: C, 12.7%; H, 0.48%; F, 44.7%.

The IR spectrum for  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$  shows the following peaks: 3083 (vw), 1618 (m), 1333 (vw), 1294 (w), 1257 (w), 1222 (m), 1196 (ms), 1117 (ms), 1086 (m), 979 (w), 944 (m), 876 (vs), 838 (vs), 804 (m), 775 (w),

746 (w), 670 (w), 632 (vw), 604 (m), 573 (w), 547 (w), 533 (vw), 479 (vw).

GC–MS analysis shows a molecular ion peak and appropriate fragments for both *cis* and *trans* isomers of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$ , as identified by the ratios from the  $^{19}\text{F}$  NMR spectrum and the peak ratios in GC. Major peaks for *trans*- $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$  include: 380 ( $\text{M}^+$ ); 203 ( $\text{CF}_2\text{C}_2\text{H}_2^+$ ); 127 ( $\text{SF}_5^+$ ,  $\text{I}^+$ ); 126 ( $\text{C}_2\text{F}_4\text{C}_2\text{H}_2^+$ ); 89 ( $\text{SF}_3^+$ ); 76 ( $\text{CF}_2\text{C}_2\text{H}_2^+$ ); 75 ( $\text{CF}_2\text{C}_2\text{H}^+$ ); 69 ( $\text{CF}_3^+$ ); 57 ( $\text{C}_3\text{H}_2\text{F}^+$ ); 31 ( $\text{CF}^+$ ). Major peaks for *cis*- $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}=\text{CHI}$  include: 380 ( $\text{M}^+$ ); 203 ( $\text{CF}_2\text{C}_2\text{H}_2^+$ ); 127 ( $\text{SF}_5^+$ ,  $\text{I}^+$ ); 126 ( $\text{C}_2\text{F}_4\text{C}_2\text{H}_2^+$ ); 75 ( $\text{CF}_2\text{C}_2\text{H}^+$ ).

### 3.6. Reaction of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ with $\text{CF}_2=\text{CF}_2$

Into a 100 ml Carius tube containing 0.36 g of Hg and 3.04 g (8.47 mmol) of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ , 0.83 g (8.29 mmol) of  $\text{CF}_2=\text{CF}_2$  was added at  $-196$  °C. The reaction mixture was irradiated for 5 days with shaking (five times in 24 h). An additional 0.12 g (1.2 mmol) of  $\text{CF}_2=\text{CF}_2$  was added and irradiated for 14 days with shaking (five times in 24 h). After the volatile materials had been removed at  $-24$  °C, distillation of the remaining non-volatile material at reduced pressure gave 0.92 g of colorless liquid  $\text{SF}_5(\text{C}_2\text{F}_4)_2\text{I}$  (b.p., 72–79 °C at 92 mmHg). The lower boiling fraction (45–72 °C) and the volatile material were returned to the reaction vessel and allowed to react for an additional 13 days. Distillation, at reduced pressure, of all of the products gave 1.32 g (2.9 mmol) of colorless liquid (b.p., 71 °C at 104 mmHg) in 34.3% yield.

Analysis: calculated for  $\text{SF}_5(\text{C}_2\text{F}_4)_2\text{I}$ : C, 10.58%; H, 0.00%; F, 54.4%; found: C, 10.63%; H, <0.1%; F, 54.2%.

The IR spectrum for  $\text{SF}_5(\text{C}_2\text{F}_4)_2\text{I}$  shows the following peaks: 1309 (vw), 1227–1217 (s, b), 1154 (vs), 1114 (m), 1067 (wm), 1044 (vw), 918 (s), 885 (vs), 838 (m), 815 (vw), 794 (vw), 786 (vw), 769 (m), 732 (w), 720 (vw), 687 (w), 669 (m), 653 (m), 610 (m), 588 (m), 570 (m).

GC–MS analysis of the fraction boiling at 72–79 °C at 92 mmHg shows a molecular ion peak and appropriate fragments for both  $\text{SF}_5(\text{C}_2\text{F}_4)_2\text{I}$  and  $\text{SF}_5(\text{C}_2\text{F}_4)_3\text{I}$ . Major peaks for  $\text{SF}_5(\text{C}_2\text{F}_4)_2\text{I}$  include: 454 ( $\text{M}^+$ ); 327 ( $(\text{CF}_2)_4\text{I}^+$ ,  $(\text{CF}_2)_4\text{SF}_5^+$ ); 239 ( $\text{C}_3\text{F}_4\text{I}^+$ ,  $\text{C}_3\text{F}_4\text{SF}_5^+$ ); 208 ( $\text{SC}_2\text{F}_8^+$ ); 181 ( $(\text{CF}_2)_3\text{CF}^+$ ); 177 ( $\text{SF}_5\text{CF}_2^+$ ,  $\text{CF}_2\text{I}^+$ ); 131 ( $\text{C}_3\text{F}_5^+$ ); 127 ( $\text{SF}_5^+$ ,  $\text{I}^+$ ); 119 ( $\text{C}_2\text{F}_5^+$ ); 100 ( $\text{C}_2\text{F}_4^+$ ); 89 ( $\text{SF}_3^+$ ); 69 ( $\text{CF}_3^+$ ). Major peaks for  $\text{SF}_5(\text{C}_2\text{F}_4)_3\text{I}$  include: 554 ( $\text{M}^+$ ); 319 ( $\text{MF}^+ - \text{SF}_5$ ,  $\text{I}^+$ ); 281 ( $\text{C}_6\text{F}_{13}^+$ ); 231 ( $\text{C}_5\text{F}_9^+$ ); 227 ( $\text{C}_2\text{F}_4\text{SF}_5^+$ ,  $\text{C}_2\text{F}_4\text{I}^+$ ); 181 ( $\text{C}_4\text{F}_7^+$ ); 177 ( $\text{SF}_5\text{CF}_2^+$ ,  $\text{CF}_2\text{I}^+$ ); 169 ( $\text{C}_3\text{F}_7^+$ ); 131 ( $\text{C}_3\text{F}_5^+$ ); 127 ( $\text{SF}_5^+$ ,  $\text{I}^+$ ); 119 ( $\text{C}_2\text{F}_5^+$ ); 100 ( $\text{C}_2\text{F}_4^+$ ); 89 ( $\text{SF}_3^+$ ); 69 ( $\text{CF}_3^+$ ).

### 3.7. Reaction of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ with $\text{CHF}=\text{CF}_2$

Into a 300 ml Carius tube containing 0.36 g of Hg and 3.47 g (9.80 mmol) of  $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ , was added 0.79 g (9.63 mmol) of  $\text{CHF}=\text{CF}_2$ . The reaction mixture was irradiated for 16 days with shaking (five times in 24 h). An additional 0.54

g (6.64 mmol) of CHF=CF<sub>2</sub> was added and allowed to react for 26 days. After the volatile materials had been removed at –24 °C, distillation of the remaining material, at reduced pressure, gave 1.31 g of colorless liquid SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CHF<sub>2</sub>CF<sub>2</sub>I (b.p., 107–117 °C at 236 mmHg) in 19.4% yield.

The IR spectrum for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CHF<sub>2</sub>CF<sub>2</sub>I shows the following peaks: 2996 (w), 1887 (vw), 1714 (w), 1571 (vw), 1508 (vw), 1450 (vw), 1384 (w), 1368 (w), 1342 (w), 1278 (wm), 1200 (vs, b), 1159 (vs), 1141 (vs), 1121 (s), 1077 (m), 1043 (wm), 970 (wm), 881 (vs, b), 850 (s), 838 (s), 810 (m), 773 (wm), 734 (wm), 688 (m), 650 (wm), 607 (s), 571 (s), 528 (w), 477 (vw).

GC–MS analysis of the fraction boiling at 107–117 °C at 236 mmHg shows a molecular ion peak and appropriate fragments for SF<sub>5</sub>(CF<sub>2</sub>)<sub>2</sub>CHF<sub>2</sub>CF<sub>2</sub>I and its isomer SF<sub>5</sub>(CF<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>CFHI, as well as two additional peaks corresponding to the M<sup>+</sup> peak representing SF<sub>5</sub>(CF<sub>2</sub>)<sub>2</sub>-(CF<sub>2</sub>CFH)<sub>2</sub>I and its isomer. Major peaks for one of the single addition products include: 436 (M<sup>+</sup>); 201 (C<sub>4</sub>F<sub>8</sub>H<sup>+</sup>); 177 (SF<sub>5</sub>CF<sub>2</sub><sup>+</sup>, CF<sub>2</sub>I<sup>+</sup>); 163 ((CF<sub>2</sub>)<sub>3</sub>CH<sup>+</sup>); 131 (C<sub>3</sub>F<sub>5</sub><sup>+</sup>); 127 (SF<sub>5</sub><sup>+</sup>, I<sup>+</sup>); 119 (C<sub>2</sub>F<sub>5</sub><sup>+</sup>); 113 (C<sub>2</sub>F<sub>4</sub>CH<sup>+</sup>); 100 (C<sub>2</sub>F<sub>4</sub><sup>+</sup>); 89 (SF<sub>3</sub><sup>+</sup>); 82 (C<sub>2</sub>F<sub>3</sub>H<sup>+</sup>); 69 (CF<sub>3</sub><sup>+</sup>); 51 (SF<sup>+</sup>, CF<sub>2</sub>H<sup>+</sup>); 31 (CF<sup>+</sup>); 28 (C<sub>2</sub>H<sub>4</sub><sup>+</sup>). For the second single addition product, the major peaks include: 436 (M<sup>+</sup>); 209 (C<sub>2</sub>F<sub>3</sub>HI<sup>+</sup>); 201 (C<sub>4</sub>F<sub>8</sub>H<sup>+</sup>); 190 (CF<sub>2</sub>HI<sup>+</sup>); 163 ((CF<sub>2</sub>)<sub>3</sub>CH<sup>+</sup>); 159 (CHF<sub>2</sub>I<sup>+</sup>); 131 (C<sub>3</sub>F<sub>5</sub><sup>+</sup>); 127 (SF<sub>5</sub><sup>+</sup>, I<sup>+</sup>); 119 (C<sub>2</sub>F<sub>5</sub><sup>+</sup>); 113 (C<sub>2</sub>F<sub>4</sub>CH<sup>+</sup>); 100 (C<sub>2</sub>F<sub>4</sub><sup>+</sup>); 89 (SF<sub>3</sub><sup>+</sup>); 82 (C<sub>2</sub>F<sub>3</sub>H<sup>+</sup>); 69 (CF<sub>3</sub><sup>+</sup>); 51 (SF<sup>+</sup>, CF<sub>2</sub>H<sup>+</sup>); 32 (CHF<sup>+</sup>); 31 (CF<sup>+</sup>); 28 (C<sub>2</sub>H<sub>4</sub><sup>+</sup>). GC–MS analysis for the double addition product gave two peaks, each showing a molecular ion peak at 518, corresponding to two isomers in which the hydrogen could be on the carbon next to the iodine or on an internal carbon (see Table 1).

## Acknowledgements

We are grateful to the National Science Foundation (CHE-9632815) and the Petroleum Research Foundation (ACS-PRF 31099-AC1) for support of this work.

## References

- [1] R.E. Banks and R.N. Haszeldine, *Adv. Inorg. Radiochem.*, **3** (1961) 337.
- [2] R.A. Bekker, B.L. Dyatkin and I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12** (1970) 2738.
- [3] J. Hutchinson, *J. Fluor. Chem.*, **3** (1973/1974) 429.
- [4] G.L. Gard and C. Woolf, *J. Fluor. Chem.*, **1** (1971/1972) 487.
- [5] H. Wessolowski, G.V. Rosenthaler, R. Winter and G.L. Gard, *Z. Naturforsch., Teil B*, **46** (1991) 123.
- [6] H. Wessolowski, G.V. Rosenthaler, R. Winter, G.L. Gard, G. Pon and R. Willett, *Eur. J. Solid State Inorg. Chem.*, **29** (1992) 1173.
- [7] J. Wessel, H. Hartl and K. Seppelt, *Chem. Ber.*, **119** (1986) 453.
- [8] R.E. Banks, M.G. Barlow, R.N. Haszeldine and W.D. Morton, *J. Chem. Soc., Perkin Trans. I* (1974) 1266.
- [9] J.C. Hansen and P.M. Savu, US Patent 5 159 105, 1992.
- [10] J.C. Hansen and P.M. Savu, US Patent 5 286 352, 1994.
- [11] F.E. Behr, J.C. Hansen and P.M. Savu, *203rd American Chemical Society National Meeting, San Francisco, CA, April 1992*.
- [12] H.L. Cross, G. Cushing and H.L. Roberts, *Spectrochim. Acta*, **17** (1961) 344.
- [13] R.J. Terjeson and G.L. Gard, *J. Fluor. Chem.*, **35** (1987) 653.
- [14] R.J. Willenbring, J. Mohtasham, R. Winter and G.L. Gard, *Can. J. Chem.*, **67** (1989) 2037.
- [15] L.F. Chen, J. Mohtasham and G.L. Gard, *J. Fluor. Chem.*, **43** (1989) 329.
- [16] R.J. Terjeson, R. Willenbring and G.L. Gard, *J. Fluor. Chem.*, **76** (1996) 63.
- [17] R.N. Haszeldine and K.J. Leadham, *J. Chem. Soc.* (1953) 1548.
- [18] D.D. Coffman, *J. Org. Chem.*, **14** (1949) 747.