

Short communication

# A facile preparation of ICF<sub>2</sub>CF<sub>2</sub>I and its reaction with ethylene

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Received 28 February 1997; accepted 16 June 1997

## Abstract

A facile preparation of ICF<sub>2</sub>CF<sub>2</sub>I in high yield is carried out using a halogen lamp. In a similar manner, ICF<sub>2</sub>CF<sub>2</sub>I reacts with ethylene to give ICH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I. © 1997 Elsevier Science S.A.

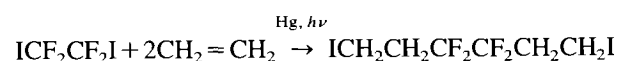
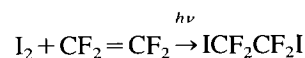
**Keywords:** Diiodotetrafluoroethane; Preparation and reaction with ethylene

## 1. Introduction

In 1949, tetrafluoro-1,2-diiodoethane was prepared by the reaction of I<sub>2</sub> with tetrafluoroethylene (TFE) in a silver-lined shaker tube at pressures of 300–370 psi; ether was used as the solvent. The reaction mixture was heated to 60 °C for 15 h and the yield was 74% based on iodine [1]. Later, in 1953, a method using I<sub>2</sub>, α-pinene, and TFE in a stainless steel autoclave was reported [2]; the yield was found to be 76%.

Several procedures have been reported for preparing not only ICF<sub>2</sub>CF<sub>2</sub>I but higher diiodo telomers [3,4]. The reactions were carried out in stainless steel cylinders under pressure and heated to 200–290 °C. The reaction of ICF<sub>2</sub>CF<sub>2</sub>I with ethylene was described in a patent issued in 1962; the methodology involved heating ICF<sub>2</sub>CF<sub>2</sub>I with ethylene at temperatures of 180–220 °C [5].

In our studies with the SF<sub>5</sub>-fluoroalkyl iodides [6] it was necessary to prepare significant quantities of ICF<sub>2</sub>CF<sub>2</sub>I. Using a technique developed for the synthesis of SF<sub>5</sub>-fluoroalkyl iodides we were successful in preparing ICF<sub>2</sub>CF<sub>2</sub>I under moderate conditions and in high yields. In this procedure, iodine and TFE were reacted together in a Carius tube or a 2 l Pyrex-glass vessel. The reactants were irradiated with a halogen lamp for periods of 12–20 days. The reaction of ICF<sub>2</sub>CF<sub>2</sub>I with ethylene to give the 1:2 adduct was carried out in a Carius tube containing mercury; this mixture was irradiated (halogen lamp) for 13 days.



The infrared spectra of the two compounds contained strong C–F bands in the 1100 to 1400 cm<sup>-1</sup> region [7]. In addition, C–H absorption bands are found for the ethylene adduct in the 2962–3001 cm<sup>-1</sup> region. The C–I stretching frequency for perfluorinated iodides is found in the 690–740 cm<sup>-1</sup> region [8]; for ICF<sub>2</sub>CF<sub>2</sub>I the band found at 698 cm<sup>-1</sup> is attributed to the C–I stretch. In the NMR spectra, the fluorine resonances for ICF<sub>2</sub>CF<sub>2</sub>I and its ethylene adduct are located at δ –52.6 and δ –115.7 ppm, respectively. These values are consistent with values reported for similar systems; for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I, the fluorine resonance was found at δ –60 ppm [9], and in SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I the fluorine resonance of the CF<sub>2</sub> group next to the CH<sub>2</sub> group was found at δ –115.9 ppm [6].

The <sup>13</sup>C chemical shift for the carbon atoms alpha to iodine in ICF<sub>2</sub>CF<sub>2</sub>I is δ +93.6 ppm; for SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>I this value was +91.1 ppm [6]. The <sup>13</sup>C chemical shifts for the α and β carbons in the ethylene adduct were found at δ –9.92 ppm and δ +35.4 ppm, respectively; in SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I, the corresponding chemical shifts were located at δ –11.61 ppm and +37.50 ppm, respectively [6]. For the γ carbons, the <sup>13</sup>C shift was found at δ +118.0 ppm.

The mass spectrum of the ethylene adduct contained the molecular ion peak (M<sup>+</sup>), the (M–I)<sup>+</sup> peak, the I<sup>+</sup> peak and other appropriate fragments.

## 2. Experimental details

The reactants I<sub>2</sub>, CF<sub>2</sub>=CF<sub>2</sub>, CH<sub>2</sub>=CH<sub>2</sub>, and mercury were obtained from Baker, PCR, Airco and Numberg Scientific, respectively. They were used as received. Infrared spectra were obtained with a Perkin–Elmer System 2000 FTIR oper-

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ating at  $1.0 \text{ cm}^{-1}$  resolution and using KBr cells. The mass spectrum was measured on a VG 7070 HS mass spectrometer operated at 70 eV. NMR spectra were obtained on a Varian EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine with  $\text{CFCl}_3$  as an internal standard or a Bruker AMX-400 operating at 100.6 MHz for carbon-13 and 400.1 MHz for proton, both using TMS as an internal standard. The radiation source was a Sylvania Capsylite Halogen Par 38 lamp (wavelengths of halogen lamps range from  $\sim 250$  to 800 nm) placed 10–12 inches away from the reaction vessel. Elemental analyses were determined by Beller Microanalytical Laboratory in Gottingen, Germany.

### 2.1. Preparation of $\text{ICF}_2\text{CF}_2\text{I}$ in a Carius tube

In a 130 ml Pyrex-glass Carius tube equipped with a Kontes Teflon stopcock, 2.80 g of powdered iodine (11.0 mmol) was added. The vessel was cooled to  $-196^\circ\text{C}$ , evacuated and charged with 1.10 g of TFE (11.0 mmol). The reaction mixture was irradiated for 7 days after which an additional 0.50 g of TFE (5.0 mmol) was added; irradiation was continued for 5 days. At the end of the reaction period no solid iodine was present. Distillation of the product gave  $\text{ICF}_2\text{CF}_2\text{I}$  as the only product (bp  $115$ – $117^\circ\text{C}$ , yield 90%).

The infrared spectrum for  $\text{IC}_a\text{F}_{2a}\text{C}_b\text{F}_{2b}\text{I}$  shows the following peaks ( $\text{cm}^{-1}$ ): 1207 (m), 1157 (vs), 1104 (vs), 974 (s), 835 (s), 698 (vs), 635 (vw), 575 (w).  $^{19}\text{F}$  NMR ( $\text{CFCl}_3$ )  $\delta$ :  $-52.6$  ppm.  $^{13}\text{C}$  NMR (TMS)  $\delta$ : 93.6 (t,t) ppm;  $J_{\alpha,a} = 318.0$  Hz and  $J_{\alpha,b} = 40.24$  Hz.

### 2.2. Preparation of $\text{ICF}_2\text{CF}_2\text{I}$ in a Carius tube as a continuous reaction

Using the Carius tube described above, 9.96 g (39.2 mmol) of powdered iodine was added; the reaction vessel was cooled to  $-196^\circ\text{C}$ , evacuated, and charged with 1.10 g (11.0 mmol) of TFE. The reaction mixture was irradiated for a total of 20 days during which time periodic measurements of the pressure were made; if the pressure was below  $\sim 0.5$  atm, additional TFE was added; four times during the 20 days, an additional 3.90 g (39.0 mmol) of TFE was added. At the end of the reaction time, no solid iodine was present; the reaction mixture was distilled giving  $\text{ICF}_2\text{CF}_2\text{I}$  in 90% yield.

### 2.3. Preparation of $\text{ICF}_2\text{CF}_2\text{I}$ in a 2 l vessel

In a 2 l Pyrex-glass vessel equipped with a Kontes Teflon stopcock, 22.42 g of powdered iodine (88.3 mmol) was added. The reaction vessel was cooled to  $-196^\circ\text{C}$ , evacuated and charged with 8.50 g of TFE (85.0 mmol) and irradiated for 5 days after which an additional 1.0 g of TFE (10 mmol) was added. The reaction mixture was irradiated for an additional 4 days; no solid iodine was observed at the end of this irradiation period. The reaction mixture was distilled giving  $\text{ICF}_2\text{CF}_2\text{I}$  in 94% yield.

### 2.4. Reaction of $\text{ICF}_2\text{CF}_2\text{I}$ with $\text{CH}_2=\text{CH}_2$

In a 100 ml Pyrex-glass Carius vessel equipped with a Kontes Teflon stopcock, 3.05 g (8.62 mmol) of  $\text{ICF}_2\text{CF}_2\text{I}$  and 0.67 g (3.34 mmol) of Hg were added. The reaction vessel was cooled to  $-196^\circ\text{C}$ , evacuated, and 0.61 g (21.7 mmol) of  $\text{CH}_2=\text{CH}_2$  was added. The reaction mixture was irradiated for 13 days with periodic shaking, (5 times per day). A white crystalline product was formed. The volatile materials were pumped away and the solid product left behind was purified by recrystallization in carbon tetrachloride, melting point  $113$ – $116^\circ\text{C}$ , 1.24 g, 35% yield. The product was sublimed at  $49^\circ\text{C}$  (0.07 Torr).

The infrared spectrum of  $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$  shows the following peaks ( $\text{cm}^{-1}$ ): 3001 (w), 3032 (vw), 2978 (vw), 2962 (vw), 1438 (s), 1429 (w), 1352 (w), 1306 (m), 1191 (s), 1186 (s), 1158 (vs), 1059 (m), 1048 (vs), 922 (m), 915 (s), 754 (w), 735 (w), 560 (w), 506 (m).

A molecular ion peak and appropriate fragments were observed in the mass spectrum. Major peaks include ( $m/z$ , mol. ion, rel.%): 410 ( $\text{M}^+$ , 43.4%), 283 ( $\text{M}-\text{I}^+$ , 100%), 155 ( $\text{M}-2\text{I}-\text{H}^+$ , 12.4%), 141 ( $\text{M}-2\text{I}-\text{CH}_3^+$ , 19.2%), 135 ( $\text{C}_6\text{F}_3\text{H}_6^+$ , 6.8%), 127 ( $\text{I}^+$ , 15.2%), 115 ( $\text{CF}_2\text{CF}_2\text{CH}_3^+$ , 8.2%), 97 ( $\text{CF}_3\text{C}_2\text{H}_2\text{CH}_2^+$ , 5.6%), 78 ( $\text{CF}_2\text{CH}_2\text{CH}_2^+$ , 5.7%), 77 ( $\text{CF}_2\text{CH}_2\text{H}^+$ , 64.5%), 59 ( $\text{CFCH}_2\text{CH}_2^+$ , 10.4%), 51 ( $\text{HCF}_2^+$ , 13.1%), 47 ( $\text{C}_2\text{H}_4\text{F}^+$ , 6.1%), 27 ( $\text{C}_2\text{H}_3^+$ , 15.0%).

The  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR results:  $^1\text{H}$  NMR (TMS)  $\delta$ : 3.22 (m) ppm, 2.65 (m) ppm.  $^{19}\text{F}$  NMR ( $\text{CFCl}_3$ )  $\delta$ :  $-115.7$  (m) ppm.  $^{13}\text{C}$  NMR, proton decoupled, (TMS)  $\delta$ :  $\alpha$ ,  $-9.92$  (s) ppm;  $\beta$ , 35.4 (m) ppm;  $\gamma$ , 118.0 (t);  $J_{\gamma,c} = 251.5$  Hz,  $J_{\gamma,d} = 40.2$  Hz.

Analysis: Calcd. for  $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ : C, 17.58; H, 1.97; F, 18.5; I, 61.91. Found: C, 17.68; H, 1.88; F, 18.7; I, 61.73%.

### 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.

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