

## ARTICLE INFO

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# DECARBOXYLATION OF 2,3,3,3-TETRAFLUORO-2-IODOPROPIONIC ACID, ITS POTASSIUM SALT AND TRIMETHYLSILYL ESTER

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**Abstract:** The preparation of 1,1,1,2-tetrafluoro-2-iodoethane by various methods has been studied, it has been shown that the best method is a method in which a solution of acid in dimethylformamide is gradually added to dimethylformamide preheated to 140°C, the mechanism of this reaction with the formation of CF<sub>3</sub>CFI – anion is proposed.

**Keywords:** iodofluoroalkanes, decarboxylation, 2,3,3,3-tetrafluoro-2-iodopropionic acid.

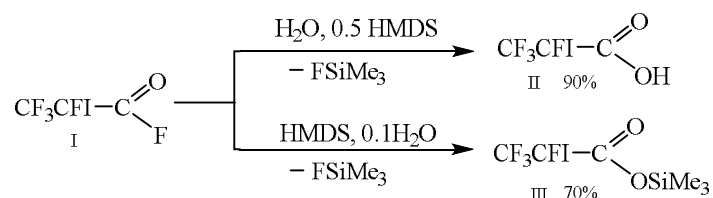
Iodofluoroalkanes are the basic synthones in organofluorine chemistry; they are widely used for fluoroalkylation of aliphatic, aromatic, heterocyclic, organoelement compounds. [1-3]. Lower iodofluoroalkanes are also used as telogens for telomerisation to form products, used for the synthesis of fluoroacids [4], fluorinated alcohols [5]; monomers for thermo- and chemically stable polymers [6].

We have recently proposed an original method for obtaining pentafluoroethyl iodide from perfluoropropylene [7], the key intermediate in which is the fluorohydride 2,3,3,3-tetrafluoro-2-iodopropionic acid I. In continuation of this work, it was proposed to obtain 1,1,1,2-tetrafluoro-2-iodoethane and 1,1,2-trifluoro-2-iodoethene using the same intermediate compound.

It is known to produce 1,1,1,2-tetrafluoro-2-iodoethane by the decarboxylation of tetrafluoropropionic acid salts in the presence of iodine in dimethylformamide with the yield about 30 % [8], through the addition of HF to 1-iodo-1,2,2,2-tetrafluoroethane in gas phase on the chrome catalyst [9], through the iodofluorination of 1,1,2-trifluoroethene by the mixture of iodine and IF<sub>5</sub> using aluminum with aluminium iodide as catalysts at temperatures 130-140°C in an autoclave [10],

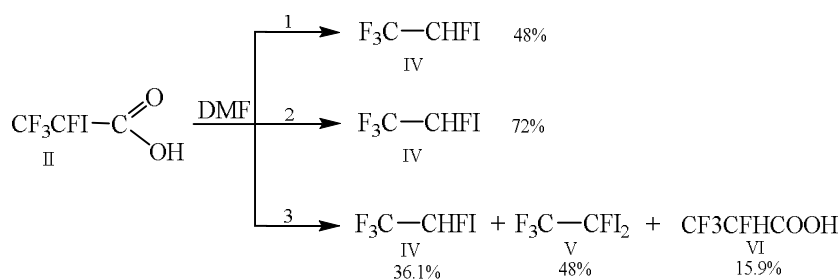
and also through the reaction of 1,1,2-trifluoroethene with ICl in HF/BF<sub>3</sub> medium at 25°C with a yield 73 % [11].

The aim of this work was to obtain 1,1,1,2-tetrafluoro-2-iodoethane and 1,1,2-trifluoro-2-iodoethene from 2,3,3,3-tetrafluoro-2-iodopropionic acid **II** and its trimethylsilyl ester **III**, which, in turn, were obtained from fluoro-anhydride **I** according to the Scheme 1 below.



**Scheme 1.**

Depending on the conditions of decarboxylation of acid **II** (Scheme 2), we obtained different results. During the decarboxylation process with simultaneous distillation of the resulting volatile products, the yield of 1,1,1,2-tetrafluoro-2-iodoethane **I** was 48% (Method 1). In the case of using the method consisting in the gradual addition of an acid solution in dimethylformamide to dimethylformamide preheated to 140°C (Method 2), it was possible to increase the yield of the desired product **IV** to 72%. However, carrying out the reaction without simultaneous distillation of volatile products (Method 3) led to an unexpected result. After isolation and comparison of GC data, <sup>1</sup>H, <sup>19</sup>F NMR spectra and mass spectra, it turned out that the reaction products in addition to **IV** are 1,1,1,2-tetrafluoro-2,2-diiodoethane **V** and 2,3,3,3-tetrafluoropropionic acid **VI**.

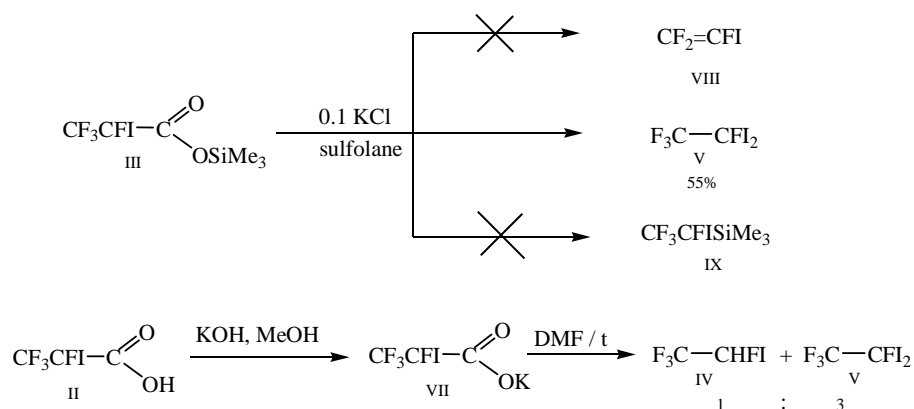


**Scheme 2.**

Decarboxylation of silyl ether **III** did not lead to the formation of the target 1,1,2-trifluoro-2-iodoethene **VII** and trimethyl(1,2,2,2-tetrafluoro-1-iodoethyl)silane **IX**, the only reaction product was 1,1,1,2-tetrafluoro-2,2-diiodoethane **V**.

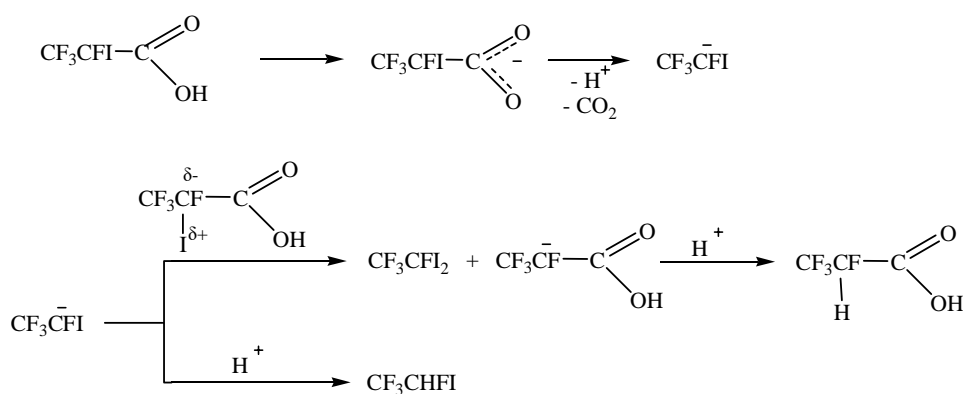
As an alternative to obtaining 1,1,2-trifluoro-2-iodoethene **VIII**, decarboxylation of the potassium salt 2,3,3,3-tetrafluoro-2-iodopropionic acid was carried out, however, in this case the

formation of the expected products did not occur, the reaction resulted in compounds **IV** and **V** in a ratio of 1:3.

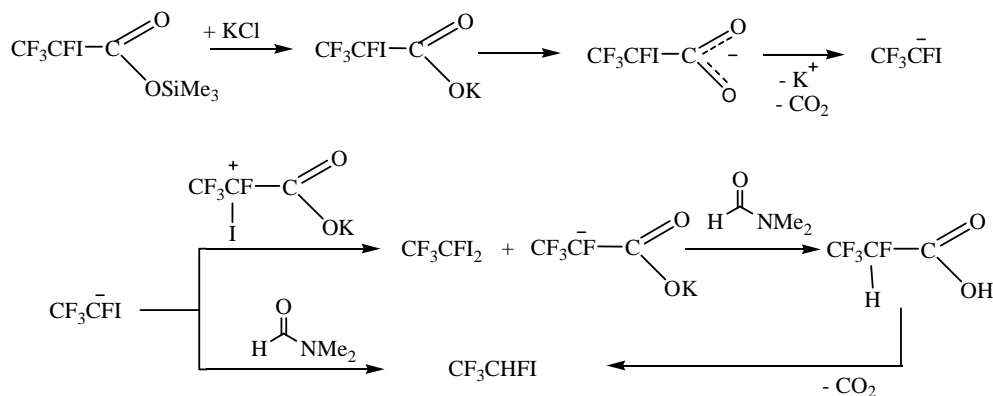


**Scheme 3.**

By analyzing the obtained experimental data, it can be assumed that, as a result of decarboxylation, a stable  $\text{CF}_3\text{CFI}^-$  anion is formed, which is reacted as shown in Schemes 4 and 5.



**Scheme 4.**



**Scheme 5.**

Thus, the formation of the diiodo derivative **V**, and not assumed alkene **VIII** or trimethylsilane **IX**, predominantly occurs.

### Experimental

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on the "Bruker AVANCE-300" spectrometer at 300 and 282 MHz correspondingly, external standard is  $\text{CDCl}_3$ . Chemical shifts for  $^1\text{H}$  NMR spectra are given in ppm relative to TMS. Chemical shifts for  $^{19}\text{F}$  NMR spectra are given in ppm relative to  $\text{CFCl}_3$ .

Fluoro-anhydride **I** was obtained as described in [7].

#### *Preparation of 2,3,3,3-tetrafluoro-2-iodopropionic acid II*

To 6.9 g (0.383 mol) of water and 31.1 g (0.192 mol) of hexamethyldisilane, while stirring, 105 g (0.383 mol) of fluoro-anhydride **I** is added dropwise. While adding fluoro-anhydride, the temperature rises to  $34^\circ\text{C}$  and the formation of trimethylsilane is observed. The reaction mass is kept at this temperature for two hours, then 15 g of fluorotrimethylsilane is distilled in vacuum into a receiving flask cooled by a mixture of dry ice with acetone. Next, the receiving flask is replaced, 0.2 g of copper powder is added to the cube and 94 g of 2,3,3,3-tetrafluoro-2-iodopropionic acid **II** is distilled as a colorless liquid. Yield 90 %, purity is 97 %, m.p.  $28\text{--}31^\circ\text{C}$ , b.p.  $67\text{--}69^\circ\text{C}/20\text{ mm Hg}$ .

$^1\text{H}$  NMR,  $\delta$ , ppm: 10.1 (c, 1H,  $\text{COOH}$ );

$^{19}\text{F}$  NMR,  $\delta$ , ppm: -142.3 (m, 1F,  $\text{CFI}$ ), -76.5 (m, 3F,  $\text{CF}_3$ ).

#### *Preparation of trimethylsilyl ester of 2,3,3,3-tetrafluoro-2-iodopropionic acid III*

To 0.7 g (0.0394 mol) of water and 64 g (0.394 mol) of hexamethyldisilane, while stirring, 108g (0.394 mol) of fluoro-anhydride **I** is added dropwise. While adding of fluoro-anhydride the temperature rises to  $46^\circ\text{C}$  and the formation of trimethylfluorosilane is observed. The reaction mass is heated to  $62^\circ\text{C}$  and kept by this temperature during 1 hour, then 10 g of the mixture of fluorotrimethylsilane and hexamethyldisilane are distilled into receiving flask which is cooled by mixture of dry ice and acetone. Further the receiving flask is replaced, 0.2 g of copper powder are added into the still and 95 g of 2,3,3,3-tetrafluoro-2-iodopropionic acid **III** are distilled as colorless liquid. Yield 70 %, purity 97 % by GC, b.p/  $52\text{--}53^\circ\text{C}/20\text{ mm Hg}$

$^1\text{H}$  NMR,  $\delta$ , ppm: 0.4 (c, 9H  $\text{SiMe}_3$ );

$^{19}\text{F}$  NMR,  $\delta$ , ppm: -138.6 (m, 1F,  $\text{CFI}$ ), -76.8 (m, 3F,  $\text{CF}_3$ ).

***Preparation of 1,1,1,2-tetrafluoro-2-iodoethane IV***

***Method 1.***

The solution of 20 g (0.0735 mol) **II** in 20 g of DMF, while stirring, is gradually heated to the temperature 135-137°C, by which gas emission begins. Then the reaction mixture is slowly heated to 145°C, and 1,1,1,2-tetrafluoro-2-iodoethane is simultaneously distilled into receiving flask which is cooled by mixture of dry ice and acetone. Yield is 48 %, purity 97 %, b.p. 39°C.

***Preparation of 1,1,1,2-tetrafluoro-2-iodoethane IV***

***Method 2.***

To 20 g of DMF, which is heated to 140°C, while stirring 20 g (0.0735 mol) of **II** is added dropwise into 15 g of DMF and 12 g of 1,1,1,2-tetrafluoro-2-iodoethane is simultaneously distilled into receiving flask which is cooled by mixture of dry ice and acetone. Yield is 72 %, purity 97%, b.p. 39°C.

***Preparation of 1,1,1,2-tetrafluoro-2-iodoethane IV***

***Method 3.***

The solution of 20 g (0.0735 mol) **II** in 20 g of DMF is loaded into a flask, provided with reflux, which is connected to deep-cooling condenser, and while stirring, gradually heated to 140°C. It is kept by this temperature during 30 minutes upon the completion of gas emission, then the reaction mass is cooled to room temperature and poured into double volume of 15% hydrochloric acid. The lower layer is separated and washed by 2x15 ml of water, dried over CaCl<sub>2</sub>. It is obtained 17 g of mixture, consisting according to GC from 36.1 % **IV**, 48% **V**, 15.9 % **VI**.

***Preparation of 1,1,1,2-tetrafluoro-2,2-diiodoethane V***

The solution of 20 g (0.0579 mol) of trimethylsilyl ester **III** and 0.4 g of potassium chloride (0.00579 mol) in 20 g of absolute sulfolane, while stirring, is gradually heated to the temperature 90-93°C, by which gas emission begins. Then the reaction mixture is gradually heated to 150°C, and 5 g of trimethylfluorosilane are simultaneously distilled into receiving flask, which is cooled by mixture of dry ice and acetone. The reaction mass is cooled to room temperature and poured into double volume of water, washed by 2x15 ml of water, dried over CaCl<sub>2</sub> and distilled. It is obtained 6.5 g of 1,1,1,2-tetrafluoro-2,2-diiodoethane, purity 96 %, b.p. 128-130°C.

<sup>19</sup>F NMR, δ, ppm: -97.7 (m, 1F, CFI<sub>2</sub>), -80.6 (m, 3F, CF<sub>3</sub>).

### ***Preparation of potassium salt of 2,3,3,3-tetrafluoro-2-iodopropionic acid VII***

To the solution of 10 g (0.0367 mol) of acid **II** in 15 ml of methanol, while stirring, 2 g (0.0367 mol) of potassium hydroxide in 7 ml of methanol is added dropwise. It is stirred during 20 minutes, methanol is distilled in vacuum of water-jet pump, the salt is dried over P<sub>2</sub>O<sub>5</sub>. The yield is quantitative.

### ***Decarboxylation of potassium salt of 2,3,3,3-tetrafluoro-2-iodopropionic acid***

In a 100 ml two-neck flask, equipped with thermometer and reflux condenser, which is connected to deep-cooling condenser, cooling by the mixture dry ice-acetone, with Tishchenko flask with concentrated H<sub>2</sub>SO<sub>4</sub>, 11 g (0.0355 mol) of **VII** in 16 g of DMF are loaded, the solution, while stirring, is gradually heated to 93°C and stirred by this temperature during 30 minutes upon the completion of gas emission. The reaction gas is cooled to room temperature and poured into double volume of 15 % hydrochloric acid, washed by 2x5 ml of water, dried over CaCl<sub>2</sub>. It is obtained 3.2 g of crude product, containing according to GC: 26 % **IV**, 74 % **V**.

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### **References**

1. Tiers G., Journal of the American Chemical Society, **1960**, 82(20), 5513.
2. Patent US 3271441 (**1966**).
3. V.C.R. McLoughlin, J.Thrower, Tetrahedron, **1969**, 25(24), 5921-5940.
4. Patent US 3351644 (**1967**).
5. Patent US 3576885 (**1971**).
6. Patent US 3862077 (**1975**).
7. V.E. Boiko, A.V. Edunov, S.M. Igumnov, Fluorine notes, **2016**, 6(109), 5-6.
8. "Syntheses of organofluorine compounds", Part 3, edited by S.M. Igumnov, E.V. Igumnova, M., "Trovan", **2015**, 214p., 3. (in Russian)
9. Patent DE 3009760 (**1981**).
10. Hauptschein M., Braid M., JACS, **1961**, 83, 2383-2386.
11. Petrov V.A., Krespan C.G., J. Org. Chem., **1996**, 61, 9605-9607.