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# Addition of some unreactive fluoroalkanes to tetrafluoroethylene. Direct catalytic synthesis of *F*-butene-2

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Dedicated to Professor Paul Tarrant on the occasion of his 85th birthday and in appreciation for his substantial and varied contributions to fluorine chemistry

#### Abstract

Condensation of trifluoromethanes,  $CF_3X$  (X = H, Cl, Br, I), with tetrafluorethylene to form the corresponding *F*-*n*-propyl adducts have been carried out with aluminum chlorofluoride as catalyst. Yields of  $C_3F_7I$  and  $C_3F_7Br$  are especially good, making these useful perfluoropropyl intermediates readily available. Details of the reactions, especially the presence of low percentages of perfluoroisopropyl iodide and bromide in the products, are accounted for by proposed mechanisms involving halonium intermediates. Longer-chain primary iodides can also be added to tetrafluoroethylene, but the final products are predominantly fluoroolefins, with pentafluoroethyl iodide as a byproduct. In the case of the addition of  $C_2F_5I$  to tetrafluoroethylene, conditions for an efficient, low temperature dimerization of terafluoroethylene to *F*-butene-2 catalyzed by a combination of  $C_2F_5I$ /aluminum chlorofluoride have been defined. Evidence for an unusual transfer of I<sup>+</sup> from the iodonium derivative of *F*-butene-2 to tetrafluoroethylene is presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Fluoroalkanes; F-butene-2

#### 1. Introduction

Additions of haloalkanes to fluoroolefins using Friedel– Crafts catalysts constitute an established and very useful synthetic method [1–3]. A number of these reactions involving simple alkyl fluorides or chlorides are effectively catalyzed by a solution of antimony pentafluoride in anhydrous HF [4–6], since this mixture provides a superacid system in which the pronounced oxidizing power of SbF<sub>5</sub> has been obviated.

Fluoride substrates requiring a stronger catalyst,  $CH_3CF_3$ [7],  $CH_2F_2$  [8], and  $CH_3F$  [8] being examples, are successfully added to fluoroolefins such as tetrafluoroethylene (TFE) with neat SbF<sub>5</sub> as catalyst. Antimony pentafluoride-catalyzed additions of chlorofluoroalkanes are limited to readily activated molecules such as  $ClCF_2CFCl_2$  [3], since they can be conducted at lower temperatures, while fluoroalkyl bromides and  $CF_3I$  are not operable; higher iodides perform poorly (vide infra). Both aluminum chloride and the more recently discovered aluminum chlorofluoride (ACF) [9] are potent Lewis acid catalysts with no oxidizing capability to cause undesirable side-reactions. ACF, in particular, has such high reactivity that it catalyzes condensation reactions of substrates resistant to the action of SbF<sub>5</sub> [1,2,10]. Sensitivity to protic impurities is a characteristic of ACF which necessitates particular care in excluding impurities such as water and hydrocarbons and which limits the range of useful substrates to those containing low amounts of hydrogen, i.e., those leading to negligible HF elimination. Within these limits, however, its range of usable substrates is broad, indeed [1,2,11,12].

#### 2. Results and discussion

Trifluoromethyl halides and fluoroform have proved to be resistant to condensation with fluoroolefins via cationic intermediates. Attempted additions to TFE of CF<sub>3</sub>H [8] have been unsuccessful with SbF<sub>5</sub> as catalyst. The case of CF<sub>3</sub>H/SbF<sub>5</sub> is instructive, since this combination does allow

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condensation reactions at elevated temperatures if a substrate more resistant to direct reaction with  $SbF_5$  than TFE is provided [13]. Thus, alkylation of pentafluorobenzene occurs in good yield to give the main product shown in Eq. (1).

$$F$$
 + CF<sub>3</sub>H - (1)

Attempted additions of  $CF_3Br$  to TFE in the presence of  $SbF_5$  carried out in this work were unsuccessful, while  $CF_3I$  suffers oxidative replacement of iodine with fluorine even at low temperature, in sharp contrast to higher perfluoroalkyl iodides, which are stable to the action of  $SbF_5$  at ambient temperature.

In contrast to the findings with  $SbF_5$ , ACF does catalyze additions of different trifluoromethanes to fluoroolefins, as is illustrated with TFE [11] Eqs. (2) and (3), confirming its increased range of catalytic activity over that of  $SbF_5$ .

$$XCF_3 + CF_2 = CF_2 \xrightarrow{50^{\circ}C} XCF_2CF_2CF_3,$$
  

$$1a, X = H, 29\%; 1b, X = Cl, 4\%$$
(2)

$$YCF_{3} + CF_{2} = CF_{2} \xrightarrow{50^{\circ}C} YCF_{2}CF_{2}CF_{3} + (CF_{3})_{2}CFY,$$
  
**2a**, Y = Br, 63%; **3a**, Y = Br, 4%  
**2b**, Y = I, 80%; **3b**, Y = I, 4% (3)

The reaction provides a simple, direct route to polyfluorinated propanes and is especially useful for the preparation of *F-n*-propyl iodide (**2b**). This precursor to perfluorinated straight-chain derivatives having an odd number of carbon atoms has generally been prepared by treatment of  $C_3F_7C(O)OAg$  with  $I_2$  [14], an expensive route, or by heating *F*-butyroyl chloride with KI at >200°C [15], which requires equipment for operation either continuously or under pressure.

The formation of detectable amounts of rearrangement products **3** along with the normal addition products **2** suggests the occurrence of a secondary reaction similar to that previously observed directly with *F*-*n*-propyl bromide and iodide [16]. The isomerizations of *F*-*n*-propyl bromide and iodide to the corresponding *F*-isopropyl halides were either quite slow or did not occur with ACF only, but proceeded with a co-catalyst such as hexafluor-opropene (HFP), suggesting further that a carbocationic species is required to promote rearrangement. In the present case, reactive carbocationic complexes **2a**' and **2b**' between trifluoromethanes and the insoluble ACF [17]<sup>2</sup> are formed



Scheme 1

presumably reversibly. The carbocationic moieties in such complexes cannot isomerize and will disproportionate only under extreme conditions, making them potentially useful promoters for ACF-catalyzed reactions. These cationic intermediates not only add to TFE, leading to product, but apparently also are capable of inducing the isomerizations noted earlier with ACF and a promoter such as HFP [16]. Low reaction temperatures limit the extent of isomerizations promoted by 2a' and 2b' via proposed intermediates 4 and 5 (Scheme 1).

As the low yield from CF<sub>3</sub>Cl attests, labilization of  $\alpha$ -F in this compound is much less pronounced than with fluorine substituents in the  $\alpha$ -position to bromine or iodine. Furthermore, ACF-catalyzed isomerization of fluorinated *vic*-dihalides is markedly more difficult with dichlorides than with dibromides, although evidence of anchimeric assistance from bridging to adjacent halogen has been adduced even for dichloride cases [16]. Our proposal of a type of anchimeric assistance (i.e., in 4; Y = Br) to account for partial isomerization of BrCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub> induced by [BrCF<sub>2</sub><sup>+</sup>·ACF<sub>2</sub><sup>-</sup>] during addition of CF<sub>3</sub>Br to CF<sub>2</sub>=CF<sub>2</sub> is in accord with the catalyzed isomerizations known to occur with primary *F*-alkyl bromides, but not occur with the corresponding chlorides [16].

The heightened reactivity of  $CF_3I$  and  $CF_3Br$  prompted a study of ACF-catalyzed reactions of higher primary *F*-alkyl iodides. In sharp contrast to n-C<sub>3</sub>F<sub>7</sub>Br (which does not react with TFE in the presence of ACF catalyst) the reaction of CF<sub>3</sub>CF<sub>2</sub>I with CF<sub>2</sub>=CF<sub>2</sub> produced, surprisingly, *F*butene-2 (**6**) along with small amounts of iodide adduct **6a** (Eq. (4)).

<sup>&</sup>lt;sup>2</sup> This paper provides evidence that the formation of polyfluoromethyl carbocations  $XCF_2^+$  (X = H,F,Cl, Br) in solution is uphill thermodynamically due to pronounced destabilizing effect of multiple fluorine substituents in carbocations of this type.

$$CF_{3}CF_{2}I + CF_{2} = CF_{2} \xrightarrow{25-30^{\circ}C} CF_{3}CF = CFCF_{3} + CF_{3}CF_{2}I$$

$$0.16 \quad 0.4 \qquad 6$$

$$+ CF_{3}CFICF_{2}CF_{3}$$

$$6a \text{ (trace)} \qquad \text{ratio } 6: C_{2}F_{5}I = 59: 41$$

$$(4)$$

Interestingly, the reaction of  $C_2F_5I$  and TFE in the presence of SbF<sub>5</sub> as a catalyst proceeds differently under similar conditions. It is much slower and does not produce butene (**6**); compound **6a** is the major product formed in low yield (10%) along with a small amount of telomeric perfluoroalkyl iodides  $C_2F_5(CF_2CF_2)_nI$  (n = 1-4, calculated yield 5%). Telomeric iodides  $C_2F_5(CF_2CF_2)_nI$  probably, result from the well-known radical telomerization reaction between  $C_2F_5I$  and TFE initiated by the oxidizer (SbF<sub>5</sub>) in a process similar to that recently described in [18] (Eq. (5)).

$$CF_3CF_2I + CF_2 = CF_2 \xrightarrow{25-30^{\circ}C} 6a + C_2F_5(CF_2CF_2)_nI$$
 (5)  
Yield: 10% 5%

Formation of the 4-carbon products in both reactions indicates that cation **7** is formed and that addition to TFE occurs, but in the case of the more powerful Lewis acid (ACF) the adduct **6a** is capable of transferring the elements of IF to another molecule of TFE under the reaction conditions. We propose that the driving force leading to formation of *F*-butene-2 is the reactive intermediate iodonium ion **8** arising from the anchimerically assisted loss of fluoride depicted by structure **9** (Scheme 2).

As is predicted by this scheme,  $CF_3CF_2I$  is reformed by net transfer of IF to TFE and can therefore serve as part of a catalyst system (along with ACF) to dimerize TFE to *F*-butene-2 (Eq. (6)).

$$2CF_2 = CF_2 \xrightarrow{25-30^{\circ}C} CF_3CF = CFCF_3$$

$$6,68\%$$

$$(6)$$

Electrophilic dimerization of tetrafluoroethylene proceeds under mild condition and produces *F*-butene-2 in moderate yield, providing easy excess to this material. The reaction is



Scheme 2.

easy to scale up and as carried out in a stirred autoclave, it was used for the preparation of several pounds of *F*-butene-2 (see Section 3). Typical yields of *F*-butene-2 are in the range 60-75%. Detailed examination of a reaction mixture shows that the main process (formation of **6**) is accompanied by the formation of a noticeable amount of isomeric *F*-hexenes, surprisingly, with *F*-3-methylpentene-2 (**10a** and **10b**, *trans*- and *cis*-isomers, respectively) being the major components of the mixture, containing also *F*-hexene-2 and *F*-hexene-3 (**11a**, **b** and **12a**, **b**, respectively; mixture of *trans*- and *cis*-isomers) and secondary iodide **6a** (Eq. (7)).

$$2CF_2 = CF_2 \xrightarrow[ACF/C_2F_5I]{25-30^{\circ}C} \mathbf{6} + \mathbf{6a} + \mathbf{10a}, \mathbf{b} + \mathbf{11a}, \mathbf{b} + \mathbf{12a}, \mathbf{b}$$
(7)

As was demonstrated in separate experiments, the formation of hexenes **11** and **12** is the result of condensation reactions of *F*-butene-2 and TFE. It is similar to ACFcatalyzed condensation of fluoroolefins such as *F*-pentene-2 and TFE [19], although the reaction of *F*-butene-2 is significantly slower (Eq. (8)).

$$6 + CF_2 = CF_2 \xrightarrow{50^\circ C, 16h} 11a, b + 12a, b$$
  
Yield of mixture 67%, at 22% conversion of 6

(8)

We believe that the formation of branched olefins **10**, however, is the result of a competitive process involving condensation of secondary iodide **6a** with TFE. Transfer of IF from intermediate **13** to TFE leads to  $C_2F_5I$  and olefin **10** as a final products (Scheme 3).

Predominant formation of olefin 10 (see Section 3) is an indication of the higher rate of the process represented by Scheme 3 compared to the rate of the reaction 6 and TFE (Eq. (8)).

Longer-chain primary alkyl iodides such as *F-n*-butyl iodide can also be induced to add to TFE using ACF catalyst, forming the corresponding olefins extended by two carbon atoms (mixture of olefins **11** and **12**). However, effective transfer of IF from both starting iodide and product to TFE produces major amounts of olefin **6** and  $C_2F_5I$  (Eq. (9)).

$$CF_{3}(CF_{2})_{2}CF_{2}I + CF_{2} = CF_{2} \xrightarrow{25^{\circ}C, 16h} 6 + 11a, b + 12a, b$$
  
+  $C_{2}F_{5}I + C_{4}F_{9}I$   
14 6 (9)



Scheme 3.

Conversion of long-chain iodides to olefins can be accomplished more cleanly with HFP as the receptor for 'IF', as indicated by the example in Eq. (10).

$$CF_3(CF_2)_2CF_2I + CF_3CF = CF_2 \xrightarrow{80^{\circ}C, 24h} 6 + 3b_{84\%} 80\%$$
 (10)

Reaction of n-C<sub>6</sub>F<sub>13</sub>I and HFP proceeds in similar fashion, producing a mixture of *F*-hexenes **11a**, **b** and **12a**, **b** and (CF<sub>3</sub>)<sub>2</sub>CFI in high yield.

The reaction patterns of fluoroalkyl chlorides, bromides and iodides found in this work and in our earlier study of halide rearrangements [16] leads to some useful general conclusions. Isomerizations of primary chlorides via chloronium ions have substantial energy barriers and have only been observed directly at high temperature, as in the special case of CHFClCF<sub>2</sub>CF<sub>2</sub>Cl at 160°C [9]. Primary F-alkyl bromides rearrange at more modest temperatures via bromonium ion intermediates, which can be generated by reaction with various fluorocarbocations. No evidence has been found so far for transferring  $Br^+$  from *n*-C<sub>3</sub>F<sub>7</sub>Br or *n*-C<sub>4</sub>F<sub>9</sub>Br to HFP even at 130°C [16]. Primary *F*-alkyl iodides isomerize more readily than the bromides [16]. In this case, evidence has been found that transfer of I<sup>+</sup> from an iodonium cation to a terminal fluoroolefin (specifically, TFE or HFP) also occurs readily.

*Vic*-dihalides rearrange via halonium ions more readily than monohalides, apparently due to the ease of removal of F- from a carbon bearing the *vic*-halogen rather than a second fluorine substituent. *Vic*-dichlorides can be isomerized to gem-dichlorides with the catalyst combination ACF/ fluoroolefin [16]. In the sterically favorable case of *F*-1,2dichloro-cyclopentane, ACF alone is sufficiently active to cause isomerization. *Vic*-dibromides in general isomerize readily to *gem*-dibromides with ACF only as catalyst. We have not examined the available, but relatively unstable ICF<sub>2</sub>CF<sub>2</sub>I.

#### 3. Experimental section

<sup>19</sup>F and <sup>1</sup>H NMR spectra were recorded on a QE-300 (General Electric, 200 MHz) or Brucker DRX-400 instruments (400.5524 and 376.8485 MHz, respectively) using CFCl<sub>3</sub> as internal standard and *d*-chloroform or *d*-acetone as a lock solvent. IR spectra were recorded on Perkin–Elmer 1600 FT spectrometer in a liquid film. CF<sub>3</sub>H, CF<sub>3</sub>Cl, CF<sub>3</sub>Br, CF<sub>3</sub>I (Aldrich), C<sub>2</sub>F<sub>5</sub>I, C<sub>4</sub>F<sub>9</sub>I (DuPont) are commercially available and were used without further purification. ACF is prepared by literature method [9,19], using reaction of AlCl<sub>3</sub> and CFCl<sub>3</sub>, stored and handled inside a dry box. Compounds **1a**, **b**, **2a**, **b**, **3a**, **b** and **6** are identified by comparison with an authentic sample. Compounds **6a** [20], **10a**, **b** [21], **11a**, **b**, **12a**, **b** [22] by comparison of NMR data to reported values.

# 3.1. Reaction of trifluoromethyl iodide with tetrafluoroethylene (TFE)

A Hastelloy 400 ml shaker tube is flushed with N<sub>2</sub> and loaded with 3 g of ACF inside a nitrogen bag. The vessel is closed, cooled down, evacuated and loaded with 60 g (0.31 mol) of CF<sub>3</sub>I and 15 g (0.15 mol) of TFE. It is kept on a shaker at 25–30°C for 16 h. The reactor is cooled to 0°C and unloaded. Excess of CF<sub>3</sub>I was distilled out of the crude product using a low temperature distillation column affording 28 g of starting iodide. The residue was distilled giving 38 g of material with b.p. 35–40°C. According to GC and <sup>19</sup>F NMR this material contains 95% of CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>I and 5% of (CF<sub>3</sub>)<sub>2</sub>CFI. Total yield on both isomers is 84.4%.

#### 3.2. Reaction of CF<sub>3</sub>Br with TFE

Using 45 g (0.3 mol) of CF<sub>3</sub>Br, 35 g (0.35 mol) of TFE, 1 g of ACF and 50 ml of dry cyclic dimer of hexafluoropropene (mixture of isomeric *F*-1,2-dimethyl- and *F*-1,3dimetylcyclobutanes) as a solvent, after 16 h at 25–30°C, 50.1 g of material with b.p. 12–13°C is isolated. According to <sup>19</sup>F NMR it is a mixture of 93% of CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>Br, 6% of (CF<sub>3</sub>)<sub>2</sub>CFBr and 1% of solvent. Total yield of C<sub>3</sub>F<sub>7</sub>Br was 67%.

# 3.3. Reaction of $CF_3Cl$ with TFE

Using 42 g (0.4 mol) of CF<sub>3</sub>Cl, 30 g (0.3 mol) TFE, 2 g of ACF and 50 ml of CDHFP, after 16 h at 50°C followed by low temperature distillation of crude product 10 g of a fraction b.p.  $-10^{\circ}$ C $-20^{\circ}$ C is isolated containing, according to <sup>19</sup>F NMR, 30% of CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>Cl and 70% of solvent. Calculated yield of C<sub>3</sub>F<sub>7</sub>Cl is 4.2%. <sup>19</sup>F NMR: -80.62 (3F, t; 8.7 Hz), -125.30 (2F, s), -69.83 (2F, q; 8.7 Hz) ppm. 22 g of polytetrafluoroethylene (PTFE) is also isolated from this reaction.

#### 3.4. Reaction of CF<sub>3</sub>H with TFE

Using 21 g (0.3 mol) of CF<sub>3</sub>H, 30 g (0.3 mol) TFE, 2 g of ACF and 30 ml of CDHFP, after 16 h at 50°C, 14.6 g of material with b.p.  $-17^{\circ}$ C to  $-10^{\circ}$ C (main fraction -16 to  $-15^{\circ}$ C), identified by <sup>19</sup>F and <sup>1</sup>H NMR as CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>H, is isolated. The yield is 29.4%. 15 g of PTFE was also isolated from this reaction.

# 3.5. Reaction of $C_2F_5I$ and TFE catalyzed by $SbF_5$

A mixture of 100 g (0.41 mol) of  $C_2F_5I$ , 5 g (0.023 mol) of SbF<sub>5</sub> and 40 g (0.4 mol) of TFE is kept in a shaker tube for 18 h at 25–30°C. The reactor is cooled to 0°C, vented, and the reaction mixture is fractionated to give 78.7 g of  $C_2F_5I$  (b.p. 10–12°C). The residue, 4.5 g of liquid, contained based on GC and NMR data 15% of  $C_2F_5I$ , 80% **6a** and 5% of  $C_2F_5(CF_2CF_2)_nI$  (n = 1-4). Calculated yield of **6a** is 3%.

# 3.6. Preparation of F-butene-2 (6)

A 240 ml Hastelloy shaker tube is loaded with 5 g of aluminum chlorofluoride (ACF) inside a nitrogen bag, cooled, evacuated and loaded with 40 g (0.16 mol) of  $C_2F_5I$  and 40 g (0.4 mol) of TFE. The reaction vessel was kept on a shaker at 25–30°C. Significant pressure drop (about 150 psi) is observed in the first 2 h. After 18 h at ambient temperature the shaker tube is unloaded, and the product (55 g) is collected in a cold ( $-78^{\circ}$ C) trap. According <sup>19</sup>F NMR the crude reaction mixture contains 41% of  $C_2F_5I$  and 59% of **6** (mixture of *trans* and *cis*-isomers, ratio 3 : 2). The calculated yield of perfluorobutene-2 is 82.5%.

#### 3.7. Preparation of 6 in stirred autoclave

The reaction is scaled up in a 11 Hastelloy stirred autoclave which is flushed with N<sub>2</sub>, loaded with 20 g ACF and 100 g of C<sub>2</sub>F<sub>5</sub>I. TFE is added at 30–35°C in 20 to 30 g increments. After addition of 400–600 g of TFE, the clave is unloaded and a new portion (100 g) of C<sub>2</sub>F<sub>5</sub>I is added and the cycle is repeated. Using 20 g of ACF, 200 g of C<sub>2</sub>F<sub>5</sub>I and 980 g of TFE, 1150 g of crude product is isolated. The distillation of crude product gives 650 g of azeoptropic mixture containing 86% of **6** and 14% of C<sub>2</sub>F<sub>5</sub>I (b.p. 0–1°C), and 220 g of material having higher b.p. The yield of **6** is 57%.

The separation of CF<sub>3</sub>CF=CFCF<sub>3</sub> and C<sub>2</sub>F<sub>5</sub>I is achieved by distillation of the mixture from dry dimethylacetamide. A first distillation [350 g of mixture of CF<sub>3</sub>CF=CFCF<sub>3</sub>/ C<sub>2</sub>F<sub>5</sub>I (86 : 14), 200 ml (CH<sub>3</sub>)<sub>2</sub>NC(O)CH<sub>3</sub>)] affords 253 g of CF<sub>3</sub>CF=CFCF<sub>3</sub> containing 2% of C<sub>2</sub>F<sub>5</sub>I. Relatively pure *F*-butene-2 [210 g of mixture *trans*- and *cis*-isomers in ratio 4 : 1, containing 0.2% of C<sub>2</sub>F<sub>5</sub>I (GC)] is isolated after a second distillation using 300 g of 98 : 2 mixture of CF<sub>3</sub>CF=CFCF<sub>3</sub>/C<sub>2</sub>F<sub>5</sub>I and 100 ml of (CH<sub>3</sub>)<sub>2</sub>NC(O)CH<sub>3</sub>).

220 g of the product with higher b.p. obtained in this reaction is distilled giving 143 g of material with b.p. 50–52°C and 24 g of residue. According to <sup>19</sup>F NMR of the main fraction is a mixture containing: *trans*-CF<sub>3</sub>CF=C(CF<sub>3</sub>)C<sub>2</sub>F<sub>5</sub> – 38%, *cis*- 9.5%; *trans*-CF<sub>3</sub>CF=CFC<sub>3</sub>F<sub>7</sub> – 7%, *cis*- 2%; *trans*-C<sub>2</sub>F<sub>5</sub>CF=CFC<sub>2</sub>F<sub>5</sub> – 29%, *cis*- 5%; CF<sub>3</sub>CFICF<sub>2</sub>CF<sub>3</sub> – 9.5%.

#### 3.8. Preparation of F-butene-2, using $n-C_4F_9I$

From 20 g (0.06 mol) of n-C<sub>4</sub>F<sub>9</sub>I, 50 g (0.5 mol) TFE and 5 g of ACF after 16 h at 25–30°C. Crude reaction mixture (65 g) contains 55% of **6**, 14% C<sub>2</sub>F<sub>5</sub>I, 21% of **12a**, **b**, 4% of **11a**, **b** and 6% of C<sub>4</sub>F<sub>9</sub>I (starting material and **6a**). After fractionation 40 g of a fraction with b.p. 0–10°C is isolated, containing, according to <sup>19</sup>F NMR, 90% of CF<sub>3</sub> CF=CFCF<sub>3</sub> (*trans*- and *cis*-isomers, ratio 3 : 2) and 10% of C<sub>2</sub>F<sub>5</sub>I. The yield of **6** is 72% (based on TFE).

# 3.9. Reaction of F-butene-2 with TFE

Using 100 g (0.5 mol) of **6**, 10 g of ACF and 50 g (0.5 mol) of TFE, after 16 h at 50°C the reaction mixture is fractionated. 70 g of **6** is recovered. The residue (30 g) according to GC and NMR data is a mixture of 25% **6**, 14.5% **11a**, 1.2% **11b**, 53% **12a** and 7.2% **12b**. Conversion of **6** is 22.5%, yield of olefins **11** and **12** 67% on converted **6**.

#### 3.10. Reaction of $n-C_4F_9I$ and hexafluoropropene

After 34.6 g (0.1 mol) of n-C<sub>4</sub>F<sub>9</sub>I, 15 g (0.1 mol) of hexafluoropropene (HFP) and 3.5 g of ACF are reacted at 80°C for 24 h, the reaction mixture is transferred into another vessel containing 3.5 g of ACF and it is charged with 7.5 g (0.05 mol) of HFP. The vessel is kept at 80°C another for another 16 h. Crude product according to GC and <sup>19</sup>F NMR data is a mixture of **6** and **3b**. Fractionation of crude product gives 10 g of the material with b.p.  $-3-2^{\circ}$ C, which is identified by <sup>19</sup>F NMR as 97% pure perfluorobutene-2 (*trans* : *cis*=81 : 19). The residue (33 g) according to <sup>19</sup>F NMR contains 71% of (CF<sub>3</sub>)<sub>2</sub> CFI, 13% of perfluorobutene-2 and 16% of starting iodide. Calculated yield of *F*-butene-2 is 84% and (CF<sub>3</sub>)<sub>2</sub> CFI -80%.

# 3.11. Reaction of $n-C_6F_{13}I$ with HFP

4.5 g (0.01 mol) of n-C<sub>6</sub>F<sub>13</sub>I and 0.5 g of ACF is placed in a heavy wall Pyrex sample tube equipped with a Teflon stopcock. The sample tube is evacuated at  $-196^{\circ}$ C and 1.5 g (10 mmol) of HFP is loaded through the vacuum line. The sample tube is kept behind a shield at 75°C for 10 h. After that it is cooled to  $-78^{\circ}$ C, opened and the reaction mixture is poured into water. The organic (lower) layer is separated, dried over P<sub>2</sub>O<sub>5</sub>. to give 5.8 g of a mixture containing 49% (CF<sub>3</sub>)<sub>2</sub> CFI, 48% of a mixture of *F*-hexene-2 and *F*-hexene-3 (ratio 23 : 77) and a small amount (2–3%) of unidentified product (probably, C<sub>6</sub>F<sub>13</sub>CF(I)C<sub>2</sub>F<sub>5</sub>). Calculated yield of *F*-hexenes is 93%, (CF<sub>3</sub>)<sub>2</sub> CFI-95%.

# 4. Conclusions

ACF catalysis of additions of trifluoromethanes  $CF_3X$  to TFE has made fluoropropanes  $CF_3CF_2CF_2X$  readily available. *F*-n-propyl iodide is a particularly useful intermediate obtainable from this synthetic method. Reactivity patterns of a series of halides in their condensation and isomerization reactions have been clarified further.

Electrophilic dimerisation of TFE catalyzed by the  $C_2F_5I/$ ACF catalytic system provides a novel, practical route to *F*butene-2, making this fluoroolefin readily available for synthetic chemists.

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#### References

- [1] C.G. Krespan, V.A. Petrov, Chem. Rev. 96 (1996) 3269.
- [2] V.A. Petrov, V.V. Bardin, in: R.D. Chambers (Ed.), Topics in Current Chemistry, Springer, Berlin, 1997, Vol. 192, pp. 39–95.
- [3] G.G. Belen'kii, L.S. German, in: M.E. Volpin (Ed.), Soviet Scientific Reviews/Sec. B. Chemistry Reviews, Harwood Academic Publishers Gmb H, New York, 1984, Vol. 5, p. 183.
- [4] G.G. Belen'kii, G.I. Savicheva, L.S. German Izv. Akad Nauk SSSR Ser. Khim. (1978) 1433.
- [5] V.A.Petrov, G.G. Belen'kii, L.S. German Izv. Akad Nauk SSSR Ser. Khim. (1980) 1099.
- [6] V.A.Petrov, G.G. Belen'kii, L.S. German Izv. Akad Nauk SSSR Ser. Khim. (1980) 2821.
- [7] V.A.Petrov, G.G. Belen'kii, L.S. German Izv. Akad Nauk SSSR Ser. Khim. (1980) 2117.
- [8] G.G. Belen'kii, V.A. Petrov, P.R. Resnick (to DuPont) PCT WO 98, 42645, 1998, CA 129 (1998) 246869.
- [9] A.C. Sievert, F.G. Weigert, C.G. Krespan, US Patent 5157171, 1992

- [10] V.A. Petrov, C.G. Krespan, B.E. Smart, J. Fluorine Chem. 77 (1996) 139.
- [11] C.G. Krespan, V.A. Petrov (to DuPont) PCT US WO 97, 02227, 1997, CA 126 (1997) 171292w.
- [12] C.G. Krespan, V.A. Petrov (to DuPont) PCT US WO 97, 02226, 1997, CA 126 (1997) 171293x.
- [13] V.V. Brovko, V.A. Sokolenko, G.G. Yakobson, Zh. Org. Khim. 10 (1974) 300.
- [14] J.H. Simons, T.G. Brice, in: J.H. Simons (Ed.), Fluorine Chemistry, New York, 1954, Vol. 2, p. 367.
- [15] C.G. Krespan, J. Org. Chem. 23 (1958) 2016.
- [16] V.A. Petrov, C.G. Krespan, B.E. Smart, J. Fluorine Chem. 89 (1998) 125.
- [17] V.A. Petrov, F. Davidson, J. Fluorine Chem. 95 (1999) 5.
- [18] C.G. Krespan, V.A. Petrov, B.E. Smart, US Patent (to DuPont) 5,574,193 (1996) CA 124 (1996) 177222.
- [19] C.G. Krespan, D.A. Dixon, J. Fluorine Chem. 77 (1996) 117.
- [20] C.G. Krespan, J. Org. Chem. 27 (1962) 1813.
- [21] P.L. Coe, A. Sellars, J.C. Tatlow, J. Fluorine Chem. 23 (1983) 103.
- [22] T.I. Filaykova, M.I. Kodess, N.V. Peschanskii, A.Ya. Zapevalov, I.P. Kolenko, Zh. Org. Khim. 23 (1987) 1858.